

T.R.
EGE UNIVERSITY
Graduate School of Applied and Natural Science

**DEVELOPMENT OF METAL AND/OR
METAL-OXIDE MODIFIED POLYMER AND
CARBON BASED COMPOSITE ELECTRODES FOR
ELECTROCHEMICAL REDUCTION OF CARBON
DIOXIDE AND DETERMINATION OF ANTIMONY
IN REAL SAMPLES**

PhD Thesis

Şebnem Gül İLARSLAN

Supervisor : Prof. Dr. Zekerya DURSUN

Department of Chemistry

İzmir

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Analytical Chemistry Third Cycle Programme

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EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

ETİK KURALLARA UYGUNLUK BEYANI

EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Doktora Tezi olarak sunduğum ***“Development of metal and/or metal-oxide modified polymer and carbon based composite electrodes for electrochemical reduction of carbon dioxide and determination of antimony in real samples (Karbondioksitin elektrokimyasal indirgenmesi ve gerçek örneklerde antimon tayini için metal ve/veya metal oksit modifiye polimer ve karbon bazlı kompozit elektrotların geliştirilmesi)”*** başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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İmzası

Şebnem Gül İLARSLAN

ÖZET**KARBONDİOKSİTİN ELEKTROKİMYASAL İNDİRGENMESİ VE
GERÇEK ÖRNEKLERDE ANTİMON TAYİNİ İÇİN METAL VE/VEYA
METAL OKSİT MODİFİYE POLİMER VE KARBON BAZLI
KOMPOZİT ELEKTROTLARIN GELİŞTİRİLMESİ**

İLARSLAN, Şebnem Gül

Doktora Tezi, Kimya Bölümü

Danışma: Prof. Dr. Zekerya DURSUN

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Bu tez çalışmasının iki temel hedefinden ilki, karbondioksitin elektrokimyasal ve fotoelektrokimyasal yöntemler ile indirgenmesi için modifiye elektrot geliştirmek, geliştirilen elektrotların yapısal ve kimyasal karakterizasyonlarını yapmak, elektrokimyasal ve fotokimyasal uygulamalarını gerçekleştirmektir. İlk olarak CO₂'nin elektrokimyasal indirgenmesi incelenmiştir. Bu amaçla, metal nanoparçacıklar (Cu ve Au) ile modifiye edilmiş polimer film; poli(p-aminofenol) kaplı camımsı karbon elektrotlar (GCE), farklı destek elektrolit (KHCO₃, NaClO₄ ve metanol) ortamlarında CO₂'in elektrokimyasal indirgenmesinin incelenmesinde kullanılmıştır. CO₂'in elektrokimyasal indirgenmesine en yüksek katalitik etkinin, 0.8 mol L⁻¹ NaClO₄ + 2 mol L⁻¹ metanol ortamında, Cu/Au modifiye poly(4-aminofenol) film kaplı GCE ile elde edilmiş.

İkinci olarak CO₂'in fotokimyasal indirgenmesi incelenmiştir. Bu amaçla, ilk olarak farklı karbon başlatıcılar (resorsin, katekol ve 4-aminofenol) kullanılarak mezogözenekli karbon malzemeler (MCM) sentezlenmiştir. Sentezlenen MCM, fotokimyasal tepkimelerde katalitik etkinin artırılması adına metal oksit fotokatalizör olan TiO₂ ile sol-gel yöntemi ile karıştırılarak MCM-TiO₂ kompoziti oluşturulmuştur. Kompozit malzemenin uygun miktardaki süspansiyonu ile hazırlanan MCM-TiO₂ kaplı GCE ile CO₂'in fotoelektrokimyasal indirgenmesi farklı destek elektrolit ortamlarında (NaClO₄, CH₃OH, KHCO₃) incelenmiş ve en iyi fotelektrokatalitik etkinin elde edilmesi

için bir seri optimizasyon çalışmaları yapılmıştır. En iyi fotoelektrokatalitik etkinin 10 µL MCM-TiO₂ süspansiyonu ile hazırlanmış GCE elektrotta, 0.5 M KHCO₃ elektrolit çözeltisinde elde edilmiştir.

Projenin ikinci amacı ise SbIII tayini için seçimli ve duyar modifiye elektrot geliştirilmesidir. Antimon (III)'ün 0.1 mol L⁻¹ HCl ortamındaki elektrokimyasal davranışının incelenmesi ve PET şişe örneklerindeki antimonun duyar ve seçimli tayininde kullanılması amacıyla, bakır(II)ftalosiyanın (CuPc) biriktirilmiş ve biriktirilmemiş, aşırı yükseltgenme yapılmamış Poly(krezol kırmızısı) film ve aşırı yükseltgenmiş Poly(Krezol kırmızısı_{ox}) film GC elektrotlar hazırlanmıştır. Hazırlanan elektrotlardan Antimon (III)' e en duyar yüzey CuPc/poly(krezol kırmızısı_{ox})/GCE olup, Antimon (III) derişimi ile pik akım yüksekliği 8.0x10⁻¹¹ – 1.0x10⁻⁹ mol L⁻¹ derişim aralığında doğrusal bulunmuş ve belirtme sınırı 1.18x10⁻¹¹ mol L⁻¹ olarak saptanmıştır (3S/m). Geliştirilen CuPc/Poly(krezol kırmızısı_{ox})/GC elektrot ile yapılan örnek analizindeki geri kazanımı %98.0–103.0 aralığında elde edilmiştir.

Optimizasyon çalışmaları sonrasında, optimum koşullarda hazırlanan metal nanoparçacık polimer modifiye elektrotlar ve karbon bazlı malzeme-metal oksit fotokatalizör modifiye elektrotların yüzey karakterizasyonları taramalı elektron mikroskobu, enerji dağılım x-ray spektroskopisi, x-ışını potoelektron spektroskopisi ve elektrokimyasal empedans tekniği ile yapılmıştır.

Anahtar Kelimeler: karbondioksit, antimon, mezo gözenekli karbon, titanyum dikosit, bakır ftalosiyanın, metal nanoparçacık, polimer film elektrotlar, modifiye elektrotlar.

ABSTRACT**DEVELOPMENT OF METAL AND/OR METAL-OXIDE MODIFIED
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İLARSLAN, Şebnem Gül

PhD Thesis, Chemistry Department

Spervisor: Prof. Dr. Zekerya DURSUN

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The first of the two main objectives of this project is to develop a modified electrode for reducing carbon dioxide by electrochemical and photochemical methods, make structural and chemical characterizations of the developed electrodes, and perform electrochemical and photochemical applications. Firstly, the electrochemical reduction of CO₂ was investigated. For this purpose, electrochemical analysis of CO₂ in different supporting electrolyte (KHCO₃, NaClO₄, and Methanol) environments, with glassy carbon electrodes (GCE) coated with a polymer film (poly(4-aminophenol)) modified with nanoparticles (Cu and Au). was used to analyze the reduction. It was determined that the best catalytic effect on the electrochemical reduction of CO₂ was obtained with Cu/Au modified poly(4-aminophenol) film GCE in 0.8 mol L⁻¹ NaClO₄ + 2 mol L⁻¹ methanol medium.

Secondly, the photochemical reduction of CO₂ was investigated. For this purpose, mesoporous carbon materials (MCM) were synthesized using different carbon initiators (resorcinol, catechol, and 4-aminophenol). To increase the catalytic effect in photochemical reactions, the synthesized MCM material was composited with TiO₂ metal oxide photocatalyst, by the sol-gel method, and MCM-TiO₂ composite material was formed. Photochemical reduction of CO₂ with MCM-TiO₂ composite GCE prepared with the appropriate amount of suspension of the composite material was investigated in different support electrolyte mediums (NaClO₄, CH₃OH, KHCO₃), and a series of optimization studies were carried out to obtain the best catalytic effect. It was observed that the best

photocatalytic result was obtained in the GCE electrode prepared with 10 μL MCM-TiO₂ suspensions in 0.5 M KHCO₃ electrolyte solution.

The second aim of the project is to develop a selective and sensitive modified electrode for the determination of antimon. Poly(krezol kırmızıısı) film and overoxidized Poly(Krezol kırmızıısı_{ox}) film GC electrodes with CuPc deposited and non-deposited, non-overoxidized Poly(Krezol kırmızıısı_{ox}) film were prepared to investigate the electrochemical behavior of antimon in 0.1 mol L⁻¹ HCl environment and to use it in the detection and selective determination of antimon in actual PET bottle samples. In the antimon determination examination performed on the prepared electrodes, the peak A_{kim} obtained with CuPc/Poly(Krezol kırmızıısı_{ox})/GCE was linear in the range of 8×10^{-11} - 1×10^{-9} nmol L⁻¹, and the limit of detection was 1.18×10^{-11} mol L⁻¹ (3S/m). The recovery for the sample analysis performed with the proposed CuPc/Poly(krezol kırmızıısı_{ox})/GC electrode were in the range of 93.0–103.0%.

After the optimization studies, surface characterizations of metal nanoparticle polymer-modified electrodes and carbon-based material-metal oxide photocatalyst-modified electrodes prepared under optimum conditions were made by scanning electron microscopy, energy dispersion x-ray spectroscopy, x-ray photoelectron spectroscopy, and electrochemical impedance technique.

Keywords: carbon dioxide, antimon, mesoporous carbon, titanium dioxide, copper phthalocyanine, metal nanoparticle, polymer film electrodes, modified electrodes.

ÖNSÖZ

Son yıllarda artan hızda birçok bilimsel araştırmada öncelikli olarak tercih edilen ve farklı konular üzerine çalışılmaya imkan sağlayan elektrokimyasal araştırmalara tez çalışmam ile katkıda bulunduğum için mutluluk duymaktayım.

Evimiz Dünya'nın son yıllarda yaşadığı en büyük problemlerden biri atmosferdeki karbondioksit miktarının artışı ve buna bağlı olarak sera etkisi nedeniyle besin ve temel yaşam döngülerini olumsuz yönde etkileyecek zincir olay ve reaksiyonların başlamış olmasıdır. Dünya genelinde, 2050 yılına kadar CO₂ salınım oranlarının sanayi şirketleri tarafından yüksek oranlarda azaltılması ve “Yeşil Kimya” altında daha temiz üretimler yapılması üzerine ciddi çalışmalar yürütülmekte ve bu çalışmalara büyük bütçeler ayrılmaktadır. Ben de doktora çalışmamda, elektrokimyasal ve fotokimyasal yöntemler kullanarak CO₂'in indirgenmesi çalışmalarına katkı sağlamak üzerine yoğunlaştım.

Bu amaçla yaptığım çalışmalar, iletken polimer kaplı modifiye yüzeylerin, altın ve bakır nanoparçacıkların sağladığı iletkenlik ve seçicilik ile desteklenerek, ortamda çözünmüş CO₂'in elektrokimyasal indirgenmesine yönelik katalitik etkinlik sağlandığını ortaya koymuştur. Buna ek olarak, yeni nesil malzemeler olarak bilinen ve birçok çalışmada farklı amaçlar ile kullanımı olan mezogözenekli karbon malzemelerin sentezlenmesini ve bu malzemelerin yarı iletken geçiş metal oksitler ile kompozit hale getirilmesini inceledim. Hazırladığım kompozit malzeme ile modifiye edilmiş yüzeylerin CO₂'in fotokatalitik olarak indirgenmesine katalitik etkinlik gösterdiği saptandı. Tezimin ikinci kısmında, günlük hayatımızda sıklıkla kullandığımız PET şişelerin sentez sürecinde katalizör olarak kullanılan antimon tayinine yönelik seçimli ve duyar yüzeyler geliştirilmiştir.

Yapılan tüm çalışmaların merdiven basamakları gibi bizleri bir adım öteye taşıyan ve aynı zamanda bambaşka bakış açıları ile bakabilmemizi sağlayan bilimsel çalışmalara, doktora tezimde yaptığım çalışmalarım ile ufak da olsa katkı sağladığım için mutluluk duymaktayım. 2013 yılında başladığım ve iş hayatım ile birlikte yürüttüğüm tez sürecimde, sevgili hocalarım başta danışmanım Prof. Dr. Zekerya DURSUN olmak üzere tez izleme komitesi üyeleri; Prof. Dr. H. İsmet GÖKÇEL ve Prof. Dr. Nuri NAKİBOĞLU'na tüm bilgi birikimini sabır ve her zamanki yol göstericiliği ile bana sundukları için minnettarım. Bu tez çalışması kapsamında yürütülen 2015-FEN-036 kodlu projem için gerekli maddi desteği sağlayan Ege Üniversitesi Bilimsel Araştırma Enstitüsüne de çok teşekkür ederim.

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Şebnem Gül İLARSLAN

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ABBREVIATIONS AND SYMBBOLS

DPASV	Differential pulse anodic stripping voltammetry
CO ₂	Carbon dioxide
CO ₂ RR	Electrochemical reduction of CO ₂
CuPc	Copper(II) phthalocyanine
CV	Cyclic voltammetry
DP	Differential pulse
EIS	Electrochemical impedance spectroscopy
GCE	Glassy carbon electrode
LOD	Limit of detection
MCM	Mesoporous carbon material
PANI	Poli(anilin)
PPAP	Poli(p-aminofenol)
SEM	Scanning electron microscopy
TEM	Transmission Electron Microscope
TiO ₂	Titanium dioxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Z	Impedance

1. INTRODUCTION

Electrochemistry is a field of chemistry in which the relationships of chemical and electrical interactions are studied. The most important part of electrochemistry studies is related to the production of electrical energy by chemical reactions or changes that occur with the passage of electric current. Electrochemistry includes many popular studies such as electrophoresis and corrosion, electrochromic displays, electroanalytical sensors, batteries, fuel cells, metal electroplating and large-scale production. It is used as a tool by scientists in electrochemical studies, analyzing trace amounts of metal ions or organic species, examining the decay rates and spectroscopic properties of intermediates such as radical ions, and examining chemical systems such as power supply design. Many electrochemical methods have been developed for this purpose. Still, it is necessary to understand the electrical properties of electrode-electrolyte interfaces to understand the applications and the basis of electrode reactions (Bockris 2000).

The physical and chemical properties of the interface used in reactions with electrochemistry at the electrode-electrolyte interface are fundamental. Because controlling one or more of these properties helps to increase selectivity and electrode activity in the electrode reactions. Although adding an electroactive species in the electrolyte solution contributes to its effect on the movement of the electrode surface, it is generally unhelpful because electrochemical events occur at the interface itself, not in the solution. For this reason, only interventions to the electrolyte solution are insufficient for the electrochemical activity at the electrode-electrolyte interface, and the electrode side often needs to be changed (Bard and Faulkner, 2022). Changes to the electrode part include modifying the electrode surface. Modifying the electrode surface has been one of the most active research topics in electrochemistry in the last three decades. Modification to the surface of an electrode gives it features such as selectivity, resistance to contamination, increasing concentration for certain species, improving electroanalytical properties, and determining the desired species in mixed matrix samples (Kissinger and Heineman, 1996; Alkire 2009).

In electrochemical methods, polymerization of monomers by chemical or electrochemical methods is also used in electrode modification. In addition,

organic and inorganic compounds, metal oxides, metal nanoparticles, carbon-based materials have also been frequently used to electrode modification in recent years (Catrinel et al., 2007, Vivek 2007).

Metal nanoparticles are specially named because of their "nanometer" particle size. The small size of the particles gives them unique surface area properties, high conductivity, and magnetic and optical properties. For this reason, it attracts great attention in modern studies (Kumar K et al., 2018). The electrodeposition is one of the methods used to modify metal nanoparticles to the electrode surface. In this method, deposition of nano-sized metals has been carried out with high purity on the electrode surface. In addition, the metal nanoparticle formation method by electrodeposition offers a low cost as it does not require high metal volumes. By changing parameters such as the concentration of the metal ion solution to be used, the applied deposition potential, and the deposition time the desired thickness, and metal nanoparticle particle structure can be obtained during the metal nanoparticle modification that will occur on the electrode surface (Ventra 2004).

Conductive polymers are another type of choice for electrode modification, either on their own or to supplement other modifiers such as metal nanoparticles. Metal nanoparticles can be dispersed into the pores in conductive polymers structures, thereby providing higher electrochemical activity (Stejskal and Sapurina, 2005). Conductive polymers can be formed on the electrode surface by chemical or electrochemical. Since a homogeneously dispersed surface is obtained in modification with conductive polymers, its use has been preferred in many studies (Inzelt, 2011).

Global warming resulting from the emission of greenhouse gases has reached alarming proportions around the world. Carbon dioxide (CO₂) is a significant greenhouse gas, and its concentration in the atmosphere has increased considerably and continues to increase. For this reason, recent studies on converting, capturing, and storing CO₂ into other usable types have attracted much attention to reducing CO₂ concentration. Electrochemical and photoelectrochemical reduction of CO₂ for conversion to other active species has been an exciting field of study by many researchers (Leung et al., 2014; Anbia

and Salehi 2016). Among these studies, the electrochemical and photochemical reduction of CO₂ has attracted the attention of many researchers due to its positive features, such as allowing it to work at ambient temperatures and pressures and the possibility of reduction at low voltages with the selection of appropriate catalyst or photocatalyst (Jin et al., 2021). Many modified electrodes have been used in the electrochemical reduction of CO₂, among which, in studies with metal/metal oxide nanoparticles, it has been determined that reduction is achieved at fast and low negative potentials. Electrodes prepared with metal/metal oxide nanoparticles such as Cu, Au, Pt, and Ni have been used in studies (Jitaru 2007). Similarly, the electrochemical reduction of CO₂ was investigated with conductive polymers due to its effect on increasing the electrode surface efficiency, and successful results were obtained (Ayдын and Köleli, 2004). Many researchers have also studied the reduction of CO₂ by photochemical methods. To examine the effects of different semiconductor photocatalysts on the photochemical reduction reaction, semiconductor metal photocatalysts were investigated by making them composite with metal nanoparticles, conductive polymers, and carbon-based materials (Khalil et al., 2019).

Electrochemical determination of analytes can also be performed with modified electrodes. With the modified electrodes, electrodes that perform sensitive determination to the desired type with high selectivity in complex matrix environments can be developed. Sensitivity, selectivity and stability are very important performance parameters in electroanalytical applications (Wang 2000). Modified electrodes are preferred in electroanalytical applications due to parameters such as performing in situ measurements, enabling faster and more sensitive analysis than instrumented measurements, and requiring a short-term pretreatment in the sample preparation procedure (Settle 1997).

1.1 The Aim of Thesis

There are basically two purposes for this thesis. The first aim is to investigate the reduction of carbon dioxide by electrocatalytic and photocatalytic methods by modifying the glassy carbon electrode (GCE) coated with conductive polymers and incorporated with metal nanoparticles (such as copper and gold, etc.), and synthesizing carbon-based materials with semiconductor metal oxide

photocatalysts (TiO_2 , ZnO , etc.) respectively. By using the cyclic voltammetry, in order to develop the electrode surface with the higher electrocatalytic and photocatalytic efficiency; a series of optimization studies such as metal ions concentration and monomer type and concentration, numbers of cycles during the electropolymerization, electrolyte solution types and concentrations, determination of initiators to be used in the synthesis of carbon-based materials, mixing with metal oxide in appropriate proportions to form composite materials were studied.

The second aim of the thesis is to develop modified electrodes for the sensitive and selective detection of antimony in PET bottle samples. For this purpose, copper phthalocyanine deposited, polymer modified GCE was developed. The surface characterizations of all the modified electrodes were characterized by cyclic voltammetry, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and electrochemical Impedance Spectroscopy (EIS).

1.2 Modified Electrodes

Modifying the electrode surface and examining and controlling its interaction with its environment has been one of the most active research topic in recent years. (Alkire 2009). A wide range of basic electrochemical research, including heterogeneous electron transfer and chemical reactivity in relation to electrode surface chemistry, electrostatic phenomena at electrode surfaces, and electron and ionic transport phenomena in polymers, for applications in chemical sensors, energy conversion and storage, electrochromic displays, corrosion protection, and electrochemical synthesis. It has provided a modern working environment that includes many study subjects such as the design of electrochemical devices and systems. (Ming Zhou et al., 2009 and Benchirouf et al., 2016).

The most distinctive feature of the modified electrodes compared to other electrodes in electrochemistry is that the selected chemical is usually bonded or coated on the electrode surface as a very thin film. Thus, with the modification provided on the surface in the form of a molecular monolayer or multiple layers of

a few micrometers thickness, chemical, electrochemical, optical, electrical, transport and other desired properties are gained to the electrode.

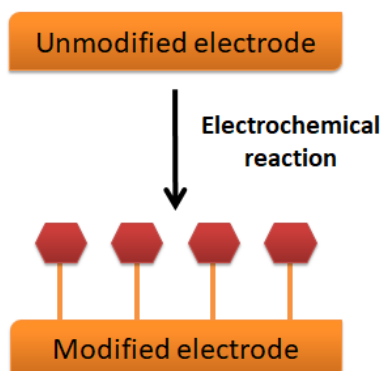


Figure 1.1 Preparation of modified electrodes (Vivek 2017).

The method to be used to modify the electrode surface has a significant short- and long-term impact on the analytical applications of the electrode. Many of these applications involve the determination of different species, including transition metal ions, peroxides, anions and organic species. Understanding the charge transfer mechanisms of chemically modified electrodes and the stability of the electrode in different environments such as low or high pH provides a basis for the development of methods based on specific reaction species (Aktürk et al., 2017, Bakır et al., 2011, Ulubay Karabiberoğlu and Dursun, 2017 and Karen and Gewirt , 2007).

The modification of the electrode surface is designed to control charge transfer rates for certain applications, such as electrocatalysis (Pei et al., 2021), solar energy conversion (Ismail et al., 2021), electrode stability improvement (Sethuraman et al., 2021), sensor development (Nurdin et al., 2022), controlled charge transfer, and electrochromism (Ezhilmaran and Bhat, 2022) (Figure 1.2). While the performance of an electrode is limited by the solution it is in, the material from which the electrode is made, and the potential applied to the surface, the ability of the electrodes to be chemically modified allows their performance to be adjusted.

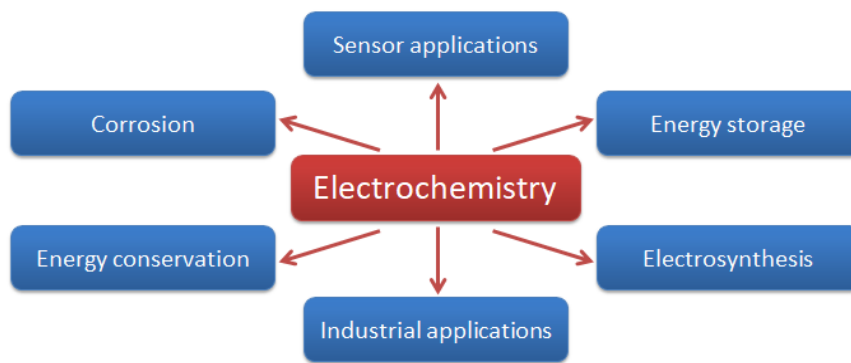


Figure 1.2 Some electrochemical technologies

In the last decade, extensive studies have been carried out on the chemical structure and modifiability of the electrode surface. It has been seen that the selection of reagents is important for chemically modifying the surface with suitable reagents to provide the desired properties and operation. It has been observed that if the appropriate reagent is selected, electrochemical reaction rates and selectivities such as electrocatalysis can be increased and adsorptive and coating effects free, special optical or excitation properties can be gained (Vivek, 2017).

1.2.1 Preparation of chemically modified electrodes

Many applications used in the preparation of chemically modified electrodes include the use of single or multilayer thin films of ionomers, redox polymers, and conductive polymers. Some methods for modifying the electrode include covalent bonding, galvanic plating, electrochemical deposition, and electropolymerization. (Takeshita et al., 2020, Koçak and Dursun, 2013, Srinivasan et al., 2020, Chen et al., 2020, Cho et al., 2015, Wang et al., 2016, S. Koçak and Dursun, 2013).

One of the benefits of using electropolymerization reactions in electrode modification is that by changing the experimental conditions, the surface properties of the polymer film can be changed, so that specially developed electrodes can be prepared for certain applications. For this purpose, various techniques have been developed to prepare different types of modified electrodes. Figure 1.3 outlined the four possible routes for the preparation of CMEs.

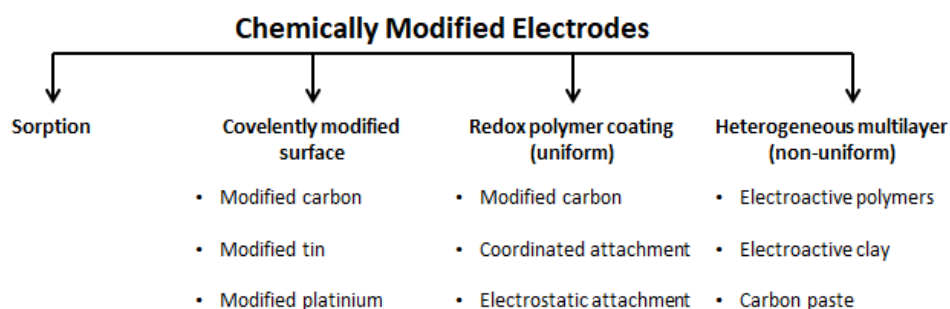


Figure 1. 3 Schematic representation for various kinds of CME preparation routes (Catrinel et al., 2007)

Ionomer loading polymers are polycation or polyanion ion exchange polymers containing electroactive species. Ion exchange polymers are bonded to the electrode surface by coating by rotating the electrode or by evaporating the solvent when immersed in the solution containing the electroactive species or species. The electroactive species binds to the ion exchange polymer via electrostatic force. One of the most widely known and used ion exchange polymers is the perfluorosulfonate ion exchanger Nafion (Lane and Hubbard, 1972).

At the study of Lane et al, they investigated the electropolymerization of pyrrole, aniline or N-methylpyrrole in the presence of polyanions such as poly(vinylsulphate) and poly-(styrenesulfonate) and found that there is an electroactive ion in a wide potential range (Lane and Hubbard, 1972). In another study, electroactive inorganic cations such as $\text{Co}(2,2'\text{-bipyridine})_3^{2+}$ and $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ were included in polystyrene sulfonate (Shaw et al., 1982.). It was used by Nafion Yagi et al. to investigate the charge transfer properties of $\text{tris}(2,2'\text{-bipyridine})\text{Ru}^{2+}$ (Yagi et al., 1997). The charge transport parameters proceed through two processes: physical displacement of the electroactive center and electron exchange between the electroactive centers and electron bounce. While this method is useful in examining the charge-carrying properties of redox-active species in membranes, it has a major disadvantage that electroactive species are not bound irreversibly to the ion-exchange structure and therefore leak into the solution (Lane and Hubbard, 1972).

The redox polymers are formed by bonding a redox active centered polymer film to a redox inactive polymer. These polymers can be synthesized in large quantities and then fixed to electrode surfaces by spin coating or dip coating methods. Low solubility is one of the biggest barriers to using redox polymers. The charge transfer mechanism has been described as electron self-exchange or electron jumping only between neighboring redox centers. Such polymers show conductivity only in the limited potential range. Neelamraju et al. incorporated $\text{Fe}(\text{CN})_5^{3-}$ into poly(4-vinylpyridine) by coordination, and the polymer was attached to the graphite electrode by solvent evaporation (Neelamraju et al., 2018).

One of the most successful and sensitive ways to form a redox polymer on the electrode surface is electropolymerization using the cyclic voltammetry technique. Electropolymerization is a frequently preferred method in recent years, as it allows consistent reproducibility and monitoring of polymer film thickness. Multi-layer polymer films have more electroactive sites and up to 1000 layers can be formed on a single electrode surface under suitable conditions. (Murray et al., 1980). Iron and ruthenium complexes of 2,2-bipyridine on platinum, glassy carbon and metal oxide electrodes were modified by Ellis and Meyer and the selectivity of charge transfer to redox species was increased (Brown, 2018). Metalloporphyrins have been used in electropolymerization by several research groups. Nickel (II) and cobalt(II)-tetraphenylporphyrins with amino-, hydroxy-, and pyrrole- were used in electropolymerization by Murray et al (Bettelheim et al., 1987). The mechanisms for preparing polymeric multilayer films are based on similar principles for forming radical cations and anions that bind together.

Electronically conducting polymers are marked with delocalized extended π -electron systems. They can be formed analogously to redox polymers by electropolymerization schemes. Pyrrole, used by Diaz and Kanazawa, was one of the first compounds used to form these polymers. For example, pyrrole forms a polymeric film with the help of a radical cation intermediate (Diaz et al., 1979). In different ongoing studies, aniline, furan and other heterocyclic aromatic compounds have also been investigated. Electropolymerization is subject to Faraday's Law, so the film thickness is easy to follow.

Charge transfer within the electropolymerized film is coupled to electron jumps between chains connecting the exit or entry of counter ions to maintain charge electroneutrality during electrochemical characterization or electrical stimulation. Chain alignment plays an important role in the conductivity of these films and the kinetics of charge transfer. Film thickness is important in sensor design because analytes can migrate from the film to the electrode surface or partially to the electrode interface to enter the charge transfer electrocatalytic reaction (Azzaroni et al., 2008).

Electropolymerized thin films have been primarily preferred in the design of amperometric and spectroelectrochemical sensors, as they increase surface selectivity. Important advantages of electropolymerized thin films and coatings are their ability to control the chemical and physical behavior of the reaction system and to provide a higher effective concentration per unit area for the reactions that occur (Brown., 2018). The main challenge in electropolymer film design is to control the reactivity with the selected compounds and to adapt the appropriate molecular architecture for orientation. (Long Xue et al., 2020 and Machatschek et al., 2020). One of the most widely used technique for developing electropolymeric films on various electrode surfaces is electropolymerization by cyclic voltammetry (Dong et al., 2021). This method allows the production of polymeric films that are consistent and sensitive in terms of reactivity to specific molecular structures and compounds.

They are used as procedures for sorption-based chemically modified electrodes (CME) with altered physical and chemical interaction properties in the creation of monolayer structures. The main advantage of this method is easy surface modification and the selectivity can be increased by the presence of functional groups. The ability to provide covalent modification on the electrode surface with the help of a specific functional group is frequently used in the preparation of chemically modified electrodes. For example, glassy carbon electrodes (GCEs) formed from -C=O , C-O- and oxide electrodes with -OH functional groups are frequently used in various applications (Filink et al., 2000; Mandler and Turyan, 1996).

Factors such as the lattice arrangement of the polymer, the film thickness, the type and content of solvent in the film, and ion entry and exit in or out of the polymer film affect the electrochemical reactivity of the compounds towards polymeric films (Gvozdenovic et al. 2014, Paulson et al., 2001). A number of electrochemical techniques such as cyclic voltammetry, square wave voltammetry, spectroelectrochemical techniques and electrochemical impedance spectroscopy are also used to characterize the modified electrodes.

1.2.2 Types of chemically modified electrodes and their applications

In recent years, studies have been carried out by many researchers to modify conventional electrodes with different methods and use them in sensitization. For electrodes modification; polymers (Ulubay Karabiberoğlu and Dursun, 2017, Htut et al., 2017), metal nanoparticles (Ahmet et al, 2019, Feyami et al., 2017), carbon nanotubes (Aktürk et al., 2017, Hudari et al., 2018), mesoporous carbon materials (MCMs) (Sakai et al., 2017, Li et al, 2016) and metal oxides (Chrzescijanska et al., 2013, Rahman et al., 2016) are mainly used as a conductive modifiers.

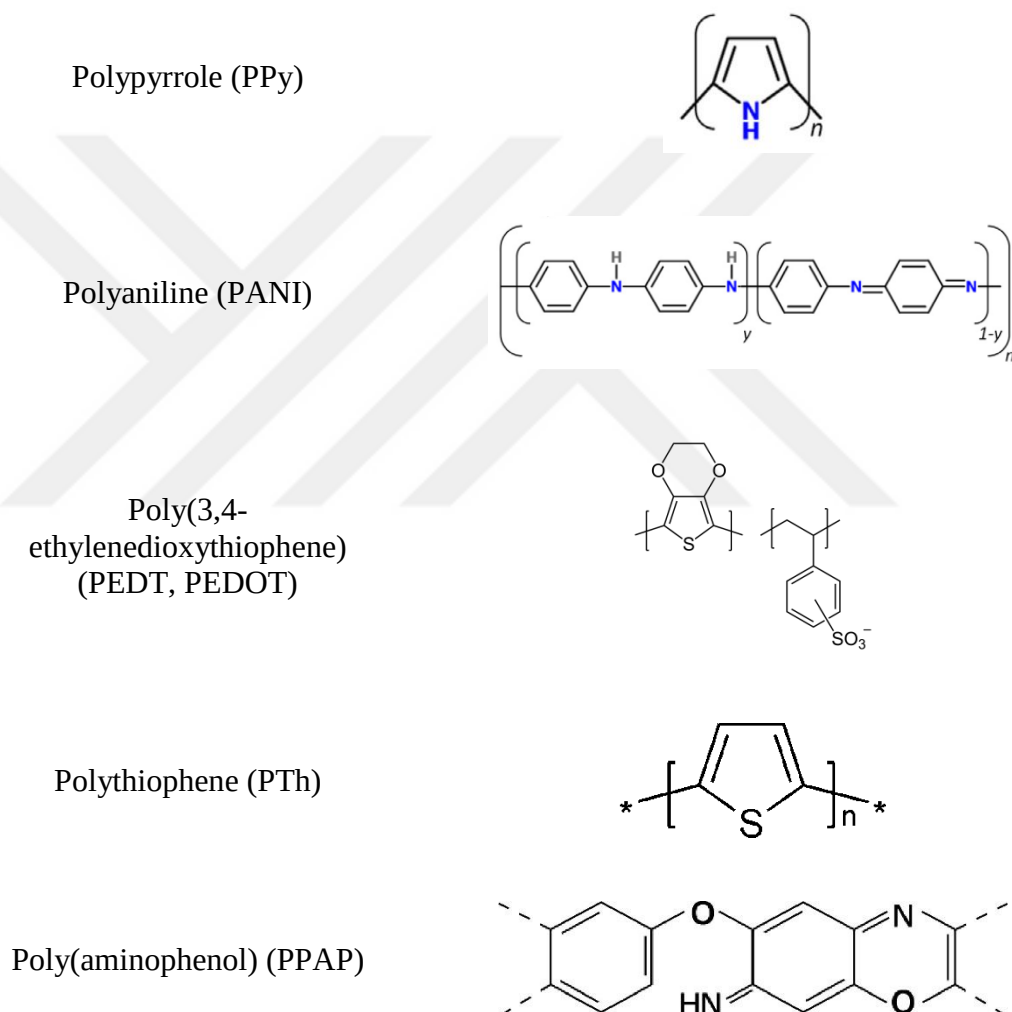
1.2.2.1 Conducting polymer films

For many years, polymers were thought to be insulators and worked in this way. In fact, until recently any electrical conduction was generally undesirable in polymers. However, the ionic properties of polymer electrolytes and polyelectrolytes have opened new horizons for the use of conductive polymers in electrochemical investigations in chemistry and physics in the last few decades (Inzelt, 2011).

The emergence of conductive polymers began in the 1970s with the discovery of a new polymer with high electronic conductivity in a partially oxidized state. Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa played a major role in this work and were awarded the Nobel Prize in Chemistry in 2000 "for the discovery and development of electronically conductive polymers" for their work. (Shirakawa et al., 1977, MacDiarmid, 2001 and Heeger., 2001). Electrochemical studies have made a great contribution to the preparation and determination of these new materials in the scientific world.

Electrochemical methods are well suited for the controlled synthesis of conductive polymers. System preparation, characterization and application of electrochemically active, electronically conductive polymer still has great popularity today. The search for specific polymer groups (Roncali., 1992 and Stejskal and Sapurina, 2005) their characterization or their application areas (Gerard et al., 2002) continues to be studied. Table 1. 1 lists a few of the commonly used conductive polymers (Kumar and Sharma, 1997).

Table 1.1 List and abbreviations of some conductive polymers



Although most redox polymers have been synthesized by chemical polymerization, the polymers can be prepared using chemical and/or electrochemical polymerization techniques. Electrochemically active groups are either incorporated into the polymer structure within the chain or incorporated as a pendant group, added to the polymer phase during polymerization, or, in the case of polymer film electrodes, fixed to the polymer network in an additional step

after the coating procedure. The second approach is typical for the ion exchange polymers detailed above. In terms of applications, inexpensive, simple, aromatic (mainly amines) benzoides (e.g. aniline (Molina et al., 2019), diphenylamine (Orlov et al, 2005)) and heterocyclic compounds (e.g. pyrroles (Maruthapandi and Gedanken, 2019, Audebert, 2010), thiophenes (Livi et al., 2014) are extremely interesting. The surface morphology of conductive polymers varies greatly according to the electropolymerization conditions. The effect of pH on the electropolymerization of aniline monomer was investigated, and it was observed that the species formed by pH differences also changed. (Sapurina and Stejskal, 2011). Some of conductive polymers have been frequently prepared by for electropolymerization which are summarized as follows.

Polypyrrole (Ppy)

Polypyrrole (Ppy), whose chemical structure is indicated in Table 1.1, is one of the most studied conductive polymers in many different studies. Ppy is often chosen because it has many excellent properties and sensitivities that make it a "smart" biomaterial. (Garner et al., 1999, B. Garner et al.,1999). Some of the most important are their high in vitro and in vivo biocompatibility (Kim et al, 2006). These parts have high chemical stability (Bousalem et al 2004.) and conductivity in air and water (Li et al, 2004).

In addition to its positive properties, unfortunately, Ppy is very difficult to process after synthesis, because its molecular structure is not thermoplastic, so it does not remain mechanically flexible after synthesis and becomes insoluble in water (Bousalem et al 2004.). Today, PPy is used in numerous applications, including fuel cells (Woon Lee et al., 2006), corrosion protection (Castano et al., 2004), computer displays (Woon Lee et al., 2006), biosensors (Castano et al., 2004) and drug delivery systems (Castano et al., 2004).

Polyaniline (PANI)

Polyaniline (PANI) is the most studied conductive polymer after Ppy. It exists in various forms known as pernigraniline, emeraldine and leucoemeraldine depending on the level of oxidation, the most stable and conductive of which is the half-oxidized emeraldine form (Zhou et al., 2009). PANI is highly

advantageous because of its ease of synthesis, low cost, high environmental stability, and electrical switching properties between resistive states (Cullen et al., 2008). However, its usability in biological applications is limited due to its low processability, low flexibility and biodegradation (Huang et al., 2008). In contrast, PANI has been explored for applications such as biosensors (Liu et al., 2009), controlled drug release (Humpolicek et al., 2012), and tissue engineering (Peramo et al., 2008).

Polythiophene derivatives (PEDOT and Polythiophene)

Other conductive polymers mostly used in studies are poly (3,4-ethylenedioxythiophene) (PEDOT) and polythiophene (PTh) derivatives (Table 1.1) (Peramo et al., 2008). Compared to PEDOT, due to its chemical structure (Table 1.1), PEDOT provides better working condition by lowering the reduction and oxidation potentials. For this reason, PEDOT has better conductivity, thermal and environmental stability than PTh (Zhou et al., 2009). Today, PEDOT is used in biosensor and bioengineering field applications (Peramo et al., 2008).

Poly(aminophenol) (PPAP)

Although p-aminophenol has been used only in limited numbers in polymer synthesis, it is an interesting starting monomer due to the presence of two functional groups with different reactivity (Kurita 1990). Aminophenols contain –OH and –NH₂ groups together in their structures and have the ability to oxidize through these groups (Table 1.1). In addition, the types of these groups called “middle, meta and para” according to their syntax in phenyl rings show different electrochemical properties (Thenmozhi et al., 2011). PPAP is used as conductive polymer in biochemical and electrochemical studies for the detection of hormones alongside each other (Koçak and Dursun, 2013) and enzyme studies (Thenmozhi et al., 2011).

1.2.2.2 Metal nanoparticles

In recent years, a significant increase has been observed in "nanochemistry" studies. In the studies, multifunctional supermolecules (Gontero et al., 2017), carbon nanotubes (Tabassum et al., 2019) and metal and

semiconductor nanoparticles (Kumar K et. Al., 2018 and Suresh, 2013) were synthesized and formed the building blocks of many electronic studies, especially optical and electronic devices (Kelly et al., 2003). Metal particles are highly preferred in “nano” scale systems due to their easy synthesis and chemical interchangeability. Especially in terms of understanding the effects of optical and electronic properties and structures, metal nanoparticles provide great advantages over bulk metals because of their extremely small surface area (i.e., < 5 nm).

Methods such as photochemical and chemical reduction and electrochemical techniques (Chen et al., 2001 and Geethalakshmi, 2012, McDarby et al., 2020, Yanilkin et al., 2018 and Singaravelan et al., 2015), hydrothermal synthesis (Gan et al., 2020), RF magnetron co-sputtering deposition (Battaglin et al., 2004), sol-gel (Parashar et al., 2020), chemical reduction method (Arvizo et al., 2011) are used for the preparation and stabilization of metal nanoparticles. Among these methods, electrochemical methods are primarily preferred because of their low cost, short time, control of grain size, and low concentration but high purity metal nanoparticles (Ulubay and Dursun, 2010).

The choice of metal nanoparticle preparation method is very important, as the kinetics of the communication of metal ions with the reducing agent has a great effect on the surface structure and size after the adsorption between the substance-metal nanoparticle and the synthesis of nanoparticles. By choosing the appropriate method, the stability of the chemical, physical and physicochemical properties of metal nanoparticles can be increased (Vijayakumar et al., 2013).

There are two main basic methods for the synthesis of metal nanoparticles: top-down methods and bottom-up method, which are shown in Figure 1.4. The main differences of these methods are the starting material (Govindrao Jamkhande et al., 2019).

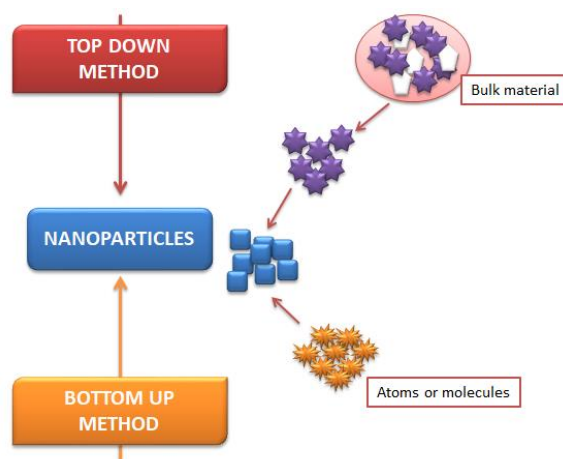


Figure 1. 4 An overview of top down and bottom up method. (Govindrao Jamkhande et al., 2019).

In the top-down method, there is a conversion from bulk materials to nano-sized particles (Figure 1.5). Nanoparticles are based on the reduction of the size of the large starting material to nano size by different chemical and physical treatment (Meyers et al., 2006). Although these methods are easy to perform, they are not suitable for the preparation of very small particles, and the observed change in the surface chemistry and physicochemical properties of nanoparticles is the biggest disadvantage (Nadagouda et al., 2011).

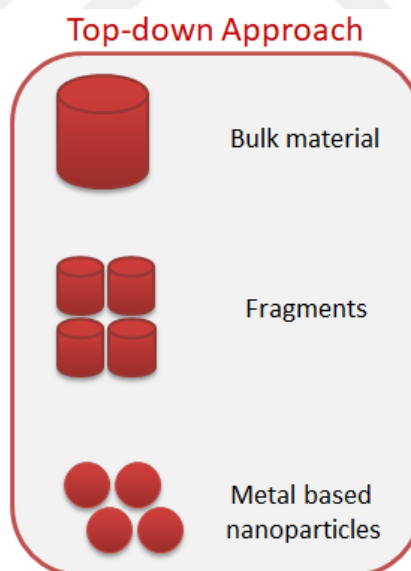


Figure 1. 5 A basic shown for top to down method (Sanchez-Lopez et al., 2020).

In nanoparticle synthesis with the bottom-up method, small particles are formed by combining atoms or molecules. With this method, firstly, nano-building blocks of nanoparticles are formed and then they come together for nanoparticle preparation (Mukherjee et al., 2001).

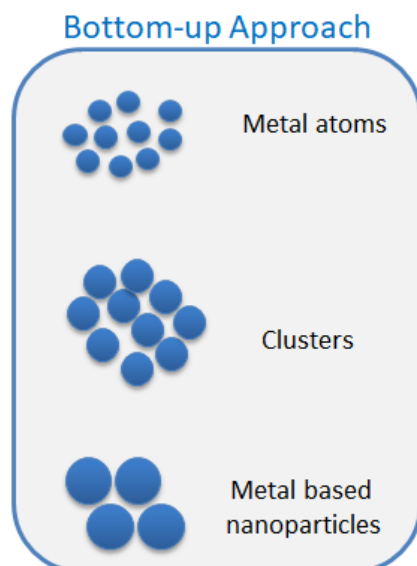


Figure 1. 6 A basic shown for down to top method (Sanchez-Lopez et al., 2020).

Compared to other metal nanoparticles, noble metal nanoparticles such as Cu, Ag, Pt and Au attract more attention by researchers. (Ramalingam et al., 2019). Especially gold nanoparticles have been frequently used in many medical, biological, chemical and physical studies in recent years due to their high stability (Hu et al., 2020). Besides, Pt is another preferred noble metal after Au nanoparticle due to its catalytic activity. However, due to its cost, many researchers have prepared nanoparticles with the help of Pt thin film and Pt alloys in order to reduce the Pt content in the electrodes (Sanchez-Ramos et al., 2022).

Cu nanoparticles have also been used in many studies due to their high availability in nature and low cost. Due to its susceptibility to oxidation under atmospheric conditions, studies are carried out to develop supporting materials to increase its sensitivity and stability (Gawande et al., 2016).

The fact that Cu can be in different oxidation stages as Cu (0), Cu (I), Cu (II) and Cu (III) allows it to enter into various reactions with both single and two electrons. Due to this feature, Cu nanoparticles are used in many nano technological applications where catalytic reactions, electro and photo catalysis reactions (Shih et al., 2013 and Yin et al., 2015).

Sun et al developed a method for the detection of protein kinase by the gold nanoparticle-based colorimetric detection method. In his studies, he performed in situ work with Au nanoparticle modified electrode. He used

electrochemical impedance spectroscopy for the variability of the surface properties. They have shown that new optical or electronic biosensors can be developed with their studies (Sun et al., 2017).

Mori et al., in their study, aimed to develop a bio device that can be used for the determination of enzyme structure and activity by placing gold nanoparticles between the enzyme and the electrode surface. For this, he investigated the enzymatic and electrochemical properties of Quinone-dependent glucose dehydrogenase absorbed into gold nanoparticles of different grain sizes. As a result of the examinations made with the cyclic voltammetry technique, they found that the use of 20 nm size in the gold nanoparticle provided the best results (Mori et al., 2021).

According to Song et al study, Cu nanoparticles investigated the electrochemical transformation of CO₂. For this purpose, Cu nanoparticles were studied by linear scanning voltammetric method using N-doped graphene electrode. According to their findings, they found that CO₂ was converted to ethanol (84%) with high faradaic efficiency (Song et al., 2016).

As a result, metal nanoparticles continue to be used in electrochemical, physical and biological studies due to the large surface area and their contribution to increasing the electrocatalytic efficiency.

1.2.2.3 Mesoporous carbon materials (MCMs)

Today, the use of porous carbon-based materials has gained importance in many modern studies and technologies such as purification of water and air, catalysis, energy applications, energy storage and chromatography, due to their high surface area, large pore volume, chemically inertness and mechanical strength. Porous carbon materials, depending on their pore widths; classified as microporous (<2 nm), mesoporous (2-50 nm), and macro porous (>50 nm) (Figure 1.7) (Ryoo et al., 2001).

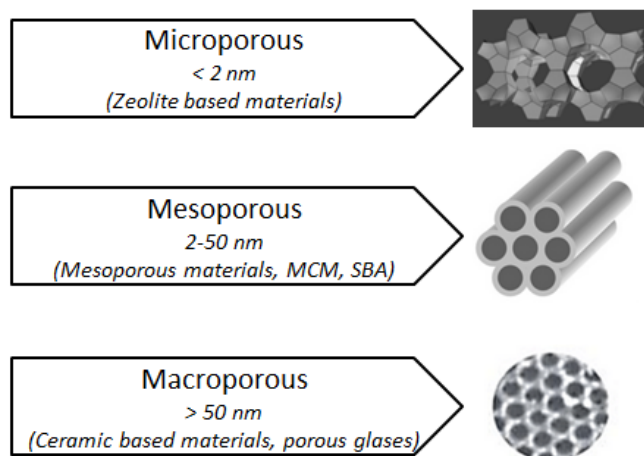


Figure 1. 7 Classification of porous materials according to IUPAC (Chaudhary et. al., 2017).

Porous carbons are generally obtained by activating natural or synthetic starting materials after the carbonization procedure. The microporous structure of most porous carbons makes them usable in many applications such as molecular sieving, adsorption and catalytic reactions (Foley, 1995). In addition, they can be used for methods such as adsorption of large molecules such as vitamins, optic, chromatographic applications, or for carbon-based materials such as electrochemical capacitors and lithium batteries (Figure 1.8). For such applications, choosing mesoporous carbon materials with different dimensional structures ranging from 2-50 nm provides more advantages (Kyotani., 2000, Asgari et al., 2015 and Karimi et al., 2016). For all these reasons, interest in the use of porous carbon has increased considerably in recent years.

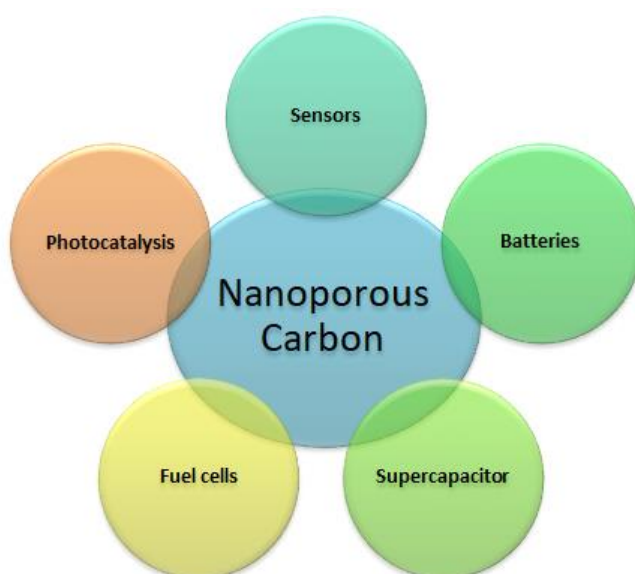


Figure 1. 8 An illustration of the synthesis and applications of micro and mesoporous carbons. (Benzigar et al., 2017).

In order to prepare carbon-based materials in structures developed for special applications; 1) activation of carbon by physical or chemical treatment at surface temperature (Shou et al., 2015), 2) carbonization of carbon initiator consisting of thermosetting and thermally unstable component (Liang et al., 2008), 3) self-assembly using soft template with condensation and carbonization (Liang and Dai, 2006 and Ghimbeu et al., 2014)) and 4) synthetic methods have been developed such as resynthesis with pre-hardened templates by impregnation, carbonization, and de-stencil removal (Ryoo et al., 2001). These methods include the so-called (3) soft template synthesis and (4) the hard template synthesis; they have been used frequently in recent years because they are the most successful methods in the control of pore structures, pore distribution and especially in the preparation of mesoporous structures.

Hard templating method for MCMs

As shown in Figure 1.9, mesoporous silica is used as a template or pre-synthesized in hard template synthesis. The carbon initiator is then filled into the pores and carbonization is performed. Finally, the silica template is removed from the medium by using NaOH or HF at the appropriate concentration (Jun et al., 2000).

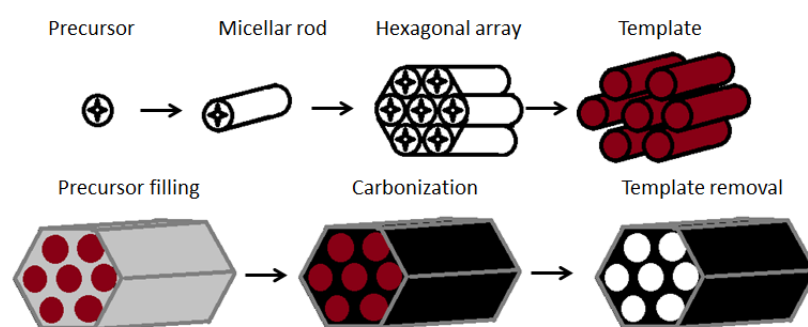


Figure 1. 9 An illustration of hard template based synthesis of MCMs . (Jun et al., 2000).

Porous silica was first discovered by Yanagisawa et al. in 1990 (Yanagisawa et al., 1990). As a result of the ongoing studies, the subject has gained great popularity with the synthesis of MCM-41 (material-41) with the liquid crystal coating mechanism. Because MCM-41 materials have attracted a lot of attention due to their special surface areas, which vary in the range of 1-10 nm and can be over $700 \text{ m}^2 \text{ g}^{-1}$ (Kresge et al., 1992 and , Beck et al., 1992). In the

following years, many new mesos such as SBA-1,(Huo et al., 1994 and Kim et al., 1999) SBA-2,(Huo et al., 1995) MCM-48,(Alfredsson and Anderson, 1996 and Sayari 2000) SBA-6,(Sakamoto et al., 2000) SBA-8,(Zhao et al., 1999) SBA-n porous structure has been developed.

Soft templating method for MCMs

The soft template synthesis used to produce porous carbons is shown in Figure 1.10. In soft template synthesis, the block copolymer directly self-assembles to form MCM (Fig. 1.10-A), followed by solidification by condensation (Fig. 1.10-B), and finally MCMs are obtained by carbonization of carbon initiators (Fig. 1.10-C) ((Liang et al., 2008 and Lu et al., 2008). In soft template synthesis 1) the ability of the organic initiator to self-assemble on the mesostructured, 2) the capacity of crosslinked initiators around the organic template, without affecting the mesostructured in the following steps, and 3) Requirements such as the strength of the carbon initiators that guide the structure during condensation and solidification are very important.

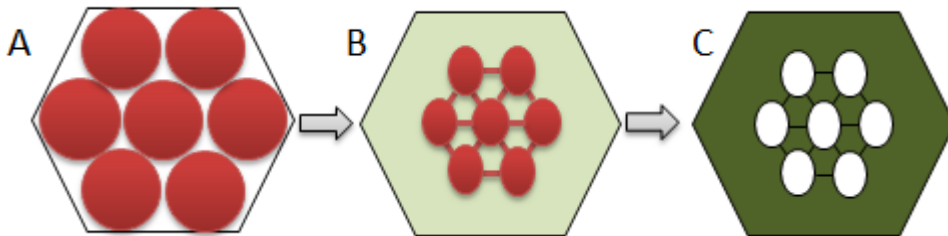


Figure 1. 10 Schematics illustration of soft template based synthesis of MCMs. (Shou et al., 2015).

The biggest advantage of soft template synthesis over hard template synthesis is that it does not require sodium hydroxide (NaOH) or hydrogen fluoride (HF) solution used in hard template synthesis to remove the silica template. However, it has disadvantages such as complex step processes, low self-assembly rate, limited number of initiators, and obtaining OMC products with less usage (Liang and Dai, 2006 and Ghimbeu et al., 2014). Therefore, the use of hard template synthesis is more common.

Ordered mesoporous carbon films have been successfully prepared via the the so-called evaporation induced self-assembly (EISA) pathway by using

resorcinol as the carbon precursor in non-aqueous solution under nearly neutral conditions (Meng et al., 2005), or by using resorcinol formaldehyde (RF) resin as the carbon precursors under acid conditions (Tanaka et al., 2005) and basic conditions (Liu et al., 2007). In addition to the techniques mentioned, mesoporous carbon film structures were prepared by the evaporation-induced self-assembly (shortly called EISA) method using resorcinol-formaldehyde as a carbon initiator in non-aqueous solution under neutral conditions (He et al., 2012). However, the EISA method is not suitable due to difficulties such as large amount of organic solvent evaporation requirement, sample collection, and proper reactor design. However, the reaction takes about 3-7 days to complete. For this reason, studies have been carried out on the development of a method in which self-assembly and condensation occurs rapidly at room temperature (Yan Huang et al., 2008 and Liu et al., 2011).

RF resin is an organic monomer frequently used in synthesizing mesoporous carbon via carbon gel and organic sol-gel. It can be used as a catalyst with both acid and base in the polymerization reaction of resorcinol with formaldehyde (Figure 1.11). In the presence of a catalyst, formaldehyde is activated by the protonation reaction. Protonated formaldehyde reacts with the active sites of resorcinol to form the labile hydroxymethyl group. When the base is used as a catalyst, the reaction between resorcinol and formaldehyde can take place at ambient temperature (Xu et al., 2012).

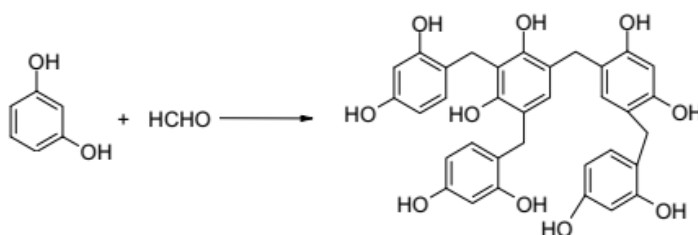


Figure 1. 11 Schematics illustration of synthesis of mesoporous RF polymer (Xu et al., 2012).

It is a very interesting subject because of the studies carried out on mesoporous carbon materials, both on the development of synthesis methods and on the surface modifications of the obtained synthesis products. In the following paragraphs, literature informations are explained about some studies with MCM.

Park et al., study, prepared the anatase TiO_2 phosphocatalyst by synthesizing it together with the ordered mesoporous carbon CMK-3. The morphology of the prepared CMK-3 supported TiO_2 surface was elucidated by X-ray diffraction, nitrogen physisorption and electron microscopy techniques. Photocatalytic efficiency of Rhodamine 6G dye solutions was investigated by using CMK-3 supported TiO_2 prepared under UV light. When the study was analyzed in parallel with commercial photocatalyst P25 and TiO_2 , it was observed that the prepared material provided higher efficiency than commercial catalysts (Park et al., 2008).

Pérez-Rodríguez et al. investigated the electrochemical reduction of CO_2 in 0.1 M KHCO_3 , using regular mesoporous carbons (OMCs) for catalyst support of Pd nanoparticles. OMC materials were synthesized using the SBA-15 stable template. Tetraethyl orthosilicate (TEOS) as silicone initiator and Pluronic P123 (P123) as surfactant were used, TEOS/P123 material was prepared using 2 or 5 mass ratios. After purification with NaOH, ethanol or HF, silica particles were removed and OMCs with different surface structures were obtained. Pd nanoparticles were deposited on this synthesized OMC material and the Pd/OMC electrocatalyst to be used in electrochemical studies was prepared. It has been found that the TEOS/P123 ratio has an effect on the formed OMC surface, and it has an effect on the electrochemical reduction of CO_2 in these OMC materials. The best results were observed with a mass ratio of 5 for TEOS/P123 (Pérez-Rodríguez et al, 2020).

Zhai et al. synthesized an ordered mesoporous carbon/nickel nanoparticle composite material using from resol, tetraethyl orthosilicate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and triblock copolymer F127, and removed the silicates in the environment with NaOH. According to the results of the investigation, they found that the MCM/Ni composite materials with low Ni content have regular and 2D hexagonal shape, large pore structure, high surface area and large pore volume. In their study with this superparamagnetic modified material, they found that excellent adsorption properties were provided for the fuchsin-based paint material and they developed an easy separation procedure (Zhai et al., 2011).

The Pt/CMK-5 catalysts exhibited superior electrocatalytic mass activity toward oxygen reduction in a half-cell configuration, compared to the Pt particles supported on conventional porous carbons such as carbon black, activated carbon and activated carbon fiber. The origin of such high catalytic activity of CMK-5 carbon supported Pt catalysts was attributed to the high metal dispersion and mesoporous structure of the CMK-5 carbon support.

The use of OMC materials from fuel cells was investigated by Joo et al. In the presence of H₂ gas, they provided a homogeneous distribution of Pt initiator (H₂PtCl₆) on the hexagonal CMK-5 mesoporous structure by wet impregnation. Although the Pt loading of the particle size on CMK-5 of the obtained Pt catalyst was twice as much by weight, it could be controlled below 3nm. It was observed that the prepared Pt/CMK-5 catalysts showed higher electrocatalytic activity towards ORR in the judgment cell configuration compared to conventional porous carbons such as carbon black, activated carbon. This source of high catalytic activity was attributed to the carbon support material and porous structure of CMK-5 to metal dispersion by Joo et al (Joo et al., 2001).

1.3 Electrochemical Reduction of Carbondioxide

The history of fossil fuel consumption dates back to the industrial revolution. Since those days, the use of fossil fuels has continued to accelerate with the increase in industrialization. The most significant disadvantage of using fossil fuels is that they cause carbon dioxide (CO₂) emissions due to chemical reactions. While the global CO₂ concentration decreased in 2020, it increased to 36.3 gigatons, with a 6% increase in 2021 and 2022 (Liu et al., 2022).

The most common method for reducing the increased CO₂ concentration is converting CO₂ into useful forms. The methods used for this purpose are divided into two as chemical and physical (Rogelj et al., 2016).

Biochemical (Sultana et al., 2016), electrochemical (Zheng et al., 2018), photochemical (Habisreutinger et al., 2013), radiochemical (Grodzowski and Neta, 2001) and thermochemical methods (Navarro-Jaén et al., 2021) are used for the chemical conversion of CO₂ in the atmosphere (Figure 1.12). Among these methods, the reduction of CO₂ by the electrochemical process; is one of the most

preferred methods because of its advantages such as i) being able to work at ambient temperature and pressure, ii) the working potential of the formed species, being able to be changed by parameters such as electrolyte solution selection, catalyst, iii) storing electrons in the reaction.

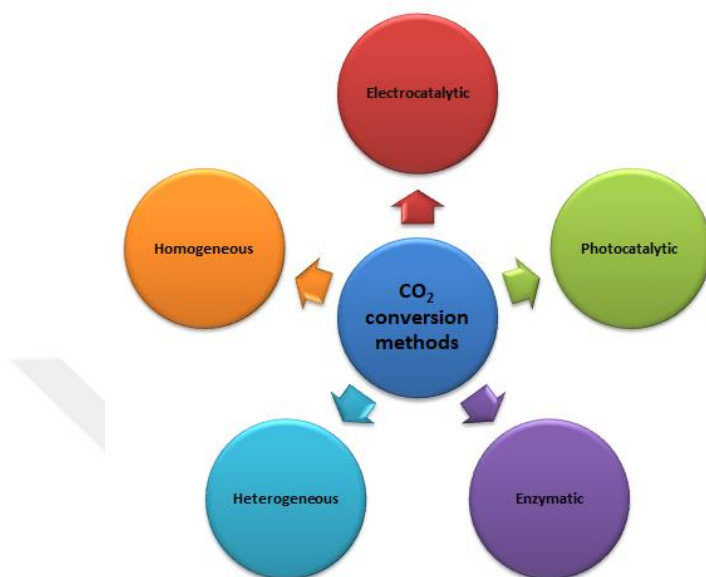


Figure 1. 12 Chemical methods for CO₂ conversion

Since CO₂ contains two concentric, four-electron delocalized p-bonds, its existing bonds have triple-bap-like properties and are of high thermal stability. Therefore, a high overpotential is required for CO₂ activation. This leads to low energy efficiency. As a result, the electrochemical reduction of CO₂ (CO₂RR) is a complex process. The recovery products of CO₂ from 1967 to the present are shown in Figure 1.13 (Jin et al., 2021).

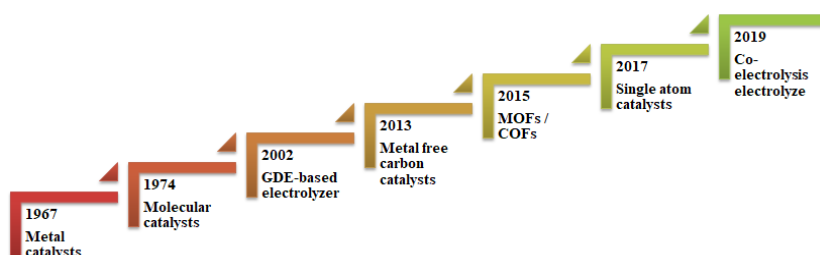


Figure 1. 13 Short summarize of developments in the electrochemical conversion of CO₂ (Jin et al, 2021).

CO₂RR can occur at low and high temperatures, in aqueous and non-aqueous media, by reduction with 2, 4, 6, and 8 electrons, and the main types formed are carbon monoxide (CO), formic acid (HCOOH), oxalic acid (H₂C₂O₄)

or oxalate, formaldehyde (CH_2O), methanol (CH_3OH), methane. (CH_4), ethylene (CH_2CH_2), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) (Qiao et al., 2014). CO_2RR electrochemical half-reactions and standard electrode potentials are given in Table 1.2.

Table 1.2 Standard potentials of CO_2 in aq. solutions (V vs.SHE) at 1.0 atm and 25°C (Bard et al., 1985).

Half-electrochemical Thermodynamic reactions							Electrode potentials (V vs. SHE) under standartd conditions
CO ₂ (g)	+	4H ⁺	+	4e ⁻	=	C(s) + 2H ₂ O(l)	-0.210
CO ₂ (g)	+	2H ₂ O(l)	+	4e ⁻	=	C(s) + 4OH ⁻	-0.627
CO ₂ (g)	+	2H ⁺	+	2e ⁻	=	HCOOH(l)	-0.250
CO ₂ (g)	+	2H ₂ O(l)	+	2e ⁻	=	HCOO ⁻ (aq) + OH ⁻	-1.078
CO ₂ (g)	+	2H ⁺	+	2e ⁻	=	CO(g) + H ₂ O(l)	-0.106
CO ₂ (g)	+	2H ₂ O(l)	+	2e ⁻	=	CO(g) + 2OH ⁻	-0.934
CO ₂ (g)	+	4H ⁺	+	4e ⁻	=	CH ₂ O(l) + H ₂ O(l)	-0.070
CO ₂ (g)	+	3H ₂ O(l)	+	4e ⁻	=	CH ₂ O(l) + 4OH ⁻	-0.898
CO ₂ (g)	+	6H ⁺	+	6e ⁻	=	CH ₃ OH(l) + H ₂ O(l)	-0.016
CO ₂ (g)	+	5H ₂ O(l)	+	6e ⁻	=	CH ₃ OH(l) + 6OH ⁻	-0.812
CO ₂ (g)	+	8H ⁺	+	8e ⁻	=	CH ₄ (g) + 2H ₂ O(l)	-0.169
CO ₂ (g)	+	6H ₂ O(l)	+	8e ⁻	=	CH ₄ (g) + 8OH ⁻	-0.659
CO ₂ (g)	+	2H ⁺	+	2e ⁻	=	H ₂ C ₂ O ₄ (aq)	-0.500
CO ₂ (g)	+	2e ⁻	=	C ₂ O ₄ ²⁻ (aq)			-0.590
CO ₂ (g)	+	2H ⁺	+	2e ⁻	=	CH ₂ CH ₂ (g) + 4H ₂ O(l)	-0.064
CO ₂ (g)	+	6H ₂ O(l)	+	12e ⁻	=	CH ₂ CH ₂ (g) + 12OH ⁻	-0.764
CO ₂ (g)	+	12H ⁺	+	12e ⁻	=	CH ₃ CH ₂ OH(l) + 3H ₂ O(l)	-0.084
CO ₂ (g)	+	9H ₂ O(l)	+	12e ⁻	=	CH ₃ CH ₂ OH(l) + 12OH ⁻	-0.744

The activity and selectivity of CO_2RR are mainly determined by the binding energy of the intermediates associated with each of the multiple reaction steps along the reaction pathway. The binding energies of different intermediates are proportionally related via thermodynamic scaling relationships. Therefore, we cannot optimize the critical power of a particular arbitrator without affecting the other. Furthermore, hydrogen bonding on catalysts should also be considered, given that the hydrogen evolution reaction (HER) is the dominant competitive reaction in aqueous solutions. Therefore, strategies should be adopted to break scaling relationships and suppress HER to increase the activity of CO_2RR and improve the selectivity of the CO_2 product (Verma et al., 2019). In the following section, the materials used in the interface for the electrochemical reduction of CO_2 are detailed.

Metal Based Electrocatalysts

In recent years, the use of metal-based electrocatalysts such as metals, oxides, sulfides, and alloys has become widespread in the electrochemical

reduction of CO₂. These materials generally facilitate electron transfer due to their high conductivity and surface active sites, so metal-based catalysts significantly affect their catalytic performance. They are widely used in CO₂RR since the metal-based catalysts' surface structure can be controlled, and the system can be changed, affecting the catalytic efficiency and stability (Chen et al., 2012).

Cu electrodes consisting of Cu₂O layers obtained with Cu foil annealed at 130°C and 500°C were prepared for the CO₂RR study by Li et al. It has been determined that Cu₂O layers formed in different micron thicknesses include electrodes that cannot be distinguished from crystallized Cu. It has been found that the high roughness provided by the prepared Cu₂O electrode requires 0.5 V less overpotential than the Cu electrodes for the reduction of CO₂. As a result, CO₂RR was supplied by the metal-based electrocatalysis method and allowed the development of suitable catalysts for electrolytic fuel synthesis (Li et al., 2012).

Another metal-based catalyst used in the electrochemical reduction of CO₂ is those containing silver. Lu et al. worked with conventional polycrystalline Ag electrocatalyst in their study. They developed a CO₂RR sensitive electrocatalyst with a selectivity of 92%, which is approximately 3000 times higher than its polycrystalline counterparts under 0.5V medium-extreme potential. At the same time, they have seen that the electrocatalyst have approximately 150 times larger surface area than the conventional ones, therefore, the thermodynamic barrier is more easily overcome in the reduction of CO₂ (Lu et al., 2014).

Single-Atom Catalysts (SAC)

Although positive and promising results have been obtained, the cast metal catalysts may adversely affect the CO₂RR activity or selectivity. For this reason, SACs, known as single-atom catalysts, can provide the advantages of homogeneous and heterogeneous catalysts with metal atoms dispersed on a solid substrate with a single catalyst (Yuanjun Chen et al., 2018). Since the valence electrons in the d-band of a metal atom in SACs are close to the Fermi level, it allows fast electron transfer. It supports the absorption of CO₂ intermediates by allowing the high activation barrier to be easily overcome. Single-atom catalysts can only catalyze single-molecule reactions and provide increased stability due to

the strong bonding force between the metal atom and the coordinated regions. For this reason, SAC catalysts are considered promising for CO₂RR.

In their study, Jiao et al. showed that CO₂RR could be converted to CO with Cu₁⁰-Cu₁^{x+} atom pair. In their research, Cu₁⁰ adsorbed CO₂, and Cu₁^{x+} adsorbed H₂O, thus reducing the CO₂ activation energy. As a result, HER, the highest peaks for CO₂RR, was almost eliminated, and CO₂RR was achieved with very high efficiency (92%) (Jiao et al., 2019).

Similarly, Ren and coworkers prepared a bimetallic diatomaceous Ni-Fe electrocatalyst that supports each other on nitrogen-doped carbon for CO₂RR. With the catalyst they prepared, they performed a high-resistance CO₂RR, with an efficiency of over 90% in the potential range of 0.5-0.9 V and an efficiency of 99% after 30 hours (Ren et al., 2019).

Metal-Free Carbon-Based Materials

Metal-free carbon-based materials have been used in many recent studies in many fields due to their properties, such as resistance to high temperatures, high surface area width, excellent electrical conductivity, being found in nature, and acid-base resistance. In addition, C-based materials have negligible activity for CO₂RR as they cannot activate the CO₂ molecule. On the other hand, C has different allotropic forms due to its wide variety of hybrid orbitals, such as sp, sp², and sp³. This feature allows it to adjust the pore size and material curvature by adjusting its physical and chemical properties (Liu et al., 2017; Duan et al., 2017).

The work with metal-free carbon material for CO₂RR was first described by Kumar et al. In their study, they synthesized the poly(acrylonitrile) polymer using carbon nanofibers and reported that they achieved 13 times higher current density than CO₂RR with Ag catalyst (Kumar et al., 2013).

In another study, N-doped CNTs were studied. In this study, the conversion of CO₂ to CO was investigated. It has been reported that the presence of graphitic, pyridinic and pyrrolic N in the N-CNT structure has a positive effect

on CO₂RR and can selectively reduce CO₂ to CO by significantly reducing the overpotential (Sharma et al., 2015).

Cathode Materials

Metal complexes and transition metals are used in CO₂RR by many researchers because they can facilitate the bond between metal-CO₂ and have vacant d orbitals that assist reduce the removal of reduction products from the surface (Qiao et al., 2014). In Figure 1.14, metals that are frequently used in CO₂RR are shown. The transition metals used in CO₂RR and the resulting species are detailed.

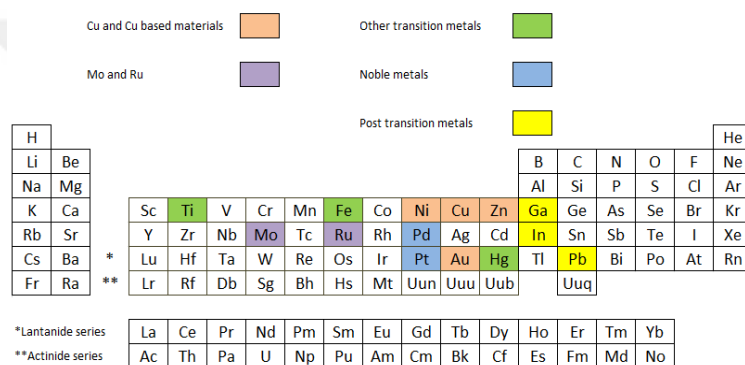
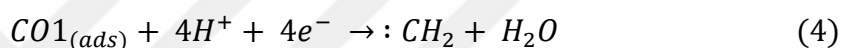
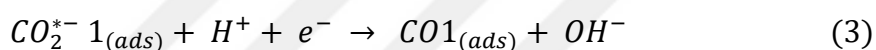
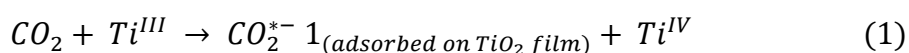


Figure 1. 14 Active metals that use for CO₂RR (Albo et al., 2015).

Titanium.

In normal conditions, titanium (Ti) has no significant catalytic activity toward CO₂ electrocatalytic reduction (Noda et al., 1990). However, TiO₂ has shown some activity in photocatalysis and electrocatalysis for CO₂ electroreduction (Mori et al., 2012). When TiO₂ is used as an electrocatalyst, a thin TiO₂ film or mixtures of TiO₂ and other metal oxides are usually deposited on a Ti electrode substrate to catalyze CO₂ electroreduction. As examples, in one of the studies, TiO₂, TiO₂-Ru, TiO₂-RuO₂, and TiO₂-Pt were deposited on a Ti wire by thermal deposition, and a thin film electrode was prepared and tested for CO₂RR. In another study, metal oxides (such as RuO₂, TiO₂, MoO₂, and Co₃O₄) were deposited on Ti foil and used in CO₂RR (Cueto et al., 2006).

Poly(ethylene) (PE) synthesis from CO₂ was performed by using a nano-TiO₂ film electrode in a mixture of water and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIm-BF₄) at room temperature and ambient pressure by Chu et al. In their study, working in EMIm-BF₄ solvent environment, high CO₂ concentration was formed because it provides a highly selective and efficient environment for CO₂RR. The reactions that occur are explained by the (1)-(5) reactions. According to the report of Chu et al., it was observed that PE could be synthesized thanks to the high pressure in the pores of the nano-TiO₂ film structure (Chu et al., 2008).



Nickel, Iron and Cobalt

The species formed by CO₂RR at the electrodes of transition metals such as Fe and Ni, under normal conditions and in aqueous solutions, are H₂ and CO or hydrocarbons. These metals are highly active for hydrogenating CO or CO₂ in heterogeneous catalytic reactions such as the Fischer-Tropsch reaction. Hara et al., in their work with the iron electrode, CO₂RR with 60% faradaic efficiency, have succeeded in producing formic acid (Hara et al., 1995). Similarly, Kudo et al. produced small hydrocarbons such as H₂, methane, ethylene, and ethane in CO₂RR with nickel electrodes in an aqueous medium. He also published that the faradic yield of CO₂RR on the nickel electrode under high pressure can be increased by varying the pressure and temperature (Kudo et al., 1993).

It has been reported by Fisher et al. that some Ni and Co complexes, such as Co(I)-tetraazamacrocycles, can be catalyzed in the reduction of CO₂RR to CO and H₂ in an aqueous solution at >90% efficiency. In their study, it was found that charge transfer to cobalt-bound CO₂ is stable in the reduction of CO₂. They also saw that the hydrogen bond interactions between the anode-hydrogen bond also contribute to the electron transfer in CO₂RR (Fisher and Eisenberg, 1980).

Copper

A study was performed by Jitaru and Gattrell, different metal based electrodes were used for CO₂RR in the KHCO₃ media, the formation of reduction product species were varied depending on the electrode type; for example, methane with copper, carbon monoxide with silver and gold, and formic acid for cadmium have been reported (Jitaru 2007, Gattrell et al., 2006).

The copper-based electrodes used in CO₂RR can be classified as Cu electrodes, Cu electrodeposited on GCE and Cu-coated GC electrodes (Cook et al., 1990). In CO₂RR studies with Cu electrodes, hydrocarbons such as methane, ethylene, carbon monoxide, methyl alcohol, ethyl alcohol, and esters and high hydrocarbon species such as paraffin-olefin with 6 C were obtained (Noda et al., 1990; Yori 1985 and Shibata et al., 2008).

It is known that the faradaic yields of the obtained species depend on the electrolyte type, concentration, applied potential, pH value, and the purity level of the copper used on the electrode surface. In electrolysis with 99.99%, pure Cu cathode immersed in 0.5 M KHCO₃ solution saturated with CO₂, by Hori et al., depending on the solution temperature being changed between 0-40°C; Faradaic efficiency in methane formation increased by 65% and 20% for ethylene (Hori et al., 1989).

1.4 Photocatalytic Reduction of Carbondioxide

Photosynthesis is a natural process carried out by plants to convert CO₂ using sunlight. To reduce the rate of CO₂ in the atmosphere and make it usable by converting it to its active species, scientists carried out the photochemical reduction of CO₂ using sunlight many years ago. In the following years, many studies have been carried out to increase the selectivity of the formed species and to increase the reduction efficiency of CO₂.

Photocatalysis involves one or more reaction steps that occur with the help of electron pairs produced by this light on the surface of a semiconductor material illuminated by a light source of suitable energy. Reactions in this way differ from normal thermal reactions and lead to product selectivity (Olivo et al., 2018).

Unlike other reactions, the beginning of the photocatalytic reaction is the absorption of the transmitted light by the semiconductor material with the band gap. This absorbed energy is used as a reductant in the progressive reaction steps, such as water purification, self-cleaning of dyes, and photocatalytic reduction of CO_2 .

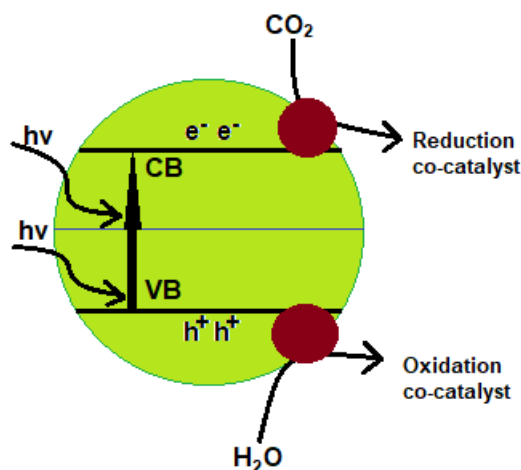


Figure 1. 15 Schematic illustration of a typical photoreaction procedure (Kan Li et al., 2016).

As shown in Figure 1.15, semiconductor materials are composed of a highly electron-weighted valence band (VB) and a high-energy conduction band (CB). Electrons transfer from VB to the vacant CB band, causing the formation of a positively charged hole (h^+) in the photocatalyst VB. This light-activated electron migration can occur with the band gap of the photocatalyst is used less than the intensity of the light. Without electron transfer from VB to CB, the photocatalytic reaction would not have occurred (Adekoyaa et al., 2019).

The most fundamental requirement for the photochemical reduction of CO_2 is developed photocatalysts sensitive to sunlight. With the photocatalyst used, selective reduction types can be formed, and efficiency can be increased. Developing suitable catalysts has been the subject of many researchers' work for years (Das et al., 2014). The results of the studies can be summarized with the photocatalyst classification indicated in Figure 1.16.

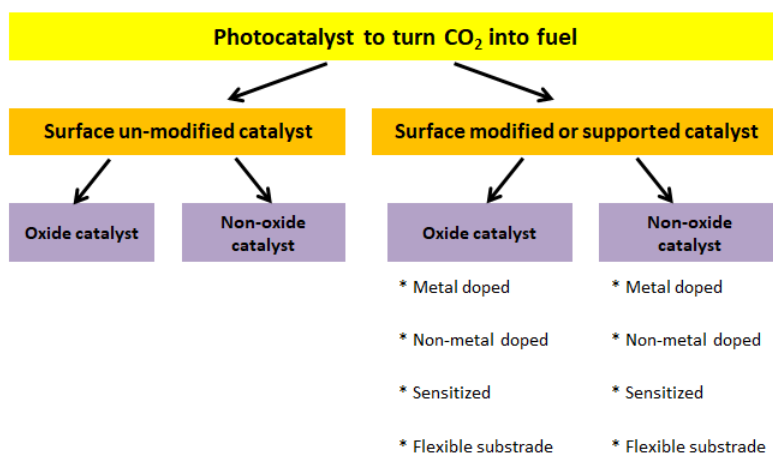


Figure 1. 16 The main scheme of photocatalysts on CO₂ transformation (Das et al., 2014).

Photocatalysts used in the photochemical reduction procedure of CO₂; the way the reaction takes place, the type of light absorbed and used, and the type and efficiency that will occur after photocatalysis directly affect the parameters. For this reason, the photocatalyst to be chosen in the photochemical reduction of CO₂ is very important and has formed the basis of studies in this field (Tahir and Amin, 2013).

Metal oxides as light-sensitive catalysts are used in the conversion of organic-inorganic materials (Sivula 2013 and Lacis et al., 2010), self-cleaning (Fujishima et al., 2000 and Benedix et al., 2000), and purification (Han et al., 2009). The utility of these catalysts in the transformation of CO₂ was first suggested by Inoue et al. (Inoue et al., 1979). It is known that photocatalysts are modified with different support materials for modifications such as reducing grain size, increasing selectivity, and increasing surface area (Sakthivel and Kisch, 2003) many photocatalytic CO₂ reduction processes, are characterized in this section with sufficient information.

In the studies, many different types of photocatalysts, such as metal oxide semiconductors, sulfides, nitrides, carbides, carbon-based materials, dyes, and enzymes, have been investigated, and very productive studies have been obtained. However, metal oxide semiconductors such as TiO₂, WO₃, and ZnO are widely used as photocatalysts in the photochemical reduction of CO₂ (Zhang et al., 2018). Among these foto-catalysts, TiO₂ is the most commonly used among metal oxide semiconductors due to its properties, such as easy availability, corrosion

resistance, and strong oxidation properties (Kan Li et al., 2016). Figure 1. 17 shows the band gap of some metal oxide semiconductors

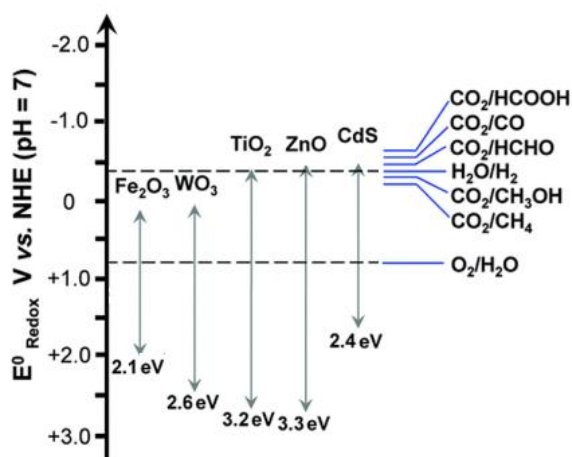


Figure 1. 17 Band gaps of various photocatalysts for CO₂ photoreduction with regard to the redox potential of other possible products at a pH: 7. (Khalil et al., 2019)

TiO₂, which is found in nature in the form of three minerals known as rutile, anatase, and brookite, is a frequently preferred metal oxide because it is inert, durable, and affordable in the photochemical conversion of CO₂ (Figure 1.18). It is known that rutile and anatase phases show better efficiency than light radiation, anatase has a bandwidth of 3.2 eV, and rutile has a bandwidth of 3.0 eV. Due to its relatively narrow band gap, the anatase form, which can absorb light in the visible region, rutile responds only to ultraviolet radiation. For this reason, the anatase phase, which can show higher activity in CO₂ photochemical conversion reactions with TiO₂, is preferred (Bouras et al., 2006).

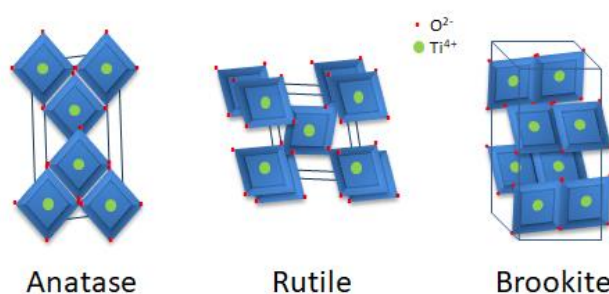


Figure 1. 18 Representations of the TiO₂ forms (Dambournet et al., 2009).

TiO₂, a semiconductor, is effective in light absorption and provides a high surface area. Although the surface area is inversely proportional to the particle size, the TiO₂ band gap is directly proportional to the particle size. However, the narrow band gap causes insufficient redox potential for oxidation and reduction

reactions (Koci et al., 2008). Figure 1.19 shows a simple photochemical mechanism of CO₂ on unmodified metal oxide.

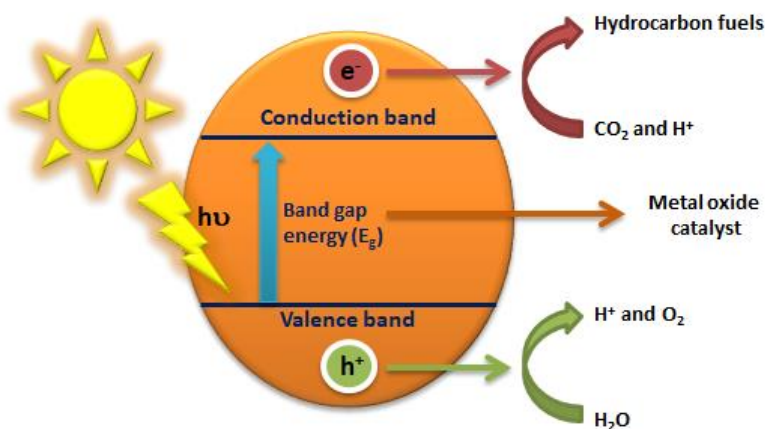


Figure 1. 19 Basic photocatalytic mechanism of CO₂ on metal oxide semiconductor (Das and Wan Daud., 2014).

Although TiO₂ is one of the most preferred metal oxides, using different metal oxides is also quite common. Inoue et al. conducted photocatalytic studies for H₂CO₃/CH₃OH under ultraviolet light using TiO₂, ZnO, and WO₃ (Inoue et al., 1979). Apart from these studies, Xi et al. synth Duan et al., synthesized W₁₈O₄₉ nanowires for photocatalytic conversion of CO₂ to CH₄ under visible radiation (band gap 2.7 eV). Thanks to the particular particle size in the structure of the synthesized W₁₈O₄₉ nanowires, success has been achieved in the photochemical reduction of CO₂ in the visible light region (Xi et al., 2012).

Metal oxides such as Ga₂O₃, ZrO₂, and MgO have also been reported, with studies having a wide band gap compared to metal oxides (Yuliati et al., 2008 and Tang et al., 2017). In these studies, CH₄ and H₂ were used as reductants for the photocatalytic reduction of CO₂, and CO was obtained as the main product (Teramura et al., 2004). It was determined that when ZrO₂ and MgO were used as metal oxide catalysts, and CH₄ was used instead of H₂ as a reducing agent, the highest reduction was obtained, and the type formed was acetate (Lo et al., 2007). Metal oxide-supported photocatalysts such as zeolite, mesoporous SiO₂, and Al₂O₃ are also frequently used. Mainly mesoporous SiO₂ provides a high surface area due to its nm pore size. The pore structure of the photocatalyst used is essential for transporting products to and from the surface (Kruk and Jaroniec, 2000).

Ti loaded on the silica matrix structure reduces the surface area of the catalyst, and the Ti content reduces the pore volume. The reduction in pore volume indicates that the semiconductor material's loading saturates the channels' space in the catalyst and helps control the catalyst size from crystal growth. High catalyst loading can cause blockage in the track, but this effect needs to be reduced (Pinho and Mosquera, 2011).

In another study, a multi-walled carbon nanotube (MWCNT) supported TiO_2 composite photo-catalyst was reported by Xia et al. MWCNT material provided a high conversion effect when supplemented with TiO_2 due to its unique electronic property (Xia et al., 2007). According to J. Qu et al., RuO_2 nanotubes on Pt electrodes provided successful results in the photocatalysis of CO_2 into methanol. In addition, the study reported that the composite electrode gave excellent results compared to the Pt electrode due to the increase in the electrode surface area after RuO_2 modification (Qu et al., 2005).

Huang et al., studied the photocatalysis of CeO_4 and Co_3O_4 , and CO_2 into methanol and ethanol under visible light Huang et al. In their study, when Co_3O_4 alone was used as a photocatalyst, methanol or ethanol could not be obtained, so they supported the photocatalyst with CeO_4 . They want to supplement with CeO_4 because it assists the increase of photoactivity when modified to other metal oxides or semiconductor materials in the photochemical reduction of CO_2 . As a result, the yields for methanol and ethanol were 1.52 and 4.75 $\mu\text{mol.g. cat.h}^{-1}$, respectively (Ying Huang et al., 2015).

Although some semiconductor metal oxides have sufficient band gap energy to increase and catalyze chemical reaction kinetics, as the energy required for excitation of the photocatalyst increases, the wavelength of the excitation light decreases, limiting their use as photocatalysts due to the shift of the electromagnetic spectrum towards the vacuum ultraviolet region. In particular, although the band gap energy of ZrO_2 has a value (5 eV) to cover many oxidation and reduction reactions, its use as a photocatalyst is limited (Karunakaran 2005).

1.5 Electroanalysis Application

In electrochemical studies, it is important to develop modified electrodes for quantitative detection for both inorganic and organic based analytes with high sensitivity and selectivity and to use them in analytical applications. In this way, steps will be taken to make laboratory-scale studies applicable to real samples and to disseminate them to field studies. With chemically modified electrodes, high selectivity can be achieved especially for substances to be determined. One of the scopes of this thesis is the determination of antimony.

In this thesis a chapter is related with a novel composite electrode which was developed by electrochemical deposition of both Copper (II) phthalocyanine-over-oxidized poly (cresol red) on glassy carbon electrode for sensitive and selective determination of antimony.

1.6 Antimony

Antimony (Sb) is a metalloid element which consist of naturally due to rock weathering, ambient deposition in the environment and uses in numerous industrial fields such as fabrication of fire retardants, glass and ceramics (Carlin 2022), batteries and Pb-Sb alloy ammunition (Johnson et al, 2005). In addition, the Sb_2O_3 compound is used as a catalyst in producing Polyethylene terephthalate (PET) (Perre et al., 2011). Ordinary concentration of dissolved antimony in uncontaminated waters is smaller than $1 \mu\text{g L}^{-1}$ (Filella et al., 2002b). Since PET bottles are food-contact materials such as drinking water, fruit juices, and carbonated drinks, EU restrictions have been introduced due to the risk of transferring from PET bottles to beverages by transport. European Union limit values are determined as $5.0 \mu\text{g L}^{-1}$ for drinking water (Council of the European Union-1998). United States Environmental Protection Agency and the Council of the European Communities accepted that antimony and its compounds are listed as pollutants and they were recommended that maximum antimony concentrations should not to exceed $5 \mu\text{g L}^{-1}$ level in drinking water (Filella et al., 2002b). Additionally, the World Health Organization was also defined the maximum antimony level as $20 \mu\text{g L}^{-1}$ in drinking water (He et al., 2012).

There are 4 main oxidation forms of Sb, Sb(–III), Sb (0), Antimony (III) and Sb (V), but it is predominantly found in nature as Antimony (III) and Sb (V). (Filella et al., 2002a). If toxicity ranking is made for Sb, (III) valence of Sb compounds show more toxic properties than (V) valence of Sb compounds, and ionic salt and inorganic forms show more toxic properties than organic Sb (Gomez Gonzalez et al., 2006 and Ulubay Karabiberoğlu and Dursun, 2017). In addition antimony species can cause several diseases such as keratitis, conjunctivitis, dermatitis etc. but they have not bioavailability (He et al., 2012, Periferakis et al., 2022). Drinking water and fruit juices bottled commercially in plastics frequently withdraws of the contamination of antimony from the vessels due to the antimony trioxide is widely used as a polycondensation catalyst during the production of polyethylene terephthalate (Perre et al., 2011).. Therefore, developing sensitive and selective methods for the detection of antimony in different samples is of significant issue. Many methods have been developed for the determination of Sb in different real samples and published studies were summarized at following paragraphs:

Lopez-Garcia et al. studied the Sb separation and enrichment using the micro-solid phase extraction procedure, the Na salt of 2-mercaptoethanesulfonate (MESNa) and Ag NPs coated magnetic particles, and the use of $\text{Pd}(\text{NO}_3)_{2,x}$ as the chemical modifier. With the magnetic field's help, a direct atomizing injector is provided for the determination of Sb. In the study, the detection limits were 0.02 and 0.03 $\mu\text{g L}^{-1}$ levels and the enrichment factor 205 and 325 were obtained (López-García ve diğerleri, 2017).

Ilander et al. used two-stage hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES) to determine arsenic and antimony concentrations in SRM 1633b - Constituent Elements in Coal Fly Ash samples. When the reading time was set to 60 seconds in the measurements perform on the device, the %RSD values for arsenic and antimony were obtained as 0.6 and 2.3. In addition, arsenic and antimony recovery tests from the SRM 1633b were performed. It was found that 96% of arsenic and 103% of antimony could be recovered in SRM 1633b. The detection limits for arsenic and antimony

were found to be 0.89 and 1.37 mg kg⁻¹ with the two-stage HG-ICP-OES performed in the fly ash sample (Ilander and Väisänen, 2011).

Lin et al. developed a method for determination of Sb species in fruit juices in Kaohsiung, Taiwan, using ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS). In their studies, Antimony (III), Sb (V), and trimethyl antimony (V) (TMeSb) species were separated by the Hamilton PRP-X100 anion exchange column in less than 8 minutes. Mobile phase – as A in 1% v/v methanol at pH 5.5 20 mmol L⁻¹ EDTA + 2 mmol L⁻¹ KHP (potassium hydrogen phthalate) as Mobile phase - at pH 9.0 at 1% v/v in methanol 20 mmol L⁻¹, 1 EDTA, 2 mmol L⁻¹ KHP, 40 mmol L⁻¹ (NH₄)₂CO₃ were used. As a result of the method used, the detection limits and %RSD values of Sb species were found to be 0.012–0.032 ng mL⁻¹ and 2.2–2.8%, respectively (Lin et al., 2017).

The most important issue in the methods to be selected in the determination of Sb is the measurability at the nanomolar level of the detection limit, the affordability of the method and providing reproducible results. Although many methods performed with the device provide low detection limits, the equipment used is not suitable for portability and the methods are relatively expensive (Ulubay Karabiberoğlu and Dursun, 2017).

Another method used for sensitive Sb determination is electrochemical techniques. These techniques provides higher sensitivity, selectivity, accuracy, relative simplicity, low costs and portable field-based equipment, therefore they have also been frequently used in trace analyzes. Especially various voltammetric methods have been described for the sensitive and selective determination of antimony.

Electrochemical methods used in the determination of antimony are anodic stripping voltammetry (ASV)), adsorptive cathodic stripping voltammetry (AdCSV) with differential pulse (DP) and chronopotentiometry (CA). Among these methods, especially in the ASV technique, the detection limits are at the nanomolar level or lower. In the ASV method, antimony (III) is electrochemically reduced to antimony (0) on the electrode surface, its concentration is increased for

an optimum time, and then anodically, antimony is oxidized and separated from the surface (Toghill et al., 2011).

In addition, adsorptive stripping voltammetric technique has been also performed by using chelating compounds in solutions for indirect determination antimony such as hematoxylin, alizarin red S, morin, chloranilic acid, oxine, rivastigmine.

Nakiboğlu et al. developed a voltammetric method using alizarin red S (ARS) as a complexing agent for the determination of Antimony (III) in drinking water samples. The method is based on observing the oxidation of the Antimony (III)-ARS complex adsorbed on the hanging mercury drop electrode (HMDE) surface. In studies performed at natural pHs, the limit of detection and the limit of quantification was calculated as 1.45 mg L^{-1} and 4.8 mg L^{-1} , respectively. In comparison, the calibration chart for Antimony (III) showed linearity in the range of $4.8\text{--}30 \text{ mg L}^{-1}$ (Nakiboğlu et al., 2013).

Vardar Segin et al. was developed an adsorptive and ASV method for Sb detection in the presence of hematoxylin using GCE. The developed method was used for Sb recovery studies from water samples and values were obtained from 97% to 102% in the presence of $0.5 \text{ } \mu\text{mol L}^{-1}$ Antimony (III) (Vardar Sezgin et al., 2017).

In other study of Vardar Segin et al., Sb was determined in the presence of rivastigmine with ASV technique at bare GCE in HCl medium. The developed method was tested for Antimony (III) recoveries from water sample and the obtained recoveries data were varied from 95.0% to 97.6% for spiked Antimony (III) (Vardar Sezgin et al., 2015).

Another ASV study was performed for selective and sensitive determination of Antimony (III) on over-oxidized poly(phenol red) modified GCE in acidic media. The developed method demonstrate great results as wide linear concentration range, low detection limit ($0.0075 \text{ } \mu\text{g L}^{-1}$), high selectivity and long storage stability towards Antimony (III) analysis. The fabricated modified electrode was used for the recovery studies of Sb in varies water samples and the

results was changed from 93.0 to 103.0% (Ulubay Karabiberoğlu and Dursun, 2017).

In another stripping study for selective and sensitive detection of antimony was carried out using hematoxylin, Cu(II) and Bi(III) ions containing medium. After the formation and adsorption of Antimony (III)-hematoxylin complex on hanging mercury drop electrode, the analytical signal was obtained by the reduction of the antimony in the adsorbed complex. The developed method display wide linear concentration range and high selectivity to Antimony (III) detection. The method accuracy for Antimony (III) detection was tested in water sample solution by recovery studies. (Şahin and Nakiboğlu, 2014).

A electrochemical reduced graphene oxide modified GCE electrode was prepared for Antimony (III) detection in in edible plants and beverage samples. The prepared electrode surface was characterized by SEM and CV, obtaining a porous surface with higher surface area compare with bare GCE. The developed method was validated with a linear range ($10\text{--}60\ \mu\text{g L}^{-1}$), detection limit ($2.5\ \mu\text{g L}^{-1}$), accuracy, repetibility and reproducibility and less then 10% RSD. The developed electrode was applied in real samples and compared with GFAAS (Liendo et al., 2022)..

1.7 Surface Characterization Techniques

Clarifying the surface morphology, surface pore structure, and diameters of the modified electrodes or the synthesized materials are very important for physics, chemistry, and biology as it provides information about the chemical structure of the prepared surface or material. Understanding the surface properties also plays an influential role in elucidating the chemical processes on the surface. Surface properties of modified or composite electrodes can be identified by electrochemical, spectroscopic and microscopic techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), X-Ray photoelectron Spectroscopy (XPS), transmission electron microscope (TEM), atomic probe microscopy (APM) have been used. With these methods, the surface structures of the new generation electrodes and the properties of the synthesized materials can be elucidated.

1.7.1 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a very powerful method for electrochemical systems among surface characterization methods. With EIS, remarkable results can be obtained about the effect of physical and chemical processes occurring under a specific potential with a single experimental setup in a wide frequency range. EIS has been widely used in many electrochemical research in recent years. In particular, it is used to illuminate electrochemical coatings, batteries, fuel cells, corrosion reactions, electrodeposition, and corrosion mechanisms.

In the EIS method, the electrokinetics are illuminated by measuring the electrode impedance in the presence of faradaic reactions at the electrode solution interface. In the electrochemical measurement performed in the EIS, the chemical transformations occurring at the electrode and solution interface are displayed with electronic equivalent circuit models. Among the interface models, the most useful is the Randles and Ershler model (Figure 1.20). According to this circuit, R_{ct} represents the charge transfer resistance, which is inversely proportional to the electron transfer rate, C_{dl} is the double-layer capacitance, R_s is the solution phase resistance, and W is the Warburg impedance due to the mass transfer limitation. According to Ohm's law, the interface impedance consists of two parts, the real number Z' and the imaginary number Z'' :

$$Z(\omega) = R_s + \frac{R_p}{1 + (\omega R_p C_{dl})^2} - j \frac{\omega R_p^2 C_{dl}}{1 + (\omega R_p C_{dl})^2} = Z' + jZ''$$

Where $j = \sqrt{-1}$

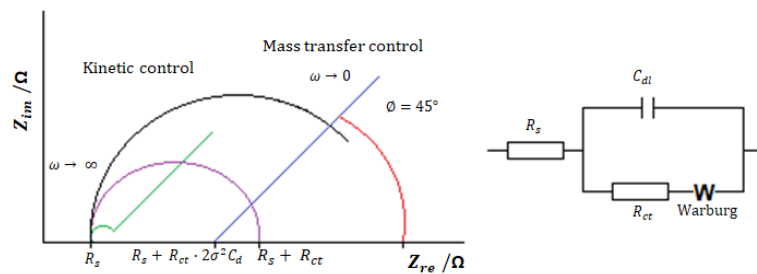


Figure 1. 20 The most generally used equivalent circuit model to investigate impedance data, i.e. the Randles and Ershler model. (Macdonald 2006).

A typical Nyquist plot is obtained in the EIS measurements, represented by the semicircle and the continuous straight line shown in Figure 1.20. The semicircle represents the electron transfer resistance observed at higher frequencies, and the straight line observed at lower frequencies represents the diffusion process. In processes with high-speed electron transfer, the impedance graph consists only of the linear part, while very slow electron transfers form a semicircular region. The diameter of the semicircle is directly proportional to the resistance to electron transfer (Suni 2006).

1.7.2 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a powerful technique for the surface examination of materials and electrodes. In the SEM technique, microscopic examination is performed on the surface by scanning the material surface with very high resolution and considerable depth of field. When the sample is irradiated with an electron beam called an electron probe, secondary electrons in the sample are emitted from the surface. The topography of the surface can be observed by taking images of the electrons separated from this surface detected on the electron probe surface. SEM measurements can enlarge the sample surface from 10 to 2,000,000 times. The actual dimensions of the structures in the image can be calculated with the scaling bar on the SEM images (Kazmiruk 2012).

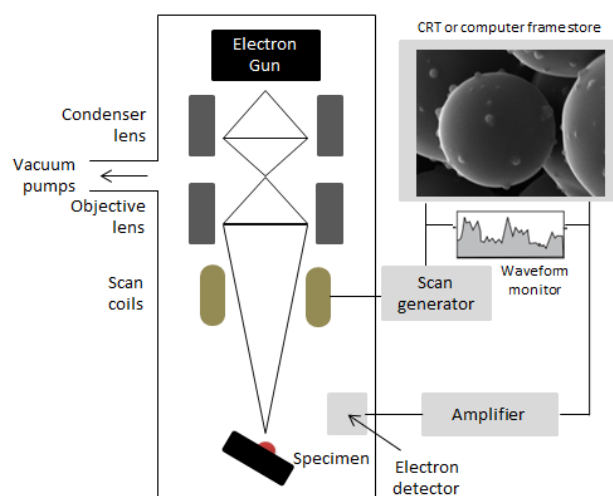


Figure 1. 21 Schematic design of a scanning electron microscope (Kelsall et al., 2005)

An essential SEM equipment is as shown in Figure 1.21, 1) the electron gun microscope column at the top, the column where the electron beam moves

down and the sample chamber, 2) the microscope is operated by computer control that performs these operations, 3) it helps to determine the structure of the sample. It includes three machines consisting of equipment.

Electrons accelerated in SEM equipment carry a significant amount of kinetic energy. When electrons with this kinetic energy arrive at the sample, they are slowed down, and dispersed as signals generated by the sample-electron interaction. These signals include secondary electrons, backscattered electrons (BSE), characteristic X-rays (photons) used in elemental analysis, and heat, which enable the production of SEM images. Among them, secondary and backscattered electrons are widely used in sample imaging. Especially backscattered electrons are very effective for fast phase separation from understanding surface morphology. (Kelsall et al., 2005)

1.7.3 Transmission Electron Microscope (TEM)

TEM equipment consists of an electron emission source, vacuum, detector and lens, and pumping unit for electron beam generation. Generally, TEM measurements consist of emitters of tungsten filament or lanthanum hexaboride. It is then passed through a high voltage source of ~100–300 kV and a magnetic field that acts as a lens. In TEM measurements, ultra-high vacuums between 10^{-7} and 10^{-9} Pa prevent electric arc formation at the cathode. A high-energy electron beam transmitted from the sample is used in surface characterizations performed with TEM (Figure 1.22).

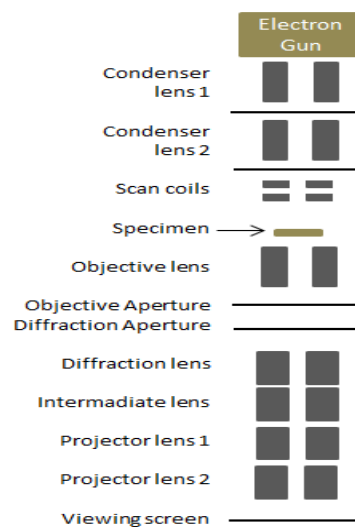


Figure 1. 22 Schematic graph of the modern TEM Champness 2001).

TEM analysis provides information about the sample's morphological, compositional, and crystallographic structure. TEMs are used in materials science, health science, and nanotechnology research. In addition, since an excellent characterization can be achieved by making micro and nano with TEM, it is possible to examine from micro size to atomic scale (Khan 2012).

1.7.4 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface-sensitive technique based on the photoelectric effect that can assign the composition of the material on the surface such as chemical state, and the overall electronic structure and density of the electronic states in the material. In the XPS method, single-energy x-rays are focused to the sample material to eject electrons, and these photoelectrons get kinetic energy by moving away from their orbits with the incoming rays. Thus, the relative concentrations of the elements can be determined by these photoelectron densities. One of the most important advantages of the XPS method is that the binding energies of the photoelectrons and the shifts in these energies can be used to illuminate the chemical state and structure of the sample (Kloprogge et al., 2020). Critical components of XPS equipment include an X-ray source, ultra-high vacuum (UHV) stainless steel chamber, electron collecting lens, electron energy analyzer, metal magnetic field shield, detector, and sample holder, as shown in Figure 1.23.

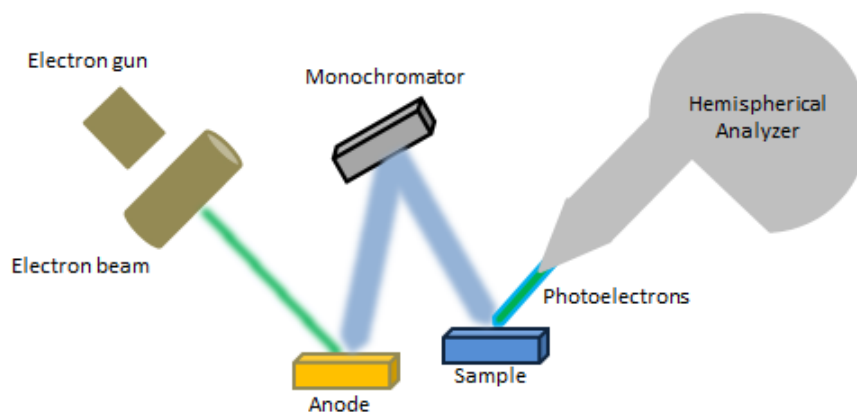


Figure 1. 23 Schematic illustration of an XPS instrument (Kloprogge et al., 2020).

When a sample analyzed in the XPS method, its surface is irradiated with monochromatic x-rays, if the atoms with electrons moving away from the surface are close to the surface ($<20 \text{ \AA}$), the probability of electrons being removed without losing kinetic energy is high. The photoelectron spectrum, which the

researchers form due to the scattering of unscattered electrons against their kinetic energies in a vacuum, is fascinating (Bard and Faulkner, 2022).

These energies allow precise characterization of the atomic structure. The measurements made give noticeable results. With XPS analysis, both elemental analysis and changes in electron density due to the formation of chemical bonds, chemical shifts, can also be examined. Photoelectron spectroscopy can show various oxidation states of a metal, for example, in oxide films on the electrode; It is widely used in the study of chemically modified electrodes and substances adsorbed on the electrodes. It is important to do such work by comparing the EB values of standard reference compounds. XPS method gives information about a few atomic monolayers on the surface (Djokić 2014).

1.7.5 Voltammetric Techniques

Voltammetry is an electroanalytical method for obtaining information about the analyte by measuring the current value as a function of the applied potential when an indicator or working electrode is polarized. This method measures the current change in the electrochemical cell under full-concentration polarization conditions (Skoog et al., 2018).

Voltammetry, a widely used analysis method recently, is a method in which substances at low concentrations can be determined. Electroanalytical procedures allow for the quantitative and qualitative determination of substances. It is frequently used in biochemistry, physicochemistry, and in the investigation of oxidation-reduction reactions that may occur in various environments in inorganic environments, adsorption events occurring on the surface, electron transfer mechanisms occurring on modified electrode surfaces, and the stability of substances in the solution environment. Voltammetric methods are frequently used to determine species that are especially important in terms of pharmaceutical, environmental and biological aspects (Saito and Kikuchi 2013)..

For analytical purposes, various forms of voltammetry are currently in use. Voltammetry is presently in use: Stripping voltammetry is now a vital trace analytical method, especially for determining metals in the environment. Differential pulse polarography and fast-scan voltammetry are essential for

identifying pharmaceutically exciting species. Voltammetric and other electrochemical detectors are frequently used in high-performance liquid chromatography (HPLC) and capillary electrophoresis. Amperometric techniques are widely used in sensor technology, monitoring titrations and biologically essential reactions. Modern voltammetric methods remain potent tools used by several different types of chemists interested in studying and exploiting oxidation, reduction and adsorption processes (Settle 1997).

1.7.6 Cyclic Voltammetry

Cyclic voltammetry is the first voltammetric method used to explain the thermodynamics of oxidation-reduction reactions, the kinetics of electron transfer, and the transport events by adsorption or diffusion to the electrode surface (Bard and Faulkner, 2001). This method measures the current change while the potential applied to the working electrode is scanned from E_{initial} to E_{final} and from E_{final} to E_{initial} (Figure 1.24). If the scan starts at the E_{initial} potential and ends at the E_{final} potential, the method is called normal pulse voltammetry. If there is a return to E_{initial} or any E_{x} potential with the same scanning rate after the E_{final} potential, it is called alternating voltammetry (Wang 2000).

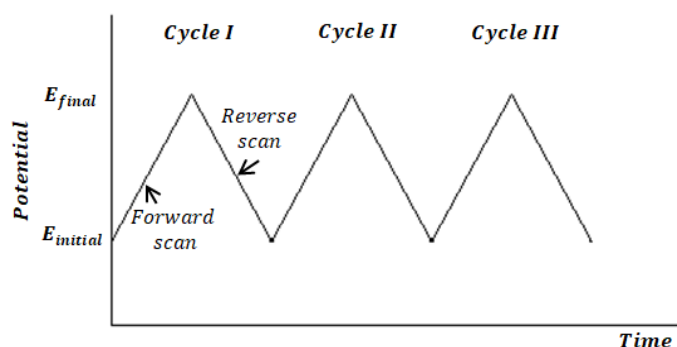


Figure 1. 24 Potential-time excitation signal in CV measurement (Wang 2000)

Figure 1.25 shows the voltammetric result of the reversible redox couple formed during a single cycle. Initially, the oxidized O form is assumed, and a potential negative sweep is selected for the first half-cycle. When the applied potential approaches E° , the cathodic current increases until it reaches its peak. After crossing the potential at which reduction occurs (at least 90 V after the peak), the scanning direction is reversed. During the reverse sequence, the R molecules are oxidized back to O, forming an anodic peak.

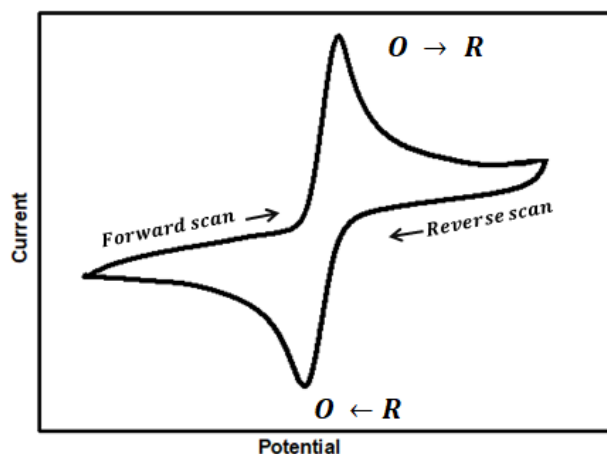
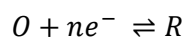


Figure 1. 25 A typical reversible CV voltammograms (Song et al., 2016).

In cyclic voltammetry, information about the reaction mechanism can be obtained by changing the scanning rate parameter. By looking at the effect of the scan rate change on the peak current, it can be concluded that the reaction is diffusion or adsorption controlled. In electrochemical reactions, if the electron transfer between the electroactive species and the working electrode occurs at the solution and electrode interface, it is called a diffusion-controlled process. If electron transfer takes place on the electrode surface, it is called an adsorption-controlled process. The linear increase of the peak current with the rise of the scan rate and the slope obtained from the plot of the scan rate logarithm-peak current logarithm close to 1 indicates that the reaction is adsorption controlled. If the slope is close to 0.5, the electron transfer occurs at the solution-electrode interface; that is, it is a diffusion-controlled process. The electrochemical reaction occurring on the used electrode surface can be grouped as reversible, semi-reversible, and irreversible (Compton 2011).

Reversible Reactions

Electrode reaction is a reversible reduction reaction by cyclic voltammetry;



In the initial state, there is only "O" substance, and no chemical reaction takes place other than electron transfer. In addition, an adsorption event does not occur on the surface. In this case, the plotted $i - E$ graph gives the voltammogram in Figure 1.25. As the scanning speed increases, the peak height also increases.

When the potential at which the "O" substance is reduced by scanning the potential in the opposite direction is reached, the "R" on the electrode surface will start to oxidize, and an anodic peak will be formed. As the potential shifts to positive during reverse scanning, the concentration of the "R" substance on the surface decreases according to the Nernst equation. The resulting "R" diffuses into the solution. As a result, the cathodic current value becomes higher than the anodic current value obtained in reverse scanning.

In reversible reactions, the electron transfer rate at the electrode surface is greater than the mass transfer rate, and the (R) / (O) ratio depends on the potential, as seen in the Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{(R)}{(O)}$$

In a reversible reaction, the peak current at 25 °C is given by the Randles-Sevcik equation.

$$i_p = (2.69 \times 10^5) n^{3/2} A C_o D_o^{1/2} v^{1/2}$$

In the equation, i_p : peak current (Ampere), D_o : diffusion coefficient of type O (cm^2/s), v : scanning rate (V/s), C_o : mother solution concentration of type O (mol/cm^3), n : number of transferred electrons and A : electrode surface area (cm^2).

With the help of cyclic voltammetry, the reversibility of a reaction can be evaluated. If the graph of the drawn string $i_p - v^{1/2}$ is linear and the graph passes through the origin, the system is said to be reversible. However, in the reversible system; $\Delta E = E_{p_k} - E_{p_a} = 59/n$ V, $|i_{p_a} / i_{p_k}| = 1$, The graph of $i_p - v^{1/2}$ is linear, E_p is independent of v , $|E_p - E_{p/2}| = 59/n$ V. Each of these criteria is needed for a reversible system. If one or more features are not valid, the system cannot be said to be reversible (Scholz 2005).

Quasireversible Reactions

In quasireversible reactions, current, electron transfer rate, and mass transfer rate are controlled together. As seen in Figure 1.30, the transition between systems occurs with the increase in scanning speed. The properties of the semi-

reversible reaction can be listed as follows; the graph of $i_p - v^{1/2}$ is non-linear, the current increases with $v^{1/2}$, E_{pk} usually shifts to negative values with scanning speed, $i_{pa} / i_{pk} = 1$ (if electron transfer coefficient (α_c) is 0.5), $E_{pk} - E_{pa}$ difference approaches $59/n$ at low scanning speeds and moves away from this value as scanning speed increases.

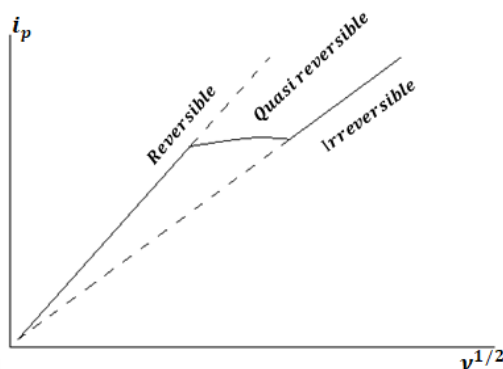


Figure 1. 26 $i_p - v^{1/2}$ graph of CV (Scholz 2005).

Irreversible Reactions

While the Nernst equation is valid for reversible reactions where the electron transfer rate is greater than the mass transfer rate on the electrode surface, this equation is not suitable for irreversible reactions where the electron transfer rate is not large enough.

The absence of an anodic peak is the most acute symptom in irreversible systems. However, not every case where the anodic peak is observed does not mean that the electron transfer step is irreversible. For example, in a reaction where electron transfer is high-speed, the oxidation peak may not be observed during reverse scanning when the product formed is rapidly converted to another substance. The following properties are used to determine whether a reaction is irreversible with the cyclic voltammetry method; No anodic peak is observed (No reverse scan peak is kept). The second i_{pk} changes in direct proportion to $v^{1/2}$. E_{pk} shifts by $30/\alpha_c n_a$ V for every 10-unit increase in scan rate at 25 °C. An irreversible system is expected to meet all of these criteria.

1.7.7 Differansial Pulse Voltammetry

In pulse voltammetry methods, constant magnitude pulses (de/dt) are applied to the working electrode with a linear potential increase for a specific time; then, the current value is measured twice. The first is calculated before the pulse is applied, with no change in potential at the beginning of the pulse, and the second is measured near the end. This measured current difference is ΔI_{puls} . A differential pulse voltammogram is obtained when this applied potential is plotted to the current difference (Wang 2000). Figure 1.27 shows the graph showing the variation of the applied potential over time.

The differential pulse voltammetry method, which is a method frequently used for analytical purposes in voltammetry, is beneficial for the determination of trace amounts of organic and inorganic species (Skoog 2018).

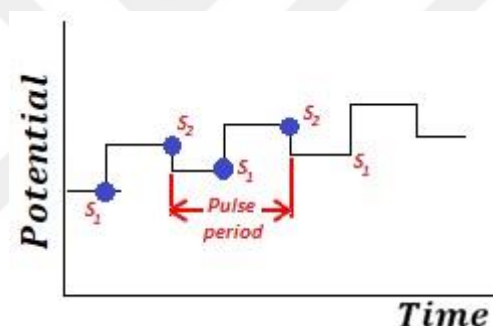


Figure 1. 27 Interpretation of potential with time in differential pulse voltammetry (Skoog 2018).

In normal pulse voltammetry, potential pulses with increasing amplitude are applied. While the pulses are used, the electrode is kept at a constant potential where no reaction will occur in the analytes. The amplitude of the pulses increases linearly with each drop. The current measurement is approximately 40 ms after the pulse application when the charge current contribution is almost zero. Due to the short pulse times, the diffusion layer is thinner than DC, so 5-10 times more sensitive measurements can be performed compared to DC due to the increase in faradaic current. In normal pulse voltammetry, the detection limit is at the level of 10^{-7} - 10^{-8} mol L⁻¹, and it is also an excellent technique for determining the diffusion coefficient (Bard and Faulkner, 2022).

1.7.8 Chronoamperometry

The chronoamperometry method involves changing the working electrode potential from the value at which faradaic reaction does not occur to the potential where the electroactive species concentrations are zero (Figure 1.28-A). In the chronoamperometry method, an unmixed solution medium and a fixed electrode are used, and the current change in the measurements is monitored. Since mass transfer occurs only by diffusion under these conditions, the current-time curve will reflect the change at high concentrations. This includes the depletion of the reactant species over time and the gradual expansion of the diffusion layer, thus decreasing the concentration gradient over time (Figure 1.28-B). Accordingly, the current decreases with time in the planar electrode, as shown in Figure 1.28-C.

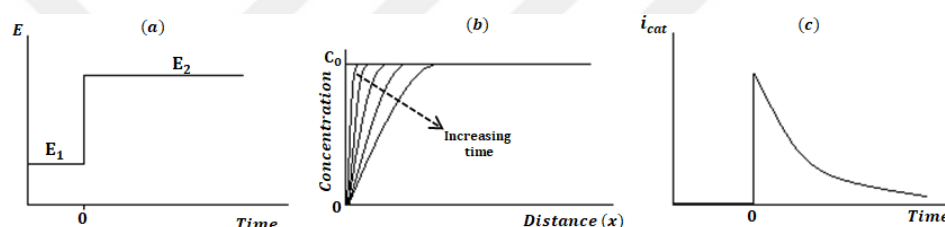


Figure 1. 28 Chronoamperometric investigation: (a) potential–time; (b) change of concentration profiles with time; (c) the consequent current–time response. (Wang 2000).

In the chronoamperometry method, comments can be made about the electrocatalytic level and stability of the catalytic system for the oxidation and reduction reaction. It also allows the determination of the number of electrons in the oxidation and reduction processes. Cottrell equation can be used to estimate the number of electrons in electron transfer (n) in chronoamperometry measurement;

$$i(t) = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = kt^{-1/2}$$

Where, i ; current density of the electrodes used (mA cm^{-2}), F ; faradaic constant (96485 C mol^{-1}), A ; electrode area (cm^2), C ; bulk concentration (mol cm^{-3}), D ; gives the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) (Wang 2000).

1.7.9 Stripping Voltammetry

Among the voltammetric techniques, the most sensitive method is stripping, which is a particularly preferred method for determining trace metals. A

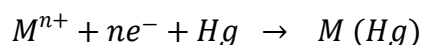
controllable deposition of the analyte achieves this method's high sensitivity and selectivity before the determination (Skoog 2018).

After the electroactive species to be measured is deposited on the electrode surface, the method is called anodic stripping voltammetry if the species is stripped by oxidation. If the type deposited on the surface is stripped by reduction, it is called cathodic stripping voltammetry. This deposited analyte, stripped from the electrode surface, is returned to the solution. This method can prevent systematic errors such as contamination and evaporation by carrying out the deposition and determination process on the same electrode surface without needing to change the container (Bard and Faulkner, 2022).

Stripping techniques are divided into three groups anodic stripping, cathodic stripping, and adsorptive stripping. In the stripping step applied in the determination of the analyte, differential pulse or square wave voltammetry is generally used.

Anodic Stripping Voltammetry (ASV)

Anodic stripping voltammetry is the most widely used stripping technique. The anodic stripping voltammetric technique is a two-step technique. In the first step, a controlled potential electrolysis is performed on the working electrode, usually a hanging mercury drop or mercury film, is kept at a negative potential enough to reduced and deposit the metal ions on the electrode surface. In this case, the reduced metal ions as metallic form are preconcentrated by electrodeposition into a small-volume mercury electrode or a thin film covered electrodes



This preconcentration process is carried out cathodically by providing time and potential control. The fact that the potential applied to the system is 0.3 – 0.5 V more negative than the E° value of the ion allows metal ions to be easily reduced. If the analysis of more than one metal ion is to be performed, a potential suitable for the species with the most negative peak potential is selected and all species are deposited on the electrode surface (Wang 2000). In the second step the

current-potential curves are obtained by re-oxidizing the analytes and generate a current signals; in general DPV or SWV ramps. The graph showing the time change of the potential in the anodic stripping voltammetry is shown in Figure 1.29.

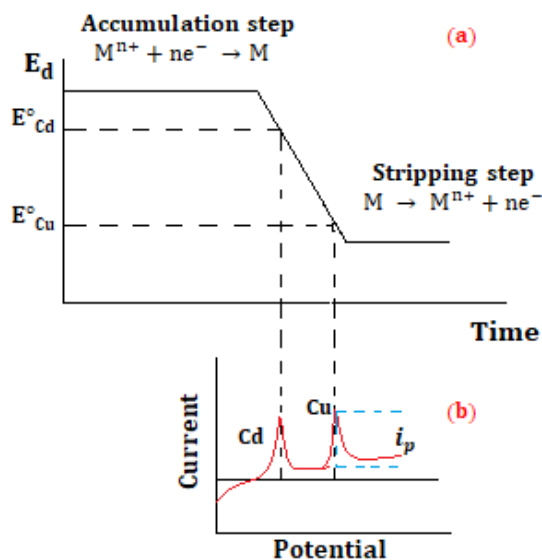
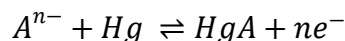


Figure 1. 29 ASV a) the potential-time graph, b) along with the consequential voltammograms (Wang 2000).

Cathodic Stripping Voltammetry (CSV)

The cathodic stripping voltammetry method is a mirror image of the anodic stripping voltammetry. After the anodic deposition of the analyte on the electrode surface, insoluble mercury salt is formed, then stripping is done by scanning the potential in the negative direction.



The determination of the analyte is carried out by using the reduction peak currents. This method is used to determine a wide range of organic and inorganic components because they can form an insoluble salt with mercury. If too much of the analyte is deposited on the electrode surface, distortion of the peaks may occur (Skoog 2018).

Adsorptive Stripping Voltammetry (AdSV)

The adsorption of ions and molecules on the surface of mercury electrodes has recently been a fascinating research topic. Adsorptive stripping voltammetry

is based on the deposition of the analyte on the surface and the reduction or oxidation of the analyte by some voltammetric methods, regardless of the adsorption mechanism and electrode reaction. Often, the reaction product is adsorbed on the electrode surface (Scholz 2005).

Despite the distinction made under stripping voltammetry, there is no significant difference between anodic and cathodic stripping voltammetry. Unlike other techniques, the preconcentration of the analyte on the electrode surface is achieved not by the electrolytic method but by the physical adsorption of the substance. Many organic species and inorganic species were determined using this technique at micromolar and nanomolar concentration levels. The adsorbed species are measured positively or negatively using a voltammetric method such as SWV or DPV to give a voltammetric signal proportional to the concentration (Settle 1997).

In the adsorptive stripping voltammetry, in the preconcentration step, the metal ion (M^{n+}) reacts with a suitable ligand (L) in the solution to form the surfactant ML_n complex. This complex is then deposited on the electrode surface in a controlled manner by adsorption. With the help of the negative potential applied to the system, the reduction process can be followed by the reduction of the metal cation in the adsorbed complex and the reduction of the ligand (Figure 1.30). As a result, adsorption peaks occur depending on the concentration of the species deposited on the electrode surface.

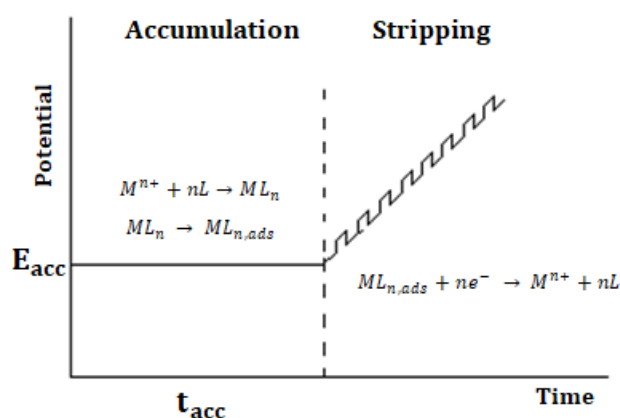


Figure 1. 30 Accumulation and stripping steps in ASV measurement of a metal ion (M^{n+}) in the presence of a suitable chelating agent (L) (Wang 2000).

2. EXPERIMENTAL

2.1 Apparatus

Voltammetric and electrochemical impedance measurements were carried out using Autolab 302 N Electrochemical Analysers with a three electrodes system consisted of a working electrode (bare GCE, Au disk, Pt disk, poly(aniline), and poly(p-aminophenol) film GCE, various metal nanoparticles modified polymer film coated GCE), a platinum wire counter electrode and an Ag/AgCl (sat. KCl) reference electrode, respectively. Cyclic voltammetry (CV), linear sweep voltammetry (LSW), differential pulse voltammetry (DPV) and chronoamperometry were used throughout the electroanalytical studies. Fiber optic illuminator with 250 W halogen bulb and F01-250 Light Guide (Titan Tool Supply Inc., USA) were used to perform photoelectrochemical experiments and illuminate the electrode surface. Thermo Scientific Apreo S and Philips XL30 SFEG Scanning Electron Microscopies were used for the characterization of modified electrode surfaces. Surface chemistry of each metal particle modified electrodes was studied by X-Ray-photoelectron Spectroscopy (XPS) using Thermo Scientific K-Alpha XPS spectrometer. FEI Tecnai G2 Spirit BioTwin CTEM was used for the characterization of metal nano particles on the electrode surfaces. Bandelin Sonorex model ultrasonic bath was used for cleaning of electrodes.

2.2 Reagents and Materials

All reagents were of analytical reagent grade. Aniline ($C_6H_5NH_2$), 4-aminophenol ($H_2NC_6H_4OH$), sodium perchlorate ($NaClO_4$), potassium bicarbonate ($KHCO_3$), sodium hydroxide ($NaOH$), copper sulfate ($CuSO_4$), sodium dihydrogen phosphate (NaH_2PO_4), disodium monohydrogen phosphate (Na_2HPO_4), graphite and cresol Red ($C_{21}H_{17}NaO_5S$) were supplied from Sigma-Aldrich. Ammonia (NH_3), sodium dodecyl sulphate ($C_{12}H_{25}NaO_4S$), N,N-dimethylformamide (DMF) (C_3H_7NO), perchloric acid ($HClO_4$), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), manganese dioxide (MnO_2), ethanol (C_2H_5OH), and methanol (CH_3OH) were supplied from Merck. Potassium antimony(III) tartrate hydrate ($C_8H_{10}KO_{13}Sb$), catechol ($C_6H_4(OH)_2$)

and resorcinol ($C_6H_6O_2$) were supplied from Sigma. Formaldehyde (CH_2O) was supplied from ISOLAB. Tetrabutyl titanate ($Ti(C_4H_9O)_4$) and copper(II) phthalocyanine ($C_{32}H_{16}CuN_8$) were supplied from TCI. Alumina powder was supplied from MetLab. Nujol was supplied from BDH. The chloroauric acid ($HAuCl_4$) was prepared by the dissolution of Au metal in 1 volume HNO_3 + 3 volume HCl . Aniline was purified three times with a steam distillation technique by rotating the evaporator.

The solutions of aniline monomer in H_2SO_4 and p-aminophenol in SDS, $NaClO_4$ and $KHCO_3$ in water, chloroauric acid in HCl and copper sulfate, Copper(II) phthalocyanine in H_2SO_4 were daily prepared by dissolving the required amount of reagent in suitable solvents. All aqueous solutions were prepared using ultra-pure water (Millipore Milli Q system (18.2 $M\Omega$)).

2.3 Methods

2.3.1 Pretreatment of GCE

Prior to use, the bare GCE was polished on a synthetic cloth with alumina powder (0.05-3 micrometer) and then ultra-sonicated successively in 1:1 pure water and absolute alcohol mixture (v/v) for 3 minutes, to get a mirror-shiny surface. GCE was also electrochemically activated by keeping 5 minutes at constant potential at 1.0 V.

2.3.2 Preparation of poly(aniline) film modified GCE

The polyaniline film was formed on the bare GCE surface in the presence of 0.1 mol L^{-1} H_2SO_4 containing 0.1 mol L^{-1} aniline monomer by cyclic voltammetry at 50 V/s, between -0.2 and 1.2 V. The film thickness was varied by changing the number of current-potential cycles. The obtained electrode was ready for use after the final wash with ultra-pure water and denoted as PANI/GCE.

2.3.3 Preparation of poly(p-aminophenol) film modified GCE

The poly(p-aminophenol) film modified electrode was prepared in 0.5 M aqueous $HClO_4$ solution containing 5 mM p-aminophenol monomer in the presence of 5 mmol L^{-1} SDS with cyclic voltammetry between -0.50 V and +2.20

V vs. Ag / AgCl (sat. KCl) at a scan rate of 20 V s^{-1} for various cycle numbers. The obtained electrode was ready for use after the final wash with ultra pure water to remove the remaining monomer adsorbed on the surface of the electrode. The polymer film electrode denoted as PPAP/GCE.

2.3.4 Preparation of Carbon Paste Electrode

The carbon paste electrode was prepared by different amount of MCM-TiO₂ composite material, Nujol (mineral oil) and graphite. In the studies, carbon paste electrodes prepared at the rates of 10% MCM-TiO₂ + 30% nujol + 60% graphite and 5% MCM + 5% TiO₂ + 30% nujol + 60% graphite carbon paste electrode were used.

2.3.5 Preparation of MnO₂-TiO₂ Composite GC Electrode

Two different metal oxide electrode materials were prepared by adding 3 ml of ethanol + 3 ml ultrapure water to 0.05 gr TiO₂ + 0.05 gr MnO₂ powder mixture and kept in an ultrasonic bath for 1 hour. Then, MnO₂-TiO₂ mixture was dried in the oven at 200°C for 30 minutes and then separately in the 500°C ovens for 1 hour. As a result, black powder mixtures were obtained. The suspension was prepared by mixing 0.06 g MnO₂ - TiO₂ + 1.00 mL ultrapure water. 20 μL of the prepared MnO₂ - TiO₂ suspension was dropped onto the GCE surface, and the electrode was allowed to dry in the oven for 30 minutes at 65°C.

2.3.6 Preparation of poly(cresol red) and over-oxidized poly(cresol red) film modified glassy carbon electrode

The electrochemical polymerization of cresol red monomer on bare GCE was performed in pH 7.0 PBS buffer solution containing 0.5 mmol L^{-1} cresol red by cycling the potential from -1.2 to 1.8 V vs. Ag / AgCl (sat. KCl) at a scan rate of 100 V s^{-1} for 30 cycles. The electrode was rinsed with water. The obtained electrode was ready for use after the final wash with ultra-pure water and denoted as PolyCrRed/GCE.

The over-oxidation of polyCrRed/GCE was carried out in 0.2 mol L^{-1} NaOH solution at 0.7 V constant potential for 100 second by chronoamperometry. The obtained electrode was ready for use after the final wash with ultra-pure water and denoted as polyCrRed_{ox}/GCE.

2.3.7 Preparation of copper (II) phthalocyanine/over-oxidized poly(cresol red) modified glassy carbon electrode

A proper amount of copper (II) phthalocyanine was dispersed in 10 mL concentrate H_2SO_4 get 5 mmol L^{-1} CuPc solution. After over-oxidation step to get $\text{CrRed}_{\text{ox}}/\text{GCE}$, the modified electrode was rinsed thoroughly with ultrapure water and transferred into a 0.01 mmol L^{-1} copper (II) phthalocyanine (CuPc) solution containing cell. The CuPc was deposited on the $\text{CrRed}_{\text{ox}}/\text{GCE}$ surface at -0.1 V constant potential for 100 s. The obtained electrode was ready for use after a final wash with ultrapure water and denoted as copper (II) phthalocyanine/ over-oxidized poly(cresol red) modified glassy carbon electrode. Here and after the modified electrode is denoted as $\text{CuPc}/\text{CrRed}_{\text{ox}}/\text{GCE}$.

2.3.8 Preparation of various metal nanoparticles modified GC electrodes

The electrochemical deposition of metal nanoparticles on PPAP/GCE and PANI/GCE was carried out by cyclic voltammetry. Au and Cu metal nanoparticles were deposited on modified electrode surfaces by CV technique with a scan rate of 50 V s^{-1} for 10 cycles at particular potential window in HAuCl_4 containing 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} CuSO_4 containing 0.1 mol L^{-1} H_2SO_4 solutions, respectively. To prepare bimetallic nanoparticles modified polymer film GC electrodes, the same procedure given above was used as consecutively deposition on the same electrode surface. The obtained metal nanoparticles modified polymer GC electrodes were ready for use after the final wash with ultra pure water.

2.3.9 Preparation of mesoporous carbon material (MCM)

Stöber method was performed with the resorcinol, 4-aminophenol and catechol precursors. According to method, an aqueous-alcoholic solution was prepared by mixing of 40 mL ethanol and 100 mL of distilled water in a 500 mL beaker at room temperature. After adding 0.5 mL of ammonia solution to the mixture under continuous stirring, 2.0 g of precursor was added under stirring for additional 0.5 h. Subsequently, 2.8 mL of 37 wt% formaldehyde was dropped into the solution and stirred for 24 h. The resulting mixture was placed in an oven for 24 h at 100°C . The resulting samples were carbonized in flowing N_2 in a programmable furnace using a heating rate of $1^\circ\text{C}/\text{min}$ up to 450°C and 650°C .

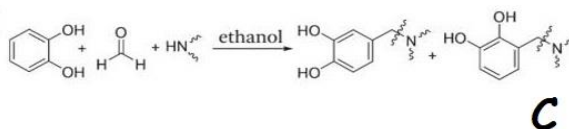
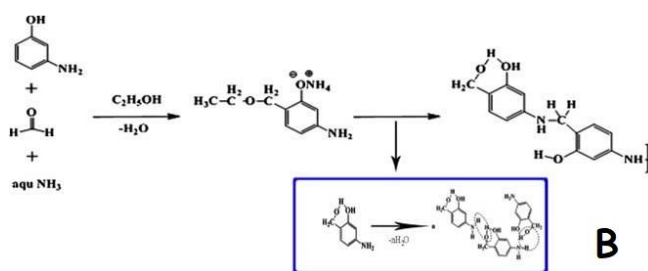
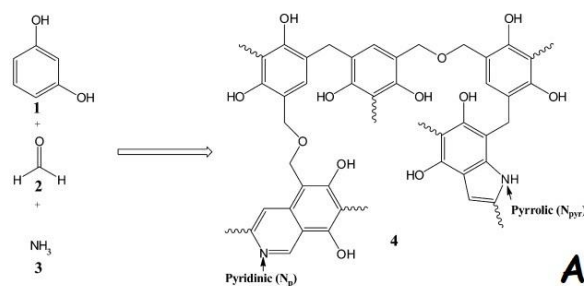


Figure 2.1 Proposed mechanism for mesoporous carbon materials synthesized with A) resorcinol, B) 4-aminophenol and C) catechol precursors respectively.

2.3.10 Preparation of MCM/TiO₂ composite materials and MCM-TiO₂/GC electrode

The MCM/TiO₂ composite material was prepared with sol-gel method. The synthesized MCM and tetrabutyl titanate were used as a carbon and TiO₂ precursor, respectively. A 1 g MCM and 1.5 mL tetrabutyl titanate was mixed at 1.5 hours in ultrasonic bath. The obtained material washed with isopropanol during the centrifuge at 10000 rpm for 30 min for 3 times. The washed material was dried at 60°C for 24 h. For the last step the material was annealed at 450° C for 3h by flowing N₂ into furnace. Finally, a 50 mg synthesized MCM/TiO₂ composite material was dispersed in the 3 mL DMF and then dropped on GC electrode for used as working electrode for photoelectrocatalytic reduction of CO₂. Preparation steps of TiO₂/MCM composite material were shown at Figure 2.2.

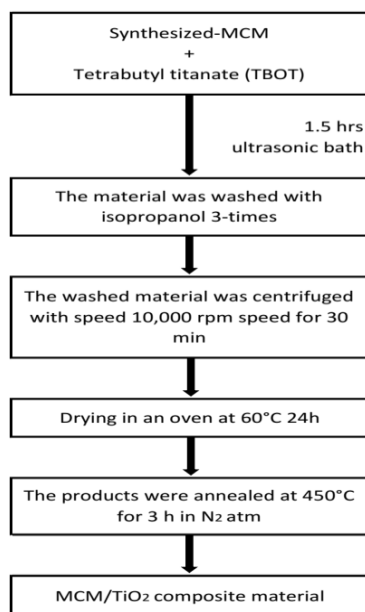


Figure 2.2 Preparation steps of MCM/TiO₂ composite material

2.3.11 Preparation of real PET samples

In order to evaluate the application of designed modified electrodes to real samples, to detect the amount of antimony (III) in plastic PET bottles were studied. A clean, empty plastic PET bottle was dried. Small pieces were cut off from dry plastic PET bottles with stainless steel scissors treated with acetone. 1 gram of the small pieces of bottles were dissolved in 1 mL of concentrated H₂SO₄ using ultrasonic bath for 30 minutes. After decomposition of PET sample, the mixture was filtered with membrane. All the preparation steps of PET bottle samples shown at Figure 2. 3. A standard addition method was used to detection of antimony in resulted plastic PET bottle sample under the optimized conditions.

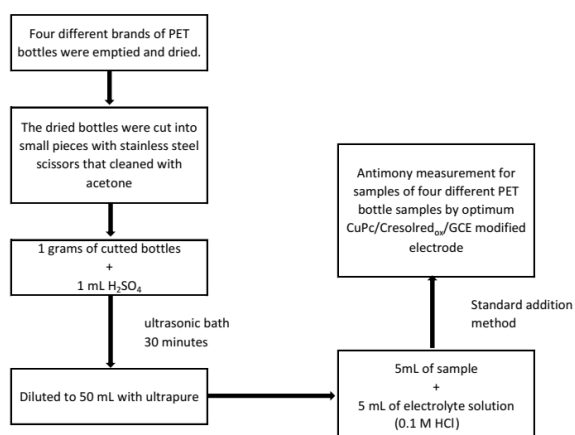


Figure 2.3 Preparation steps of PET bottle samples

3. RESULTS AND DISCUSSIONS

3.1 Preparation of polymer film electrodes

3.1.1 Preparation of poly (aniline) film modified GCE

Figure 3.1 shows the electropolymerization of 0.1 mol L^{-1} aniline monomer in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ to the GCE surface between $(-0.2) - 1.2 \text{ V}$ potentials at 50 V s^{-1} by cyclic voltammetry method. In the scan performed in the anodic direction, three well-separated peaks were observed at 0.20, 0.42, and 0.50 V potentials, respectively. The peak current of the first and third peaks were close to each other whereas some tendency to be higher than second peak. The peak potentials of the observed three peaks were shifted to positive potentials as 0.35, 0.45 and 0.55 V by increasing of scan number. All the three peaks have their cathodic counterparts, observable in the back potential scan. During the poly(aniline) electropolymerization, it was seen that the peak currents increase in parallel with the increase in the number of cycles. This indicates that poly(aniline) (PANI) polymerization has occurred on the GC electrode surface (Mu and Kan, 1996).

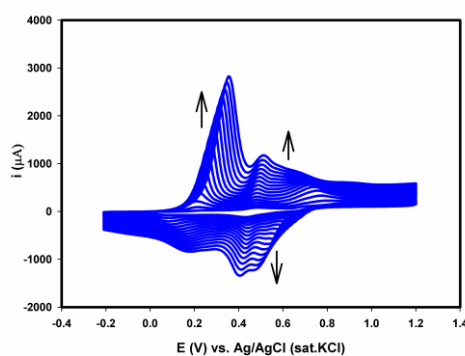


Figure 3.1 CVs of PANI electropolymerization of 0.1 mol L^{-1} aniline monomer in $0.1 \text{ M H}_2\text{SO}_4$ solution on the surface of the GCE at a scan rate of 50 V/s (for 15 cycles)

The peak observed at 0.20 V potential in poly(aniline) electropolymerization indicates the transition of PANI from the reduced leucoemeraldine (LE) state to the elevated emeraldine (EM) state. Similarly, the increase peak at 0.50 V corresponds to turn from the LE to the PANI state. Oxidation peaks at 0.42 V and 0.20 V are attributed to the p-benzoquinone reaction since intermediates are known to form during electropolymerization (Niu et al., 2003). Consecutive cycles with increasing oxidation peaks indicate the growth of

poly(aniline) film on the electrode surface. The primary mechanism is shown in Figure 3.2.

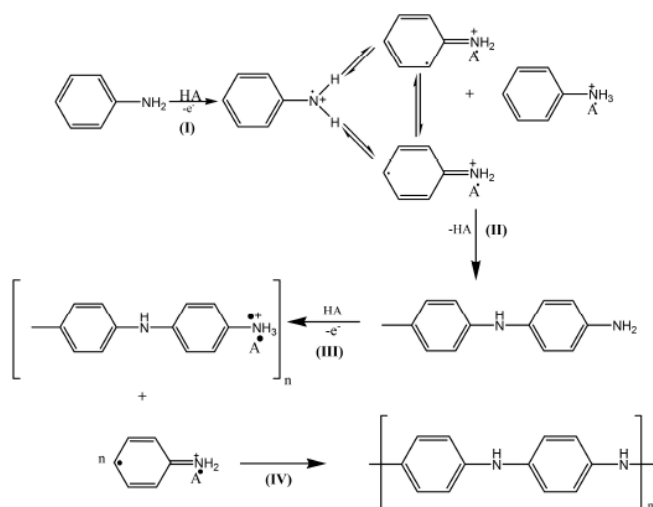


Figure 3.2 Electropolymerization mechanism of aniline to polyaniline

3.1.2 Preparation of poly (p-aminophenol) film modified GCE

The electrochemical polymerization of p-aminophenol monomer on GCE was studied in 0.5 M aqueous HClO_4 solution containing 5 mmol L^{-1} PAP in the presence of 5 mmol L^{-1} SDS by cyclic voltammetry in the potential range from -0.50 V to 2.20 V for 15 cycles (Figure 3.3).

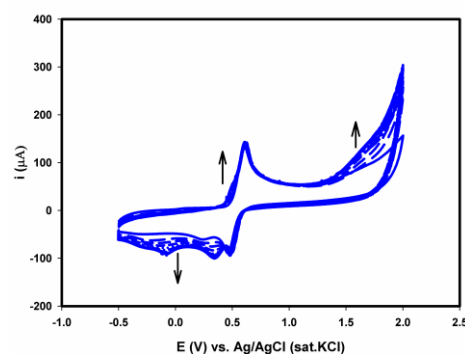


Figure 3.3 CVs of p-aminophenol electropolymerization of 5 mmol L^{-1} monomer in 0.5 mol L^{-1} HClO_4 solution on the surface of the GCE in the presence of 1 mmol L^{-1} SDS at a scan rate of 50 V/s (for 15 cycles).

The use of SDS in the electropolymerization of p-aminophenol monomer supports the increase in the monomer's conductivity (Liu et al., 2010). Due to the oxidation of p-aminophenol and the reduction of its oxidized form in electropolymerization, quasireversible peaks were observed at 0.60V and 0.52V potentials. Additionally, an irreversible oxidation of monomer wave was appeared

at 1.70 V. It is seen that these peaks increase with the increasing number of scans. However, in the first scan performed, there was only one reduction peak at 0.45 V potential and two new reduction peaks at 0.33 V and -0.88 V. The peak formed at the -0.10 V potential in the second scan can be attributed to intermediate species in the oxidation of p-aminophenol. The existence of SDS can also lead to the formation of more monocation radicals during p-aminophenol oxidation on the surface of electrode. The peak currents were increased depending on potential cycle, which demonstrating enhancement polymer content on the GCE surface.

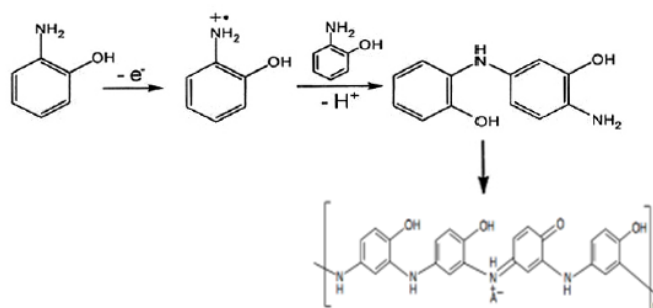


Figure 3.4 Electropolymerization mechanism of p-aminophenol

3.1.3 Preparation of poly (cresol red) and over-oxidized poly (cresol red) film modified glassy carbon electrode

The polished and cleaned GCE was placed in 0.5 mmol L^{-1} cresol red solution (pH 7.0 PBS). The poly(cresol red) film was prepared by repetitive potential cycling between -1.2 and 1.8 V, 30 times at a scan rate of 100 V s^{-1} . Figure 3.5-A shows repetitive cyclic voltammograms of 1 mmol L^{-1} cresol red in pH 7.0 PBS.

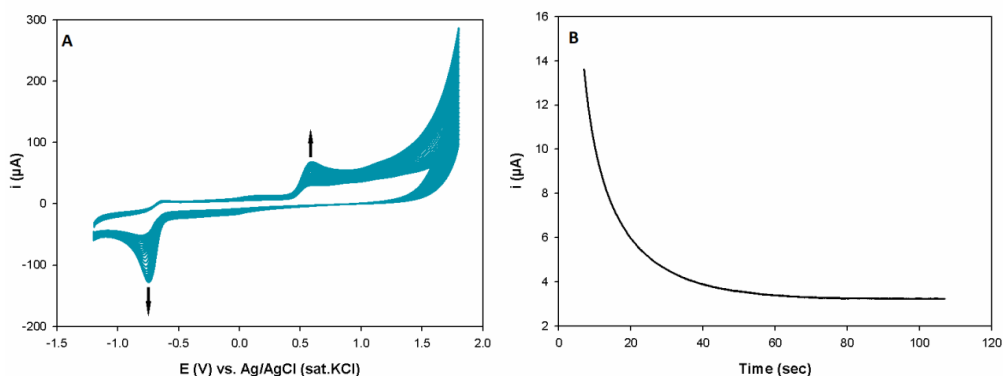


Figure 3.5 A) CVs of cresol red polymerization at a GCE electrode in pH 7.0 PBS containing 5.0 mmol L^{-1} cresol red monomer (B) over-oxidation of poly(cresol red) at 0.70 V on GCE in 0.2 mol L^{-1} NaOH solution.

During this process, the anodic peak at about 0.6 V corresponding to the oxidation of cresol red monomer and the peak height increased with increasing of scan number. A new redox couple appears at about -0.75 V in the cyclic voltammogram and the peak currents increase with successive scanning, indicating that film formation has occurred. With increasing scan number, the anodic peak potential shifts slightly in the positive direction, and the cathodic peak potential shifts slightly in the negative direction. The possible electrochemical polymerization mechanism was described as follows: orthomethyl phenol ring in cresol red was firstly oxidized to form 2-methylcyclohexadienone, and then a dimer was produced from an addition reaction between the parent molecule and the oxidized form of cresol red (Figure 3.6). This insoluble polymeric species formed by addition polymerization subsequently deposited onto the electrode.

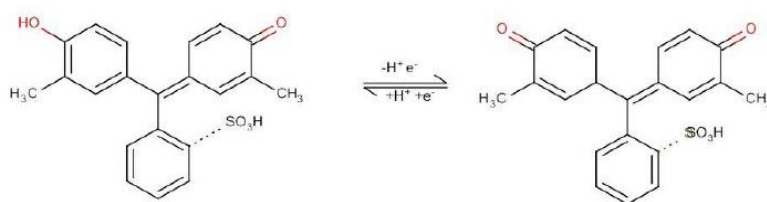


Figure 3.6 Electropolymerization mechanism of cresol red

The poly(cresolred) modified GCE was rinsed thoroughly with ultrapure water and transferred into a voltammetric cell containing 0.2 mol L⁻¹ NaOH solution for electrochemical over-oxidation of the conductive CrRed film at 0.7 V for 100 s with chronoamperometry (Figure 3.5-B).

3.1.4 Preparation of Metal Nanoparticles Modified GC Electrodes

The electrochemical deposition of gold nanoparticles on the poly(aniline) (PANI) and poly(4-aminophenol) (PPAP) film modified GCE in 1 mmol L⁻¹ HAuCl₄ + 0.1 mol L⁻¹ HCl solution was carried out in potential range between -0.9 V and +0.20 V at 50 V for 10 cycles. Figure 3. 7 A of CV showed that, Au nanoparticles obtained by Au(III) ions reduction at -0.40 V and reoxidation of Au at -0.35 V on PANI/GCE surface. For the following potential scans only a slight increase of the reduction peak current at -0.4 V was observed, and the peak potential slightly shifted to negative potentials. Figure 3. 7 B of CV showed that, It is observed that Au (III) ions are reduced to the Cu/PANI/GCE modified

electrode surface as Au⁰ nanoparticles at -0.40 V potential and oxidized at -0.35 V potential. It was observed that the peak current values increased as the number of Au nanoparticle coating increased, so it was predicted that Au nanoparticles were formed on the Cu/PANI/GC Electrode surface.

On the other hand, two reduction peaks at -0.32 V and -0.40 V were appeared for Au (III) ions to Au⁰ depends on the polycrystallographic orientation of the gold species on PPAP/GCE surface and partially reoxidation at -0.55V and -0.35 V of the reduced peaks was observed during the current-potential scan for anodic direction. Significant current increase was observed by subsequent potential scans especially on the reduction peak at -0.4 V (Figure 3.7 C). Similarly, the CV of Au nanoparticle formation on the Cu/PPAP/GCE surface is shown in Figure 3.7 D. The cathodic peak observed at -0.45 V belongs to the reduction of Au(III) ions to Au⁰ and nanoparticle formation on the surface, and the anodic peak observed at -0.35 V belongs to reoxidation. It was observed that the reoxidation potential shifted to positive potentials as the number of Au nanoparticle reduction and reoxidation cycles increased.

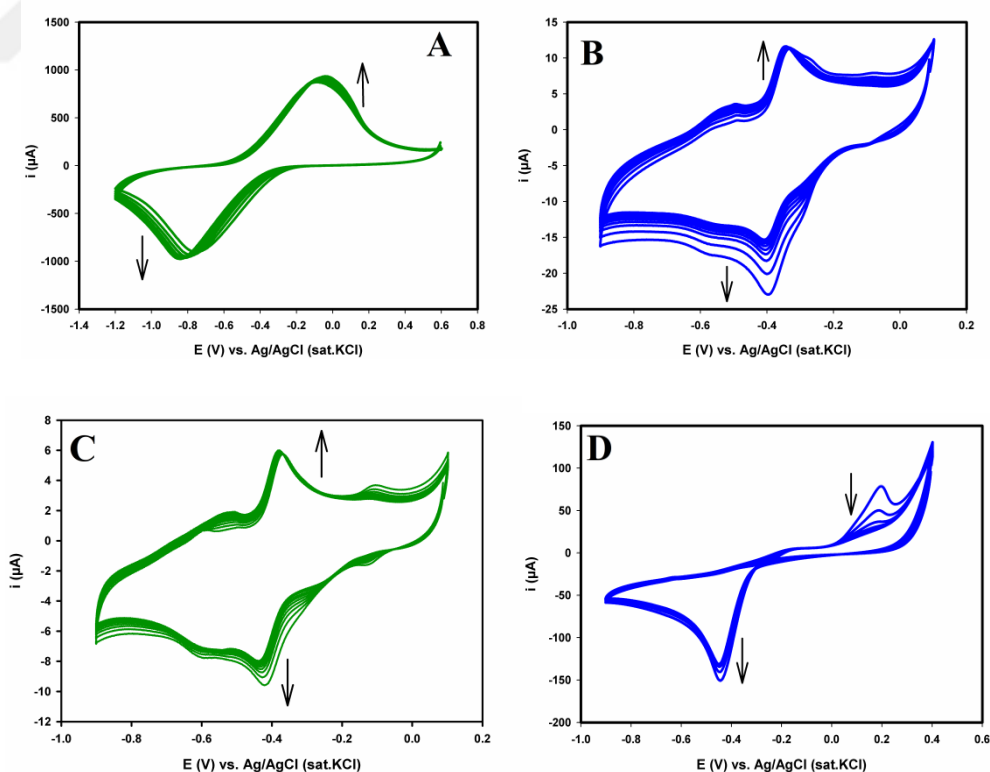


Figure 3. 7 Deposition of Au metal nano particles on A) PANI/GCE B) Cu/PANI/GCE C) PPAP/GCE and D) Cu/PPAP/GCE by CV from $1 \text{ mmol L}^{-1} \text{ HAuCl}_4$ in $0.1 \text{ mol L}^{-1} \text{ HCl}$ at 50 Vs^{-1} scan rate.

The electrochemical deposition of Cu metal particles on PANI/GCE and PPAP/GCE was achieved in the $0.1 \text{ mmol L}^{-1} \text{ CuSO}_4$ containing $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ by CV in the potential range from (-0.90V) to 0.20 V potential with 50 V s^{-1} scan rate (Figure 3.8).

A cathodic peak was observed at -0.15 V for reduction of Cu^{2+} ions to Cu metal during the potential scan from 0.50 V to -0.60 V . Two anodic peaks were appeared at -0.28 V and 0.05 V for reoxidation of the Cu metal which was formed during the cathodic potential scan (Figure 3.8 A). During the electrochemical deposition of Cu on Au/PANI/GCE (Figure 3.8 B), two reduction peaks and an oxidation peak were observed for both cathodic and anodic direction of potential scan. The reduction peak at -0.50 V and -0.72 V were for the reduction of Cu(II) ions to Cu metal depends on the polycrystallographic orientation of the Cu species on Au/PANI/GCE surface and partially reoxidation at -0.55V and -0.40 V of the reduced peaks was observed during the current-potential scan for anodic direction. In the case of the deposition of Cu on PPAP/GCE, a reduction peak at -0.65 V and oxidation peak at -0.15 V were formed due to the reduction of Cu^{2+} ion to Cu metal and reoxidation of deposited metallic Cu to Cu(II) for both cathodic and anodic direction potential scan (Figure 3.8 C). On the other hand, three reduction peaks at 0.10 V , -0.50 V and -0.82 V were demonstrated the reduction of Au(III) and Cu(II) ions respectively. The reduction peak at 0.10V could be formed due to the reduction of Au (III) ions to metallic Au due to the oxidation of Au on the PPAP/GCE. An higher reoxidation peak was also observed at -0.75 V for metallic Cu to Cu(II) during potential scan to the anodic direction (Zheng et al., 2018).

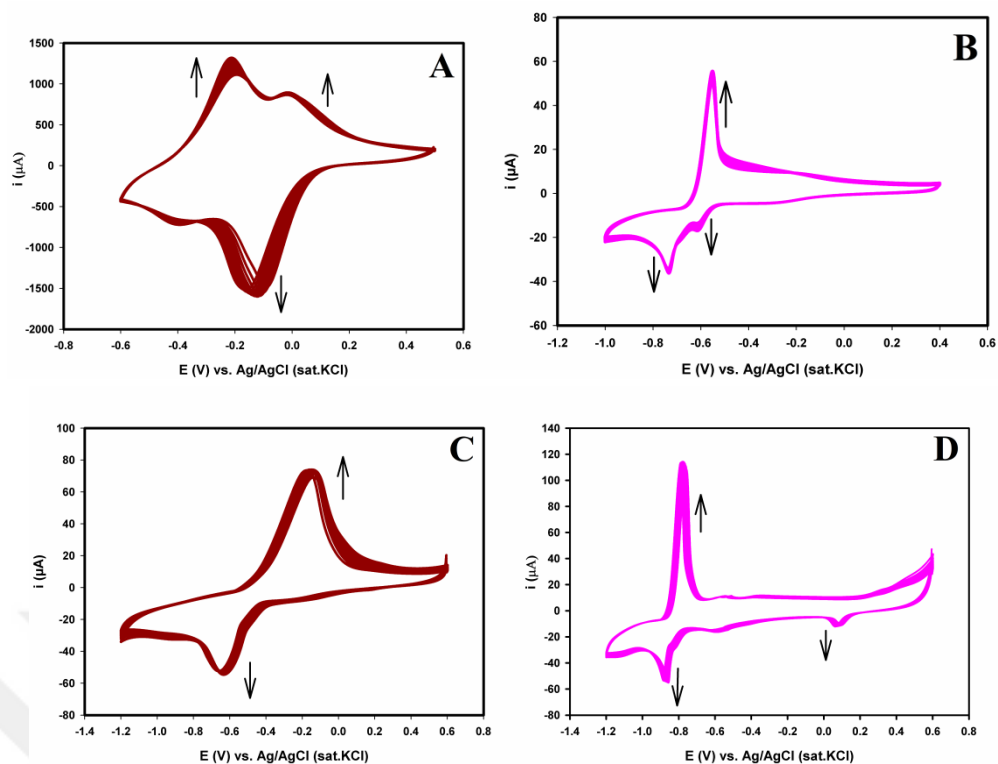


Figure 3. 8 Deposition of Cu metal nano particles on a) PANI/GCE b) Au/PANI/GCE c) PPAP/GCE and d) Au/PPAP/GCE by CV from 1 mmol L^{-1} in 0.1 mol L^{-1} HCl at 50 V s^{-1} scan rate.

3.1.5 Surface Characterization of Modified Electrodes and MCM/TiO₂

Composite Material

SEM, TEM, EDX, XPS and EIS techniques were used to identify the surface morphology, chemistry and charge/electron transfer properties of all modified electrodes.

3.1.5.1 Characterization of modified electrodes with SEM and EDX

SEM characterization of Cu and Au modified PPAP/GC electrodes

Figure 3.9 shows the SEM images of PPAP/GCE, Au/GCE, CuPPAP//GCE and successive deposition of Au and Cu particles on PPAP/GCE, which is demonstrated as Cu/Au/PPAP/GCE.

In Figure 3. 9-A almost homogeneously distributed porous PPAP polymer on GCE. These porous polymer surfaces enable to deposition of metal or metal oxide nanoparticles and prevent the agglomeration of the particles. Therefore a long term stable Au/GCE, CuPPAP//GCE and Cu/Au/PPAP/GC electrodes could be prepared. The SEM image of Au/PPAP/GCE shows Au nanoparticles were almost homogeneously deployed as distinguishable particles on the PPAP/GCE

surface (Figure 3.9-B). Figure 3.9-C displays the backscatter image of Cu/PPAP/GCE and practically round shape and bright Cu nanoparticles were distributed as heterogeneously on the PPAP polymer surface. The prepared bimetallic particles by consecutive deposition of Au and Cu on PPAP/GCE of SEM image was shown in Figure 3.9-D. As can be seen, the bimetallic nanoparticles are regularly distributed on the surface after consecutive deposition of Au and Cu on PPAP/GCE. When compared to single metal deposited on PPAP/GC electrodes, it is understood that the bi-metallic structure has a different geometry as trigonal form.

The different geometry and shape of Cu-Au bimetal particles in sem image show that Cu could be deposited mostly from metallic Au particles sites on the Au/PPAP surface. It is understood that a Cu-Au bimetallic/alloy structure could be formed on PPAP/GCE surface.

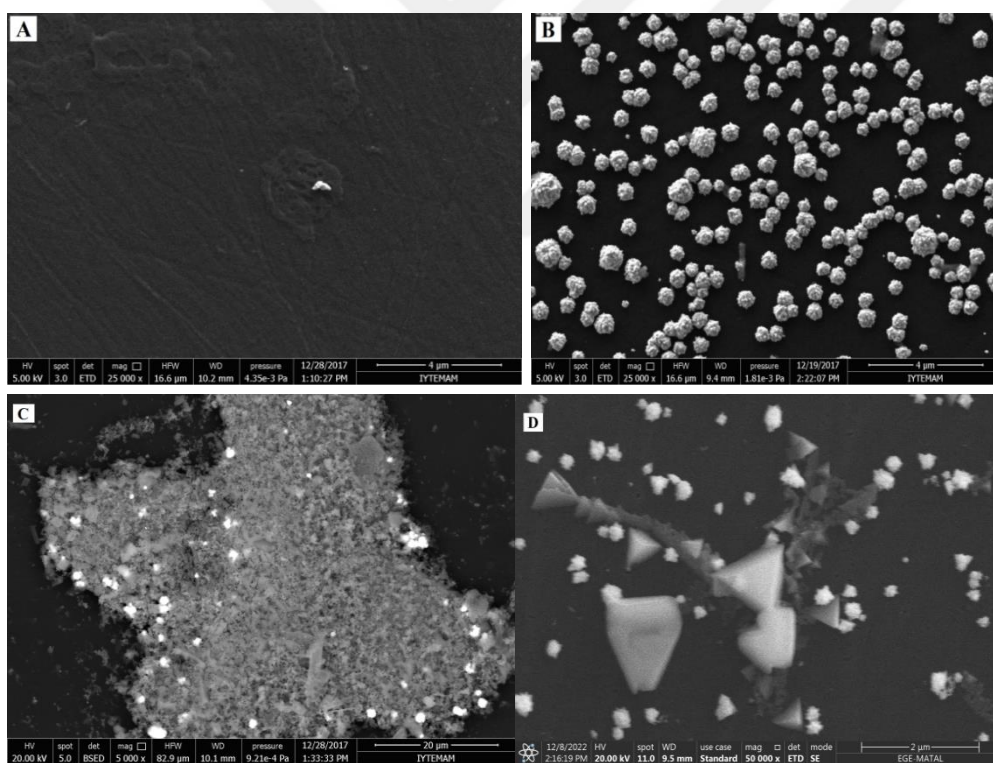


Figure 3. 9 SEM images of the (A) PPAP/GCE, (B) AuPPAP/GCE, (C) Cu/PPAP/GCE and (D) Cu/Au/PPAP/GCE.

Figure 3.10 shows the EDX images of Au/GCE, Cu/GCE and Cu/Au/PPAP/GCE. Energy dispersive X-Ray spectroscopy (EDX) study confirmed the presence of Au and Cu particles on PPAP/GCE.

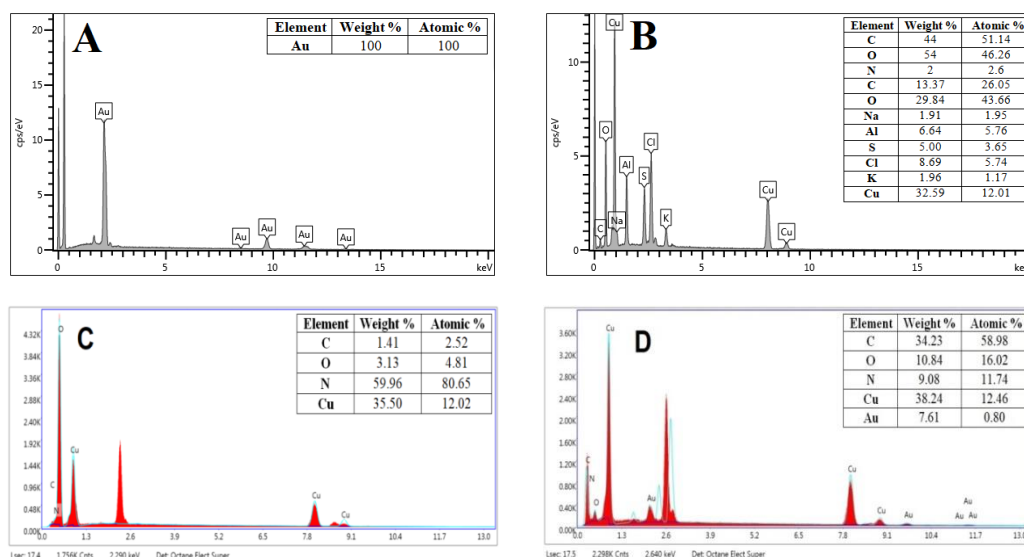


Figure 3.10 EDX results of the (A) Au/GCE, (B) Cu/GCE, (C) Cu/PPAP and (D) Cu/Au/PPAP/GCE

The weight gain of the PPAP due to the Cu and Au loading were about 17.49 % and 46.36 %, respectively, which was prepared consequently deposition Cu and Au for Cu/Au/PPAP/GCE which was prepared simultaneously deposition. Finally, it can be claimed that a uniformly covered layer of Cu and Au nanoparticles modified PPAP on the GCE can easily be prepared with the presence technique applied here according to SEM images.

SEM characterization of MC and MCM/TiO₂ composite material

Figure 3.11, 3.12, 3.13 and 3.14 show SEM images of after carbonization of mesoporous carbon based material synthesized using 4-aminophenol, catechol and resorcinol precursors, respectively. In the literature, the images obtained after SEM analysis are exactly the same as SEM analyzes for mesoporous carbon based materials. In addition, the difference in particle sizes corresponds to the definition of mesopore specified in the literature.

In MCM synthesis of from 4-aminophenol precursor, carbonization temperature was applied at two different temperatures as 450°C and 650°C. According to the SEM results (Figure 3.11), it was observed that the spheres in the MCM material structure were more clearly separated when the carbonization process was performed at 650°C compared to the carbonization performed at 450°C. The mesoporous carbon particles diameter was varied between 629- 1679 nm for 450 °C and 524- 1005 nm for 650 °C. The results indicate that almost more homogenous mesoporous carbon particles were obtained with 650 °C

carbonization temperature. At the XPS analysis in the following sections, it was determined that there were differences in the material structure at 650°C and 450°C carbonization steps, and the chemical structure supported by the literature was obtained at 650°C (Xu et al., 2012, Liu et al., 2007).

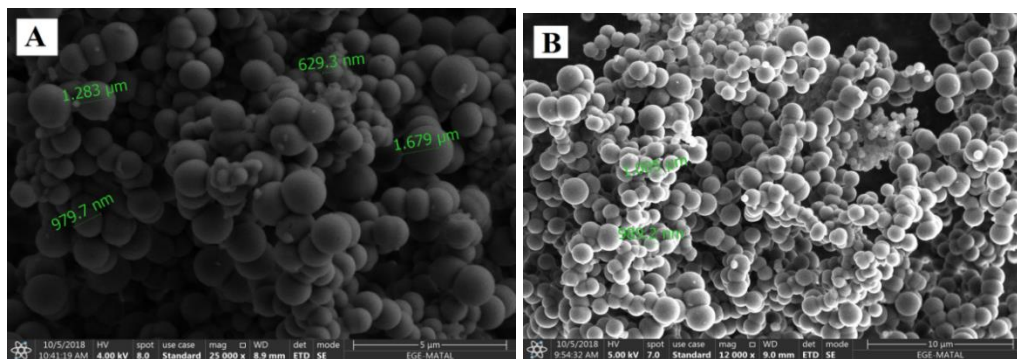


Figure 3. 11 SEM images of the MCM material synthesized by 4-aminophenol precursor material A) 450°C and B) 650°C carbonization temperature with 25000 and 12000 magnification, respectively.

In case of catechol precursors, almost similar structures were found and the mesoporous carbon particles diameter was changed in narrow range but the particles diameter were obtained in the range from 6.32 to 8.118 μm for 450 °C and 3.666 and 7.167 μm for 650 °C carbonization temperature. It is seen that the diameter of mesoporous carbon particles prepared with catechol precursor is approximately 6 times larger than those prepared with 4-aminophenol precursor for both carbonization temperatures.

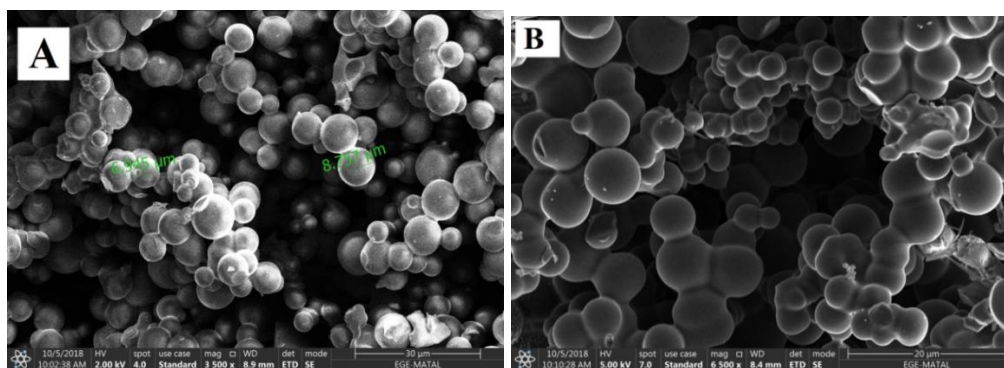


Figure 3. 12 SEM images of the MCM material synthesized by catechol precursor material A) 450°C and B) 650°C carbonization temperature with 3500 and 6500 magnification, respectively.

The SEM images with different magnification were demonstrated in Figure 3.13 at 450°C and in Figure 3.14 for 650°C carbonization temperatures for resorcinol precursor. A heterogeneous distribution of mesoporous carbon particles were formed in range of 8.554 – 1.792 μm particle diameters for 450°C carbonization temperature (Figure 3.13). On the other hand, the mesoporous

carbon particles with closer particle diameters in the 2.132 – 4.128 μm range were obtained for resorcinol precursor at 650°C

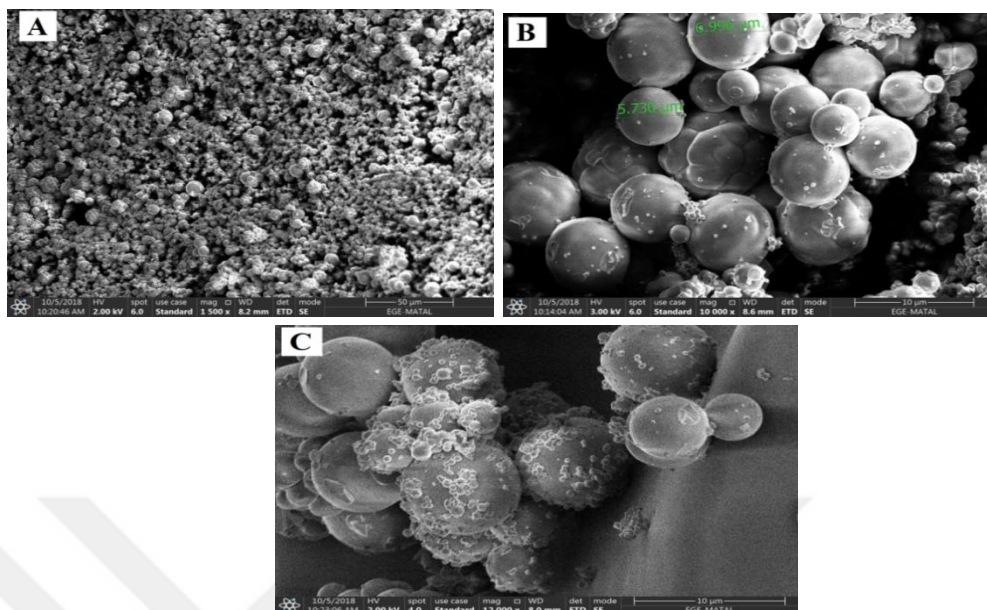


Figure 3. 13 SEM images of the MCM material synthesized by resorcinol precursor after 450°C carbonization with A) 1500, B) 10000 C) 12000 magnification, respectively.

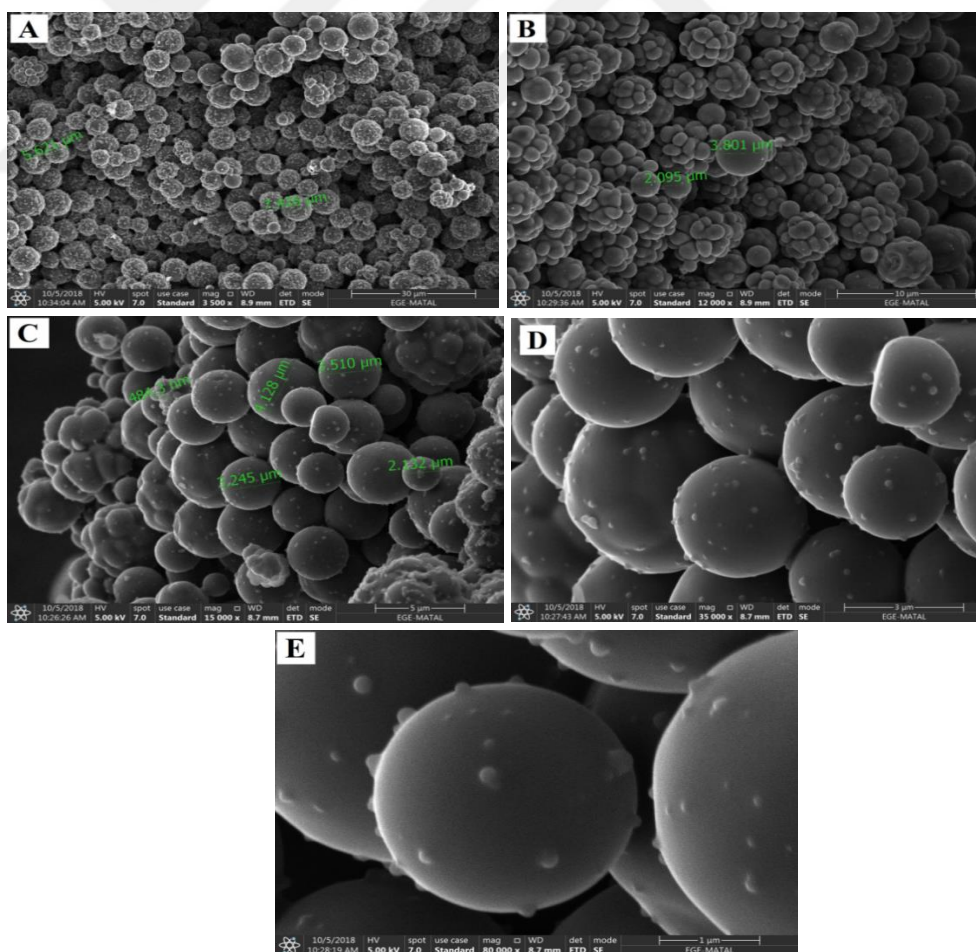


Figure 3. 14 SEM images of the MCM material synthesized by resorcinol precursor material after 650°C carbonization with A) 3500, B) 12000 C) 15000 D) 35000 and E) 80000 magnification, respectively.

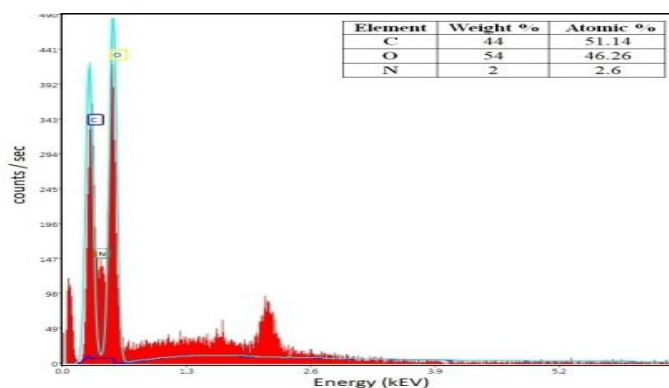


Figure 3. 15 EDX results of the MCM synthesized with resorcinol precursor.

The composite material was prepared from MCM and TiO_2 according to in section of 2.3.10 preparation of MCM/ TiO_2 composite material. Quite different SEM images were observed for MCM/ TiO_2 composite material in Figure 3.16 A and B compare with MCM. A heterogenous particle distrubition was obtained for composite material. It is understood from SEM images in Figure 3.16 A and B that when MCM and TiO_2 are brought together, they form a composite material with different morphology.

TiO_2 particles are distributed in the morphology of the composite material in a large petal shape. It is observed that SEM images of MCM/ TiO_2 composite material synthesis in agreement with literature studies (Liu et al., 2018 and Ma et al., 2013). The EDX study of MCM/ TiO_2 composite material confirmed the presence of Ti, C, N and O particles from synthesized material (Figure 3.17).

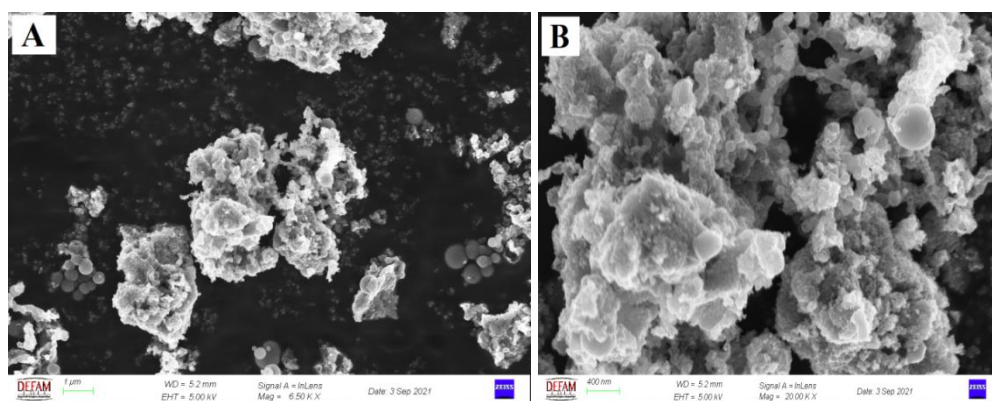
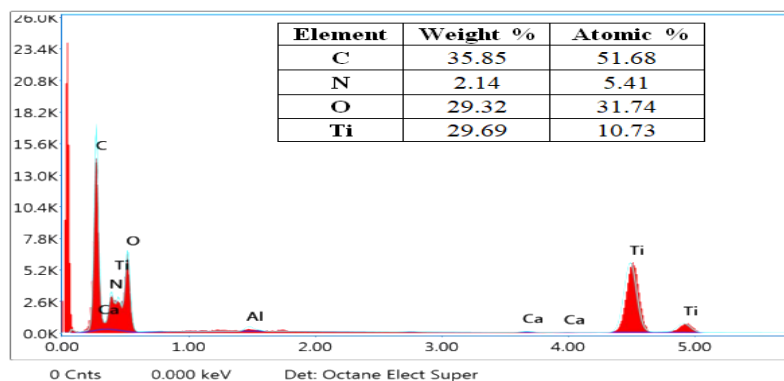


Figure 3. 16 SEM images of the MCM/ TiO_2 composite material with A) 6500 and B) 20000 magnification, respectively.

Figure 3. 17 EDX results of the MCM/TiO₂ composite material

SEM characterization of CuPc and Cresol red modified GC electrode

SEM and EDX techniques were used for characterization of poly(Cresol red)/GCE, poly(Cresol red_{ox})/GCE, CuPc/poly(Cresol red)/GCE and CuPc/poly(Cresol red_{ox})/GC modified electrodes (Figure 3.18 and Figure 3.19). Figure 3.18-A show that a porous poly(Cresol red) film was formed on the GCE surface. As seen in Figure 3.18-B, the polymer structure was branched and improved the porosity after the over-oxidation process. It is expected that the porosity and functional groups in the polymer structure sides were increased after the over-oxidation procedure (Ulubay Karabiberoğlu and Dursun, 2017).

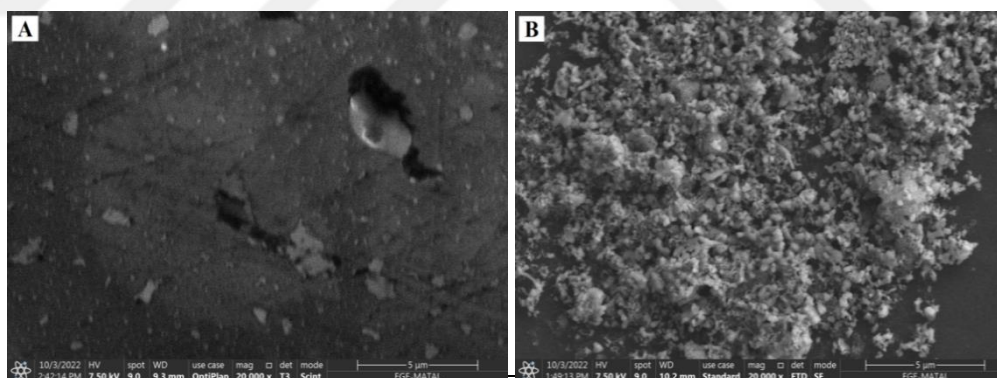
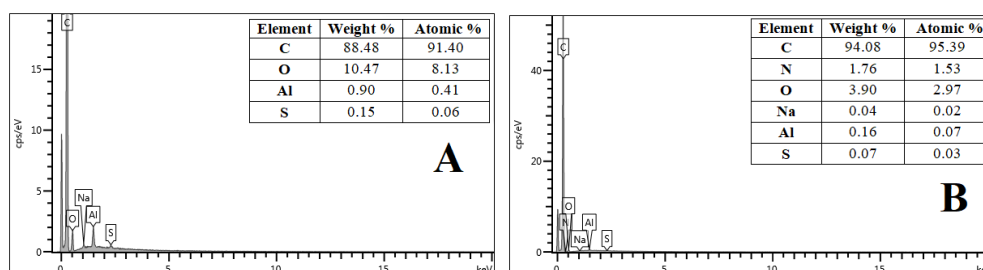
Figure 3. 18 SEM images of the A) poly(Cresol red)/GCE and B) poly(Cresol red_{ox})/GCE with 20000 magnification.Figure 3. 19 EDX results of the A) poly(Cresol red)/GCE and B) poly(Cresol red_{ox})/GCE , respectively.

Figure 3.20 shows the SEM images of the CuPc modified poly(Cresol red)/GC electrode. As can be seen from the images, CuPc is uniformly spread on

the polymer modified electrode surface. When CuPc was deposited after over-oxidation of poly(cresol red). It was observed that the morphology of CuPc modified poly (cresol red)/GCE surface was changed and rod-like CuPc structures were formed on the electrode surface in Figure 3.21, unlike Figure 3.20 (Chiu et al., 2011 and Ouyang et al., 2019). Thus, it is seen that the highly oxidized structure of the polymer also affects the CuPc structure deposited on it. The presence of Cu in EDX results shows that, CuPc was deposited on the both poly(Cresol red)/GCE and B) poly(Cresol red_{ox})/GCE (Figure 3.22) .

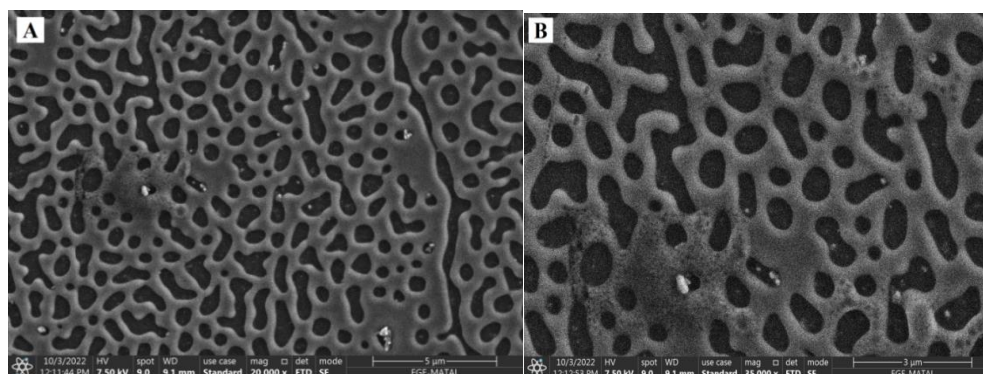


Figure 3. 20 SEM images of the CuPc/poly(Cresol red)/GCE with A) 20000 and b) 35000 magnification , respectively

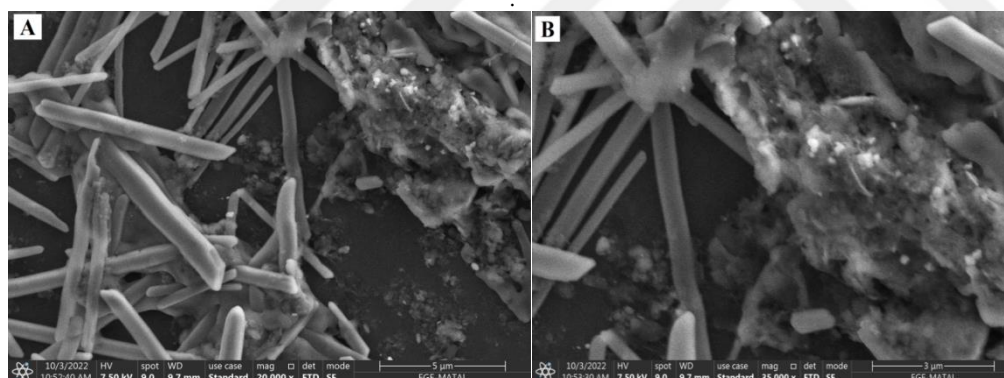


Figure 3. 21 SEM images of the CuPc/poly(Cresol red_{ox})/GCE with A) 20000 and b) 35000 magnification , respectively.

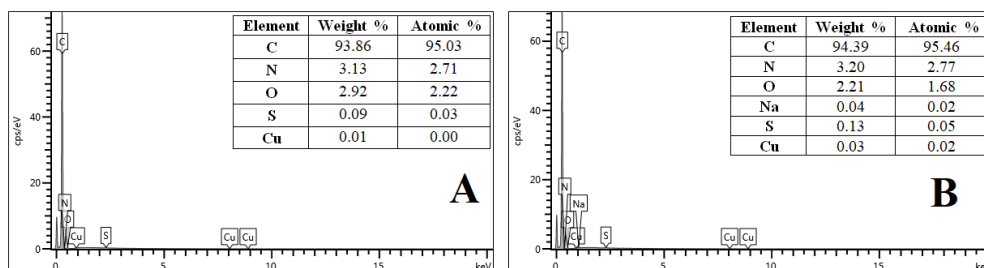


Figure 3. 22 EDX results of the A) CuPc/poly(Cresol red)/GCE and B) CuPc/poly(Cresol red_{ox})/GCE, respectively.

3.1.6 Characterization of modified electrodes by XPS

3.1.6.1 XPS chemical analysis of poly(4-aminophenol) modified GC electrode

To identify the surface composition of PPAP/GCE surface, XPS studies was performed and the spectrums were shown in Figure 3.23. Due to the molecular structure of 4-aminophenol, the presence of N, C, and O were expected in XPS survey spectrum (Figure 3.23 A). Figure 3.23 B display the high-resolution XPS spectrum of the N1s. The main peak may be deconvoluted into two peaks at binding energies (BE) 406.7eV and 401.7 eV attributed to the presence of pyrrolic N ($-NH-$), and quaternary N ($-N=C$) atoms in the polymer structure (Jia et al., 2010). The O1s core level spectrum of PPAP/ GCE was given in Figure 3.23-C. It exhibited two peaks at 532.1 eV and 532.9 eV attributed to C=O and C-O-C groups into polymer structure (Wu et al., 2020). Figure 3.23 D display the high-resolution XPS spectrum of the C1s. The main peak of C1s at 284.8 eV could be de-convoluted into four characteristic peaks corresponding to C-C (284.7 eV), C-N (286 eV), C-O (287 eV), and O-C=O (288.7 eV) groups (Hartman et al., 2019).

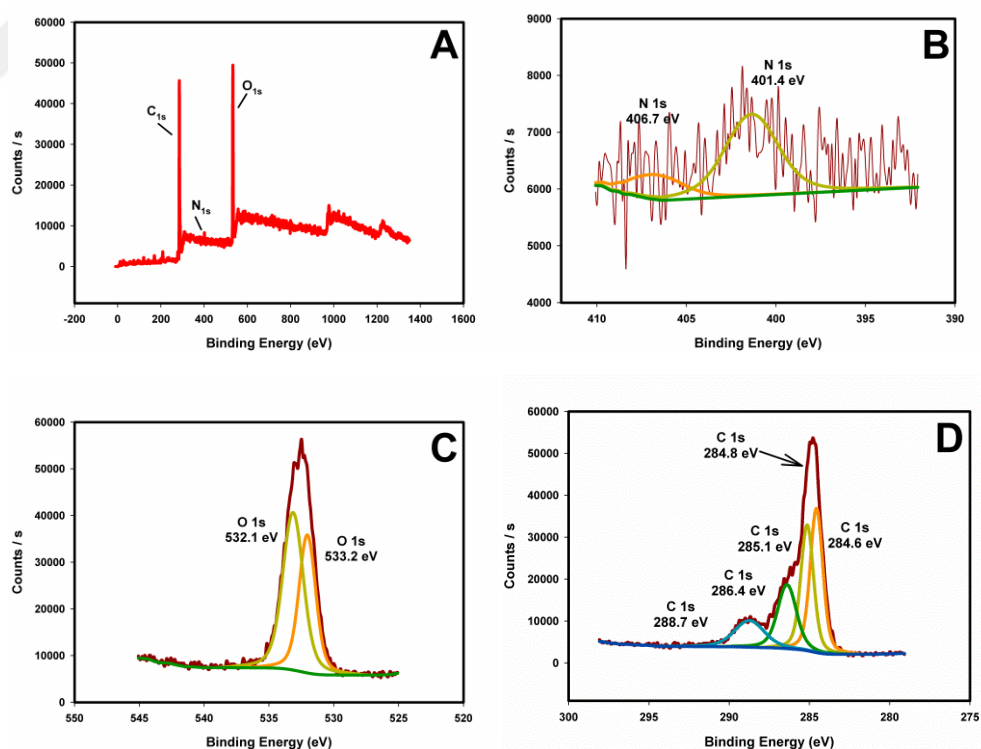


Figure 3. 23 XPS spectra of PPAP/GCE represent A) survey, B) N 1s C) O 1s and D) C 1s spectrums.

3.1.6.2 XPS chemical analysis of Cu modified PPAP/GC electrode

To identify the surface composition of Cu/PPAP/GCE and the oxidation state of Cu atoms, XPS studies were performed, and the spectrums are shown in Figure 3.23. Figure 3.24-A displays the existence of C, N, O, and Cu in Cu/PPAP/GCE. The peaks at 935 eV binding energy indicate the presence of Cu^0 and Cu^+ in the structure. The peaks between 940-946 eV binding energies indicate the presence of Cu^{2+} states, also another two satellite peaks formed at 943.88 eV and 939.8 eV also confirmed the presence of Cu^{2+} species on the PPAP/GCE surface. The binding energies of Cu 2p_{3/2} and Cu 2p_{1/2} for CuO species are shifting to positive values compare with literature data (Biesinger 2017, and Swadzba-Kwasny et al., 2011) due to an interaction between the Cu species with C and N containing PPAP surface during the electrochemical deposition of Cu with CV method.

The high-resolution XPS spectrum of the N1s (Figure 3.24-C) showed that the main peak may be deconvoluted into three peaks at binding energies (BE) 405 eV graphitic N (=C-N-C-), 402 pyrrolic N (-NH-), 395 and 390 pyridinic N (C-N-C) and 399,8 N-Cu, respectively (Huan et al., 2012, Bulushev et al., 2017). The O1s core level spectrum of Cu/PAP/ GCE was given in Figure 3.24-D. It exhibited three peaks at O 1s atom is molecularly adsorbed oxygen on Cu (533 eV), C=O (532.5 eV) and C-O-H (531.5 eV), respectively. Figure 3.24-E display the high-resolution XPS spectrum of the C1s. The main peak of C1s at 284.7 eV could be de-convoluted into four characteristic peaks relating to C-C (284.7 eV), C-N (286.0 eV), C-O (287.0 eV), and O-C=O (288.7 eV) (Hartman et al., 2019).

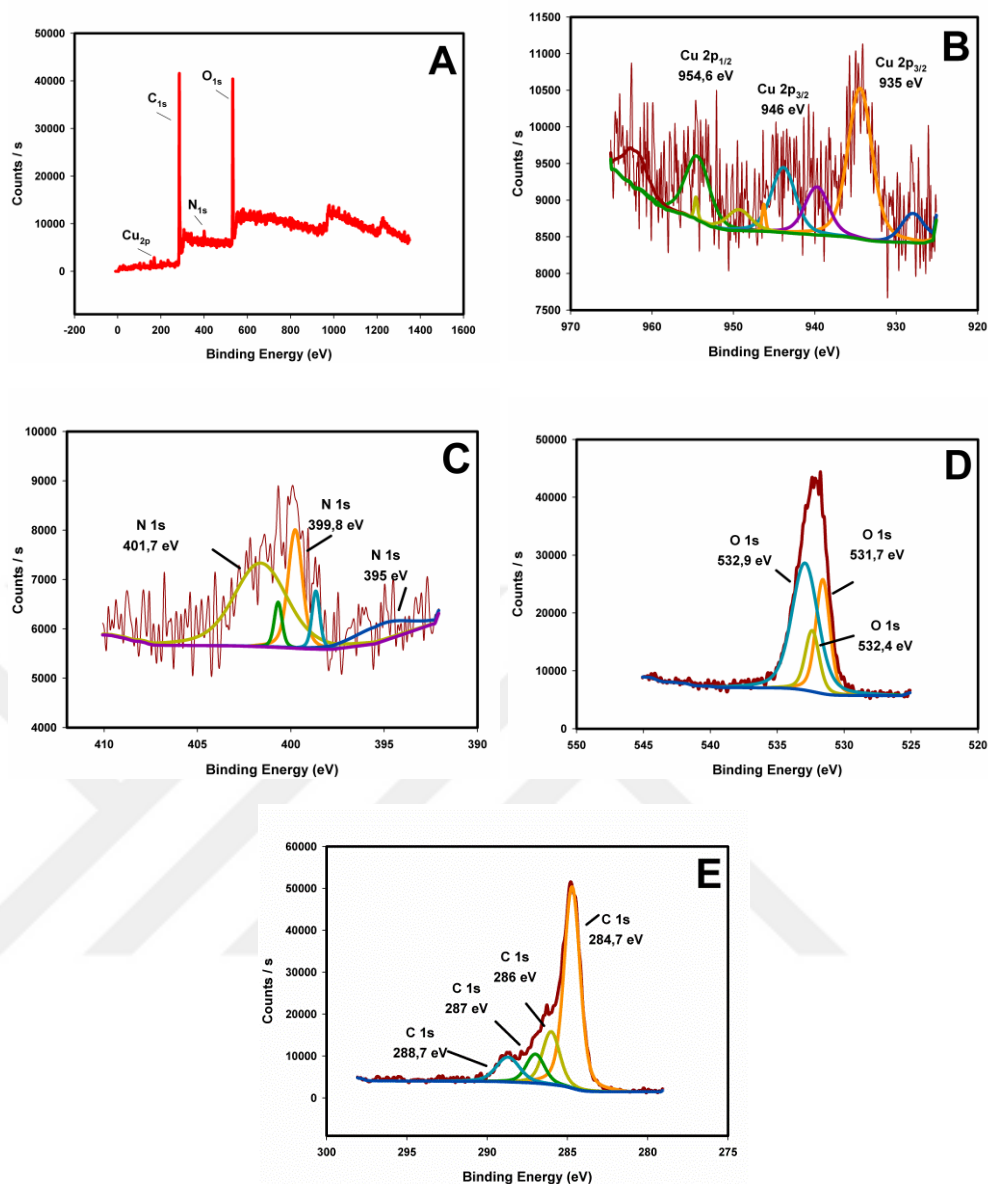


Figure 3. 24 XPS spectra of Cu/PPAP/GCE represent A) survey, B) Cu 2p C) N 1s, D) O 1s, and E) C 1s spectra.

3.1.6.3 XPS chemical analysis of Au modified PPAP/GC electrodes

Figure 3.25A display survey spectrum of Au modified PPAP/GCE. The presence of Au, C, N and O atoms were confirmed. The high-resolution Au4f XPS spectrum resolved into two spin-orbit components. The Au4f_{7/2} and 4f_{5/2} peaks observed at 87.9 and 84.3 eV binding energy, respectively. Moreover, a 3.60 eV Binding energies difference between Au 4f_{5/2} and Au 4f_{7/2} also proved the presence of Au in a metallic form. (Bakır et al., 2011).

As the above sections explain, N, O, and C atoms were expected from the polymer in the PPAP/GCE structure. When the binding energy graph of N1s

atoms was examined, it is seen that the system was in the form of -NH- (394.9 eV) and -N=C- (400.3 eV) as explained in the section above (Figure 3.25-C). Similarly, O 1s atoms in the structure are in C-O-C / C-O-H (531.6 eV) and C=O (532.7 eV), structures (Figure 3.25-D), and C1s atoms are in C-C (284.7 eV), C-N (286.5 eV), C-O (288.5 eV) structures and O-C=O (288.7 eV) (Figure 3.25-E).

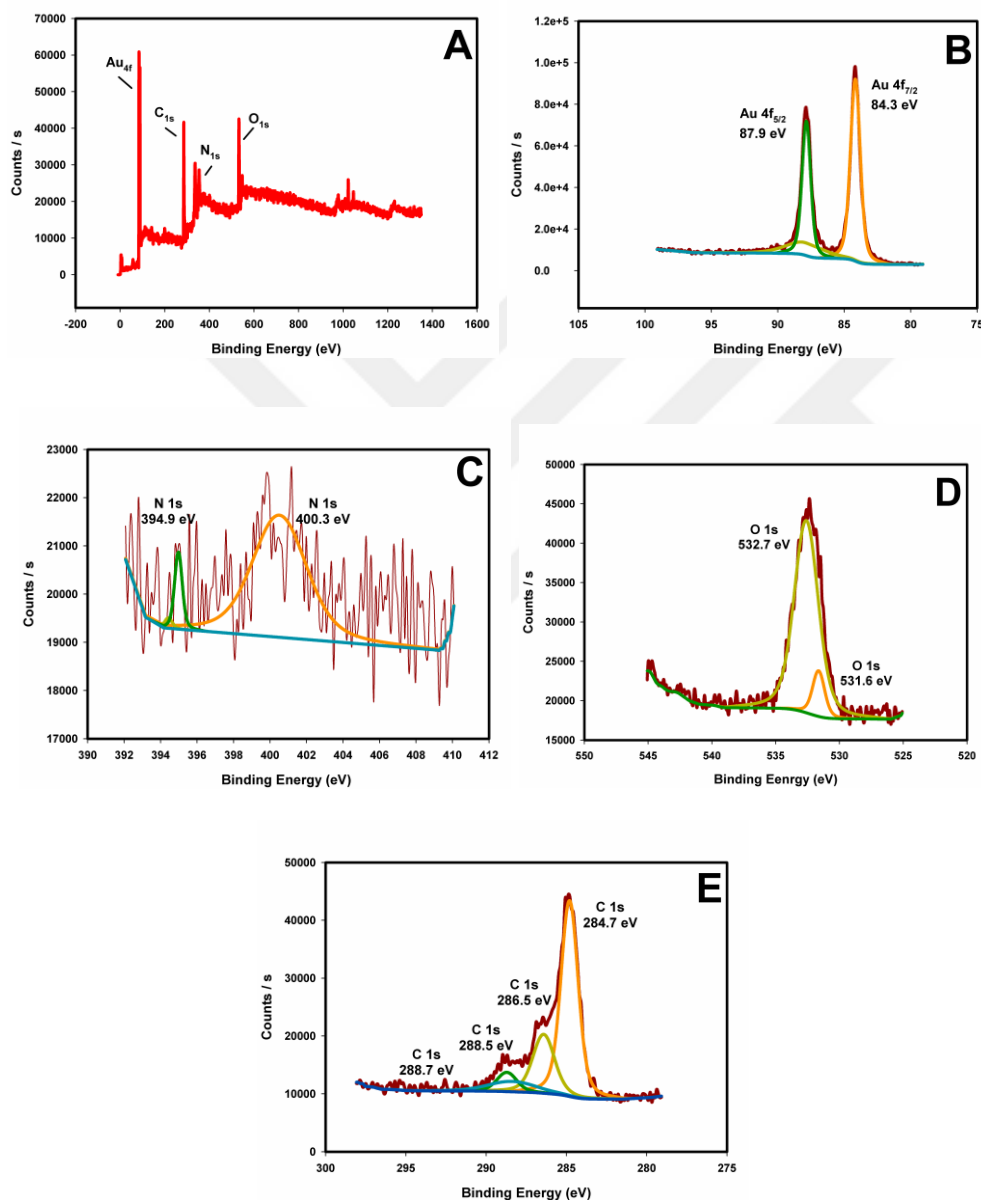
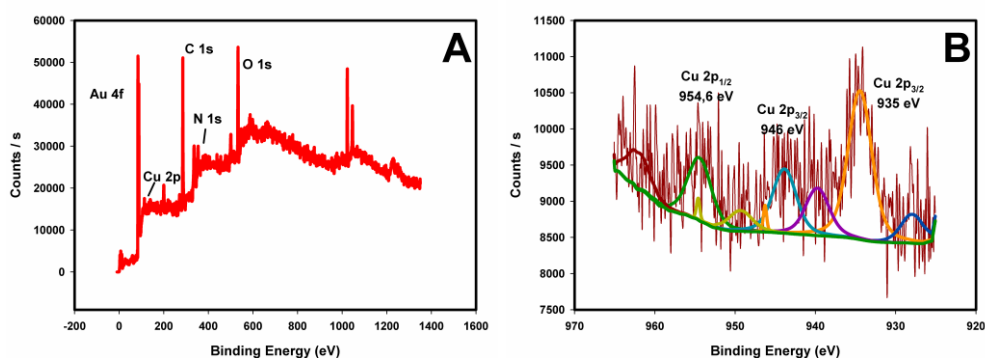


Figure 3. 25 XPS spectra of Au/PPAP/GCE represent A) survey, B) Au 4f, C) N1s, D) O1s and E) C1s spectrums.

3.1.6.4 XPS chemical analysis of Cu and Au modified PPAP/GC electrode

The surface composition and chemical oxidation states of the Cu and Au particles on the PAP were also determined by XPS. Figure 3.26A display survey spectrum of Cu-Au/ PPAP/GCE. The presence of Cu, Au, C, N and O atoms were confirmed. Figure 3.26-B and Figure 3.26-C show the comparative core-level spectra of Cu 2p_{1/2}, Cu 2p_{3/2} and Au 4f_{5/2} -Au 4f_{7/2} of Cu/Au/PPAP/GCE. The Cu 2p spectrum resolves into two spin-orbit components (Cu 2p_{1/2} and Cu 2p_{3/2}) on Cu/Au/PPAP/GCE. The main two peaks of Cu were observed at 954.5 eV and 934.2, whereas peaks of Au 4f_{5/2} and Au 4f_{7/2} were formed at 84.1 and 84.7 eV, respectively. The peaks at 930 eV and 935 eV binding energies indicate the presence of Cu⁰ and Cu⁺ in the structure, which cannot be discriminated from each other. The peaks at 940-946 eV binding energies indicate the presence of Cu²⁺ states, and another two satellite peaks formed at 943.88 eV and 939.8 eV also confirmed the presence of Cu²⁺ species on the Cu/Au/PPAP/GCE surface. The binding energies values of Cu 2p_{3/2} and Cu 2p_{1/2} could be ascribed to the presence of Cu particles surface converted to the CuO on the Cu/Au/PPAP/GCE surface. The binding energies values of Au 4f_{5/2} and Au 4f_{7/2} were indicated that Au particles were metallic form on the electrode surface.

When the N1s, O1s, and C1s atoms coming from the polymer structure are examined, it is seen that the N 1s atom in the polymer structure is 405 eV graphitic N (=C-N-C-), 402 pyrrolic N (-NH-), 395 and 390 pyridinic N (C-N-C) and 399,8 N-Cu respectively (Figure 3.26-D), the O 1s atom is molecularly adsorbed oxygen on Cu (533 eV), C=O (532.5 eV) and C-O-H (531.5 eV), (Figure 3.26-E), the C 1s atom is also C-C (284.7 eV), C-N (286.1 eV), C-O (287.1 eV) and O-C=O (288.8 eV) (Figure 3.26-F).



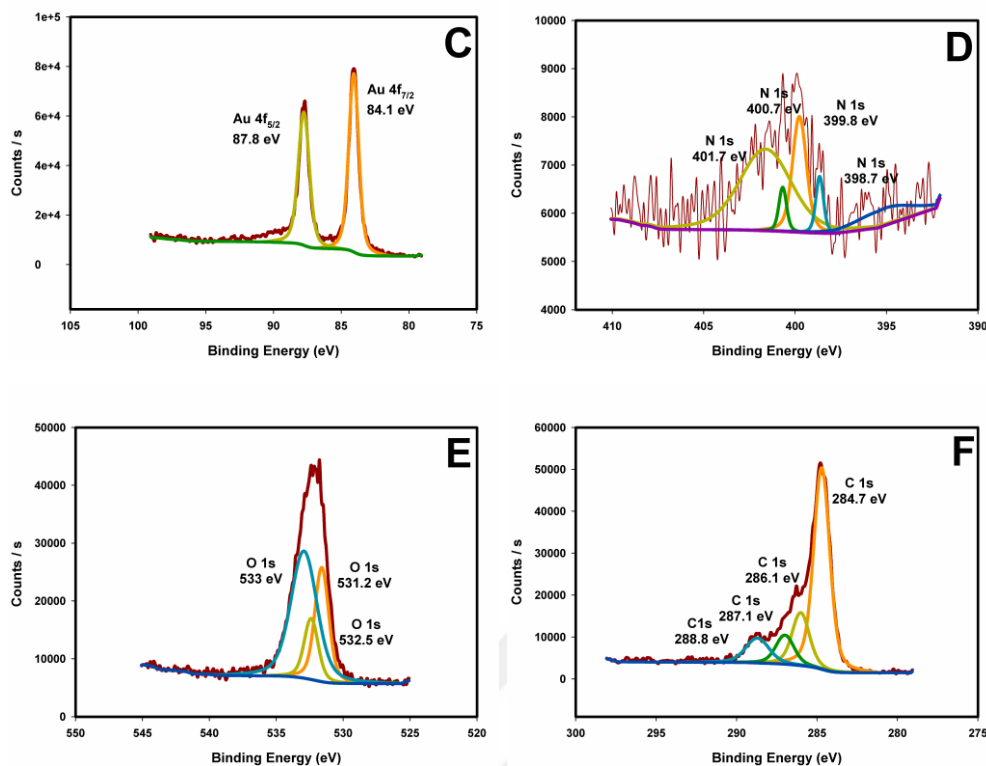


Figure 3. 26 XPS spectra of Cu/Au/PPAP/GCE represent A) survey, B) Cu2p, C) Au 4f, D) N1s, E) O1s and F) C1s spectra.

3.1.6.5 XPS analysis of MC material synthesized with different precursors

Synthesis of MC with 4-aminophenol

The mesoporous carbon materials (MCM) were synthesized with 4-aminophenol, catechol, and resorcinol precursors and the final products were identified with XPS. Figure 3.27A was displayed the survey spectrum of the MCM obtained with 450°C carbonization procedure and the presence of C, O and N atoms were detected.

The binding energies of O1s, N1s, and C1s atoms in the structure were investigated after XPS analysis, considering the molecular structure of 4-aminophenol used as an initiator. After carbonization of the synthesized MC material at 450°C, the high resolution spectrum of O1s show that three peaks at 531 eV, 532.6 eV and 533.6 eV (Figure 3.27B) attributed to C-O, C-O-C and O-C=O groups formed in MCM. The high resolution spectrum of N1s (Figure 27C) displayed two peaks at for C-N (398.2 eV), and C=N (400 eV), and the spectrum for C1s (Figure 27D) shown that the main peak may be deconvoluted into five

peaks for C-C (284.1 eV), C-O-H (284.7 eV), C-N (285.5 eV), C=O (286.4 eV) and O-C=O (286.9 eV) groups formed into MCM structure.

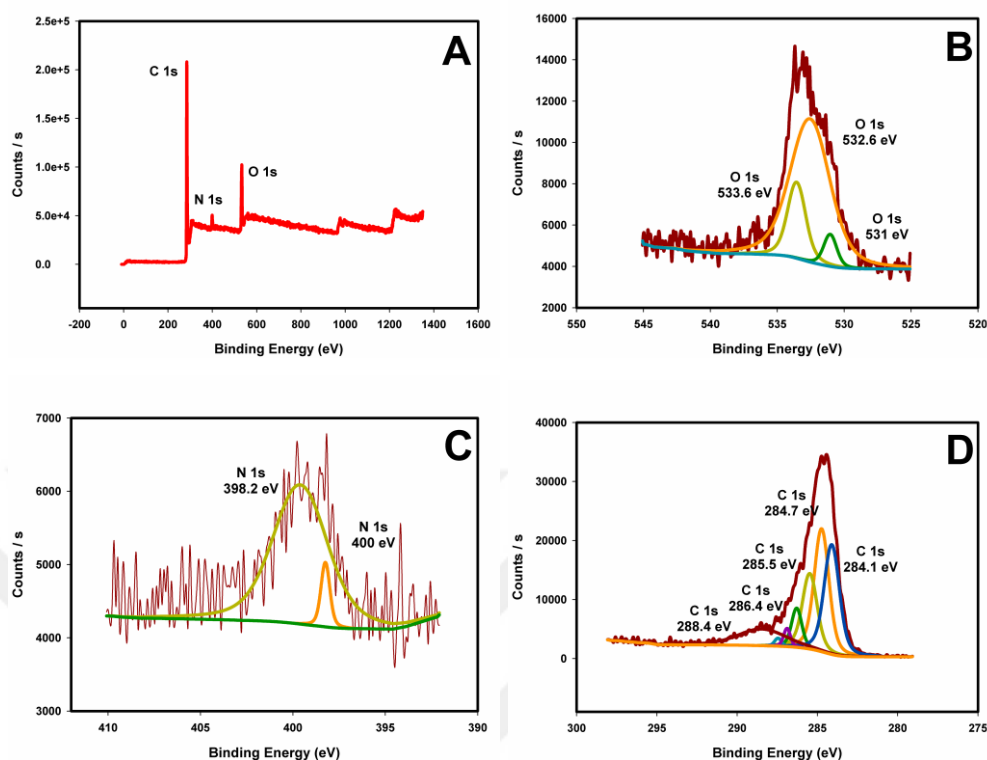


Figure 3. 27 XPS spectra of MC composite material synthesized with 4-aminophenol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectrums peaks after 450°C carbonization.

Changes in the structure were observed when the carbonization temperature was carried out at 650°C (Figure 3.28). The survey spectrum was confirmed the presence of O, N and C atoms in the structure of MCM obtained at 650 °C carbonization temperature. The high resolution spectrums displayed O-C (531 eV) and O-C=O (533.6 eV) for O1s, C-N (398.5 eV) and C=N (400.1 eV) for N1s and C-C (284.4 eV), C-O-H (285eV), C-N (285.6 eV), C-O-C (286.9 eV) and O-C=O (288 eV) for C1s groups in MCM structure. It was observed that the C was predominantly in the form of C-O-H (counts value 21716 s) after carbonization at 450°C and predominantly in the form of C-C (count value 22404 s) at 650°C, and the importance of C-O-H counts decreased to 10739s. Thus, it has been seen that there is a difference between the carbonization results of both materials at different temperatures. The carbonization temperature of 650°C creates the required material structure.

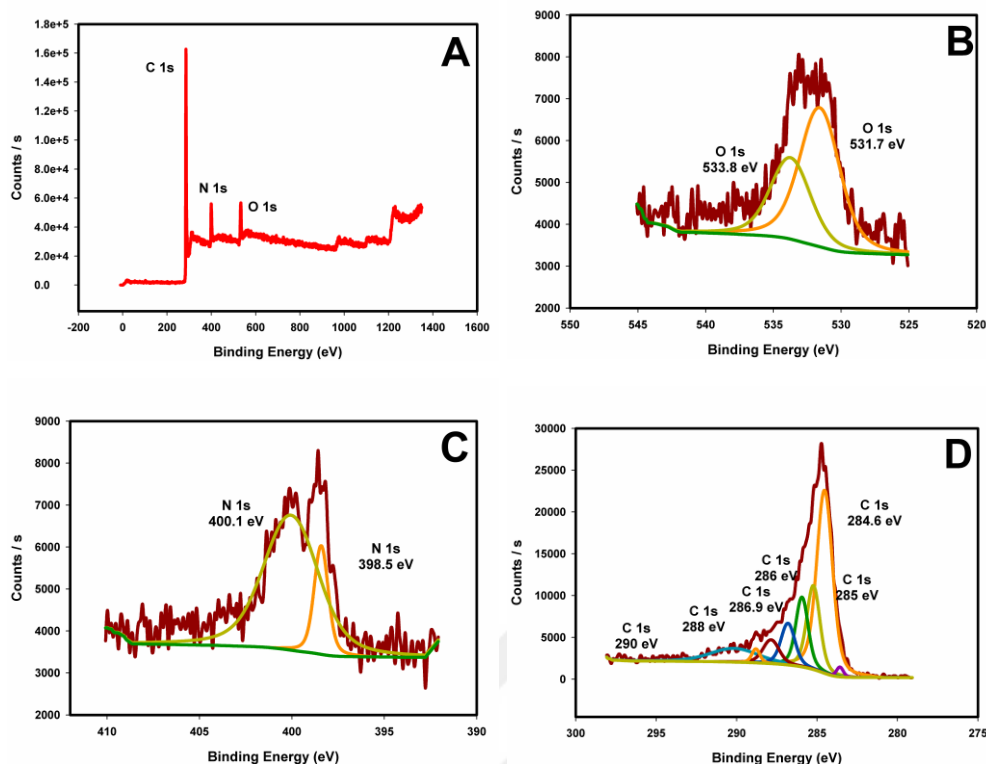


Figure 3.28 XPS spectra of MC composite material synthesized with 4-aminophenol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectra peaks after 650°C carbonization.

Synthesis of MC with catechol

XPS spectrums of MCM synthesized using a catechol initiator after carbonization at 450°C and 650°C are shown in Figure 3.29 and Figure 3.30. As detailed above, O 1s, N1s, and C1s atoms are expected in the structure. After 450°C carbonizations, it is observed that O1s (Figure 3.29 B) in the structure could be formed as C-O (531.6 eV) and carbonyl oxygen (-O=C) (536 eV), N1s (Figure 3.29 C) could be formed as pyrrolic N (-NH-) (398.2 eV), quaternary N (-N=C) (399 eV), C=N-C (399.6 eV), C-N-H (400 eV), C=N (400.6 eV) and -N-H (400.5 eV) groups structure)Figure 3.30. C 1s (Figure 3.29 D) in the synthesized material were also found to be in C-C (284.4 eV), C-O-H (285.2 eV), C-O (286.4 eV), and C=C (288.8 eV) structures.

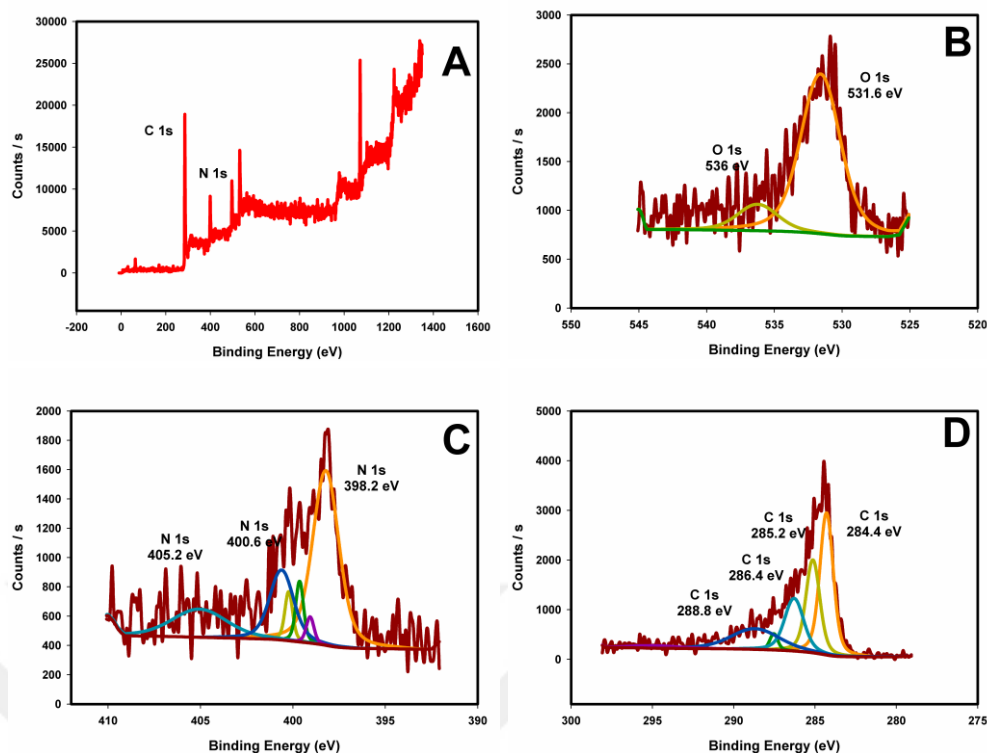


Figure 3. 29 XPS spectra of MC composite material synthesized with catechol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectrums peaks after 450°C carbonization.

In the XPS performed after carbonization at 650°C, it was observed that there were differences in the form of O, N and C atoms in the structure, as in the synthesis with the 4-aminophenol initiator. It was observed that the O1s atom was found in C-O (532 eV), C=O (537.8 eV), and C-O-H (534 eV) structures, and the structure differed according to carbonization at 450°C (Figure 30-B). It was observed that the N 1s atom was differentiated entirely according to the 450°C carbonizations, and it was found only in the pyrrolic N (–NH–) (398.7 eV) and C-N-H (400 eV) structures (Figure 3.30-C). It has been observed that the C1s atom was C-C (284.7 eV), C-O-H (285.9 eV), C=C (287.8 eV), and C=O (288.8 eV).

(Figure 3.30-D). As a result, it was observed that the carbonization process carried out at 450 and 650 °C in the synthesis using catechol caused the differentiation of oxygen and nitrogen atoms in the MCM structure.

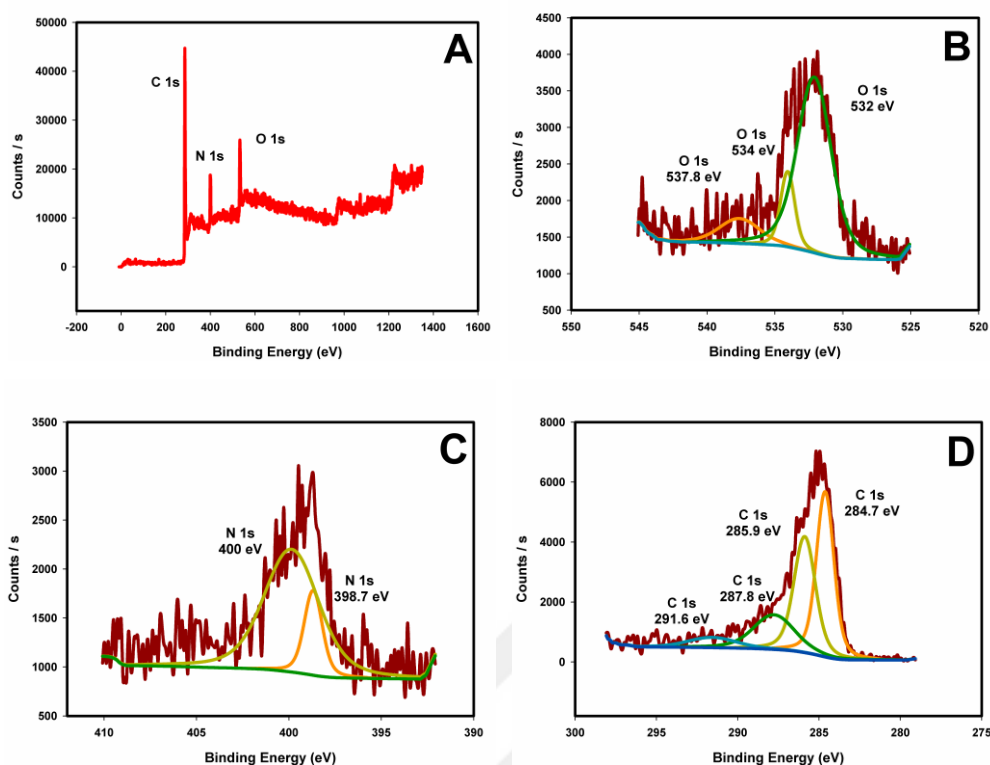
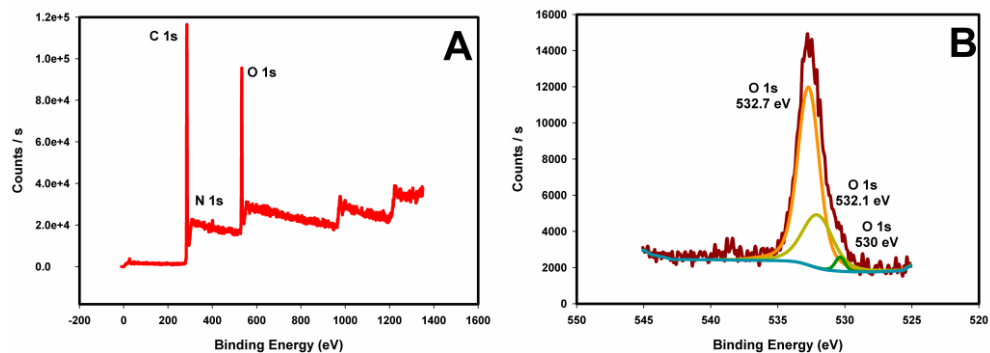


Figure 3.30 XPS spectra of MC composite material synthesized with catechol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectrums peaks after 650°C carbonization.

Synthesis of MC with resorcinol

XPS analysis of MC material synthesis with resorcinol initiator was also performed after carbonization at 450°C and 650°C (Figure 3.31 and Figure 3.32). As detailed in the above section, it was observed that there were differences in the material structures obtained after both temperatures. After carbonization at 450°C, O1s atoms were found in the MC material structure as C-O (530.3 eV), C-O-C/C-O-H (532.1 eV), and C=O (532.7 eV) (Figure 3.31-B). It has been observed that N1s atoms are in the C=N (400.8 eV) structure, while C1s atoms are in the C-C (284.3 eV), C=N (285.7 eV), and C=C (288 eV) structures (Figure 3.31-C and Figure 3.31-D, respectively).



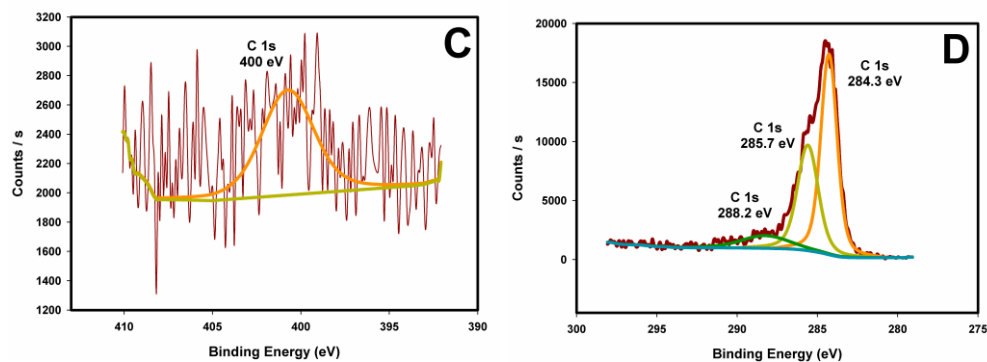
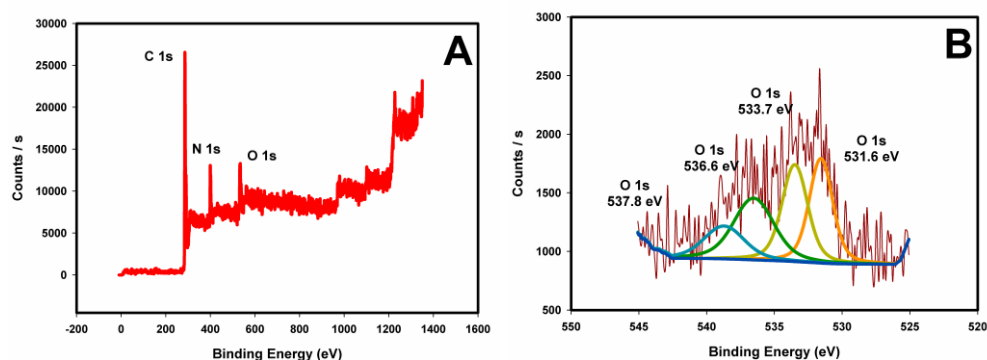


Figure 3.31 XPS spectra of MC composite material synthesized with resorcinol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectrums peaks after 450°C carbonization.

In synthesis with a resorcinol initiator, when carbonization takes place at 650°C. As seen in Figure 3.32-A survey graph, it was observed that there was a severe differentiation in terms of the species formed in all of the O, N, and C atoms. After XPS analysis, it was observed that O 1s atoms were in the form of C-O (531.6 eV), C-O-H (533.7 eV), -C=O (536.6 eV), and O-C=O (537.8 eV) (Figure 3.32-B). Completely different from the 450°C carbonizations of N 1s atoms, the peak at the primary 401 eV binding energy was divided into five peaks, each representing another N1s atom. These structures respectively; It has pyridinic N (395 eV), pyrrolic N (398 eV), C-N-H (399 eV), C=N (400 eV), and quaternary N (403 eV) structures (Figure 3.32-C). Finally, it has been observed that C1s atoms are completely differentiated like N1s atoms and exist in the form of C-C (285 eV), C-O (286 eV), C-N (287.5 eV), and C=C (290 eV) (Figure 3.32-D). As a result, in the syntheses made with all three initiators, it was seen that the carbonization temperature directly affects the structure of the formed species, and the structure specified in the literature was obtained after 650°C carbonizations (Tian et al., 2016).



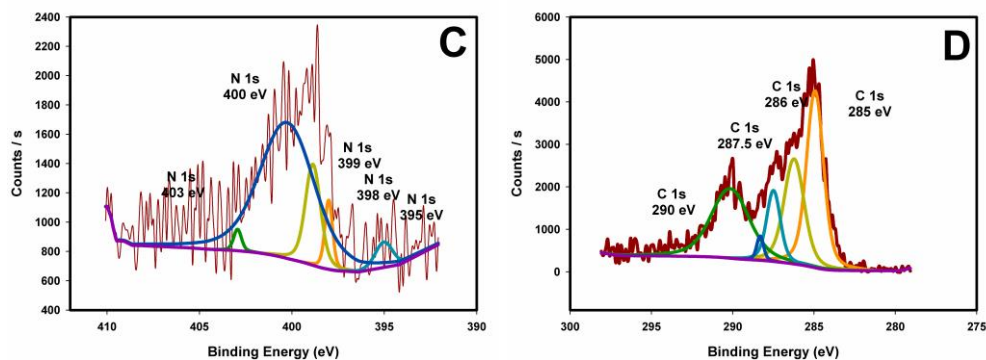
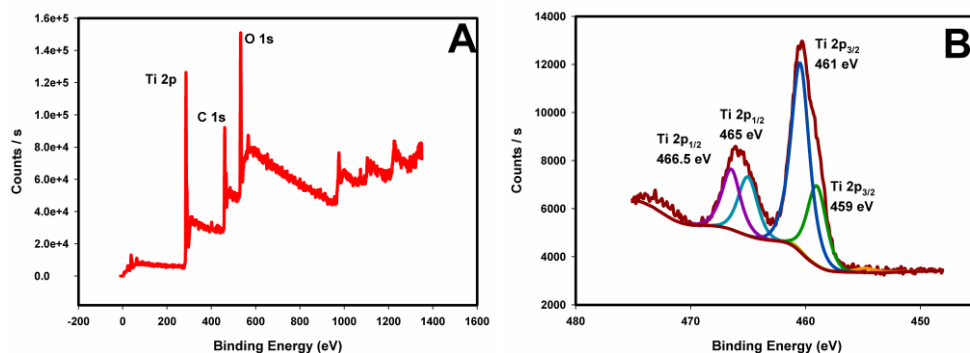


Figure 3.32 XPS spectra of MC composite material synthesized with resorcinol precursor represent A) survey spectrum, B) O1s, C) N1s and D) C1s spectrums peaks after 650°C carbonization.

3.1.6.6 XPS of MCM/TiO₂ composite material

The survey spectrum in Figure 3.33A was confirmed the presence of Ti, O, N and C atoms in the composite structure. In the Figure 3.33 B, the Ti 2p spectrum resolves into two spin-orbit components as Ti 2p_{1/2} and Ti 2p_{3/2}. There were two sharp peaks with binding energies of 465 eV and 461 eV representing Ti 2p_{1/2} and Ti 2p_{3/2}. The binding energies values of 459 eV and 461 eV were demonstrated the TiO₂ and TiO_x species. As similarly, the binding energies of 465 eV and 466.5 eV were demonstrated the Ti(IV) (TiO₂) in composite material. As a result, it is seen that the tetrabutyl titanate structure has been changed to TiO₂ (Figure 3.33-B).

The high resolution XPS spectrum for the O, N, and C atoms (Figure 3.33 C-E) indicated that the O-Ti (531.7 eV) and H-O (533.4 eV) form of oxygen atom, pyridinic N (400 eV), pyrrolic N (400.7 eV) and N-Oxide (403 eV) for nitrogen atom and C-C (284.7 eV), C-N (285.7 eV), C=O (288.8 eV) and C=C (292 eV) structures (Figure 3.33-C, D and E, respectively) (Figure 3.28-B).



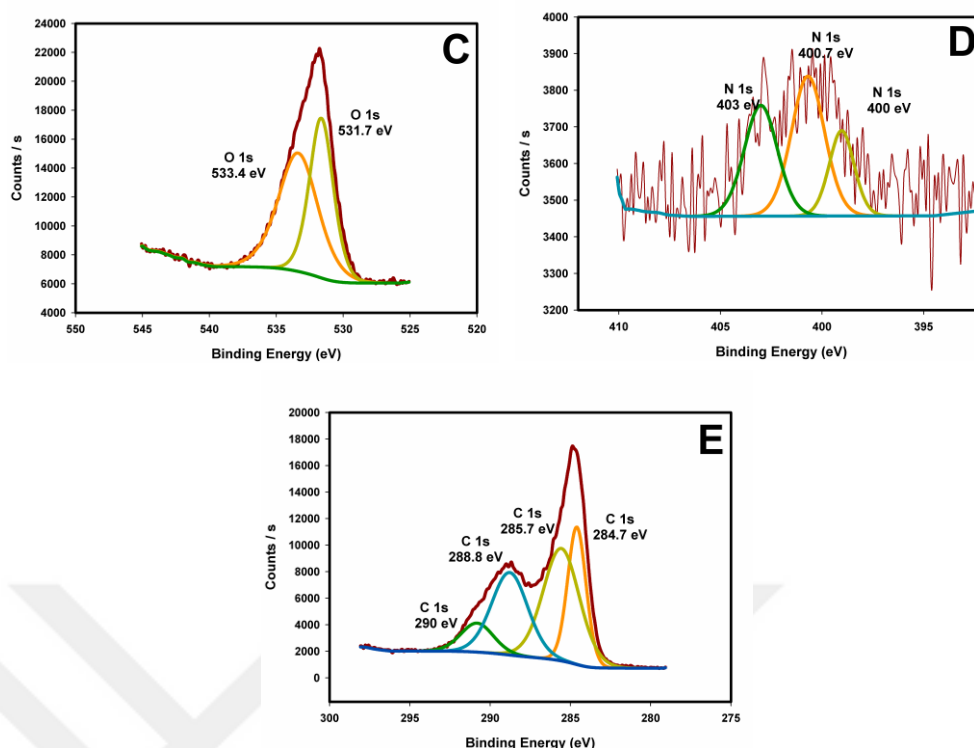


Figure 3.33 XPS spectra of MCM/TiO₂ composite material represent A) survey spectrum, B) Ti2p, C) O 1s D) N1s and E) C 1s spectrums peaks.

3.1.6.7 XPS of CuPc modified polycresol red film GC electrodes

The XPS survey spectrum of poly(cresol red) and poly(cresolred_{ox}) modified GCE were proved the S, O and C in the polymer structure (Figure 3.34A and 35A). The high resolution XPS spectra of S 2p (Figure 3.34 B) were deconvoluted into four peaks. The peaks at 168 and 164.7 eV are defined to SO_x and C–S–C, while the peaks at 170 and 163.2 are ascribed to sulfonyl groups.

The XPS spectrum of deconvoluted S2p at poly(cresolred_{ox})/GCE showed three peaks for S-O (168 eV), S=O (170 eV) and C-S (169.2 eV) as expected (Figure 3.35-B).

The high resolution O1s spectra of the poly(cresolred) and poly(cresolred_{ox}) were demonstrated in Figure 3.34C and 35C. Three oxygen component could be formed on poly(cresolred) and poly(cresolred_{ox}) for to C-C-O (531.5), S-O (532.9) and O-C=O (536.2 eV).

The curve fitting of the C1 s peaks for both poly(cresol red) and poly(cresolred_{ox}) were performed and constituents for C-H (284 eV), C-C (285 eV) (Figure 3.34D) and C-H (284.6 eV), C-C (286 eV) in the and -C=O (287 eV) (Figure 3.35D) respectively. As expected, C1s after over-oxidation of poly(cresol

red) indicates a new peak at 287 eV which can be attributed to -C=O functionality groups.

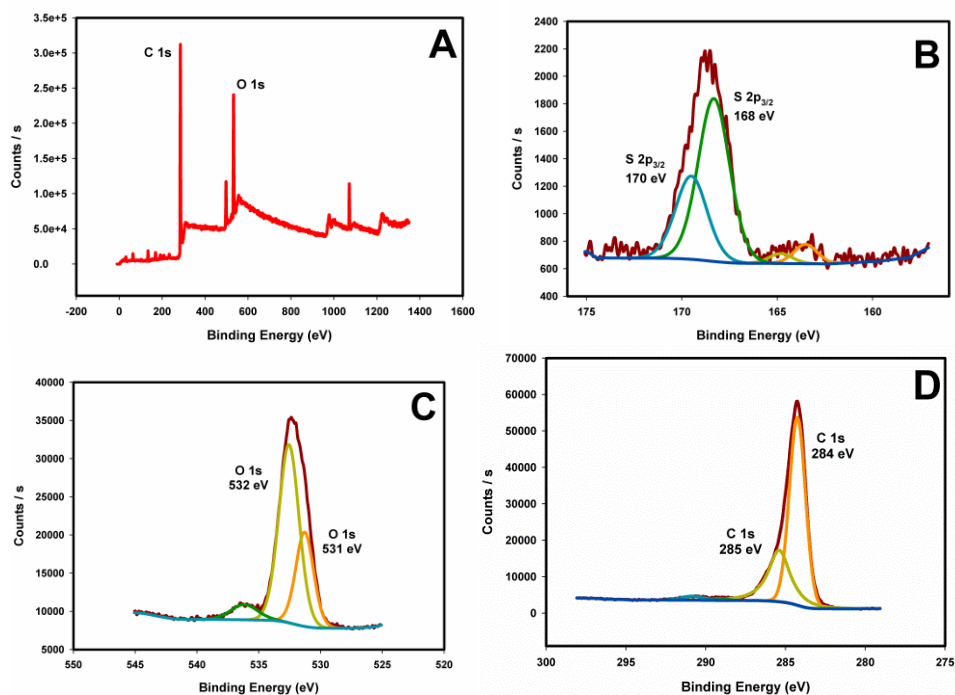


Figure 3.34 XPS spectra of poly(cresolred)/GC electrode represent A) survey spectrum, B) S 2p C) O 1s and D) C 1s spectra peaks.

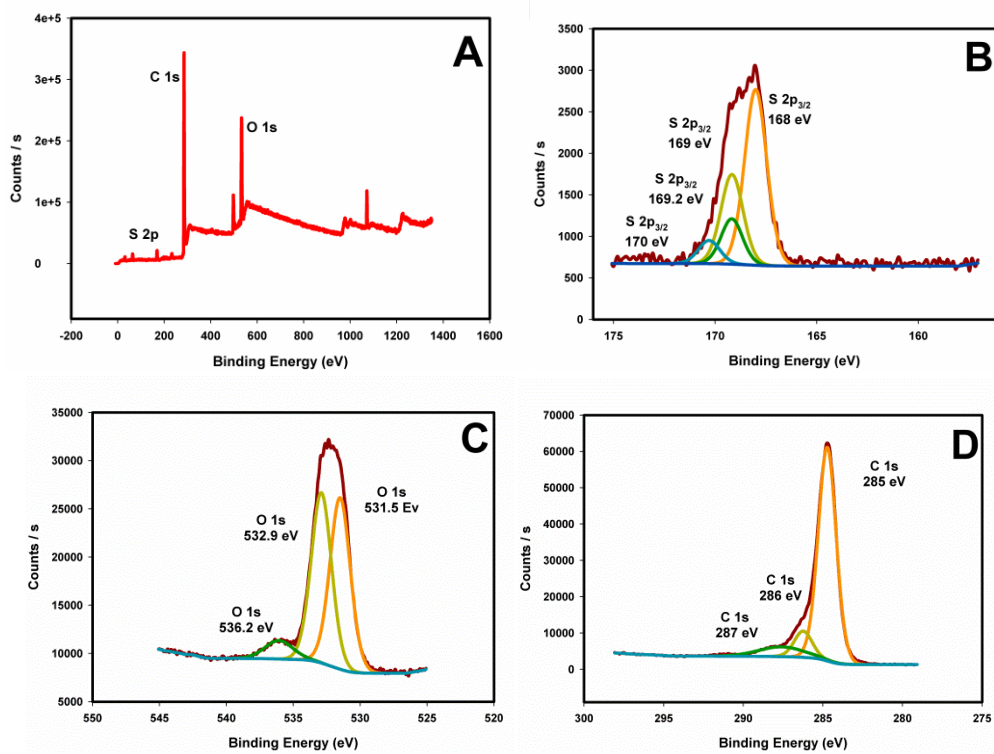
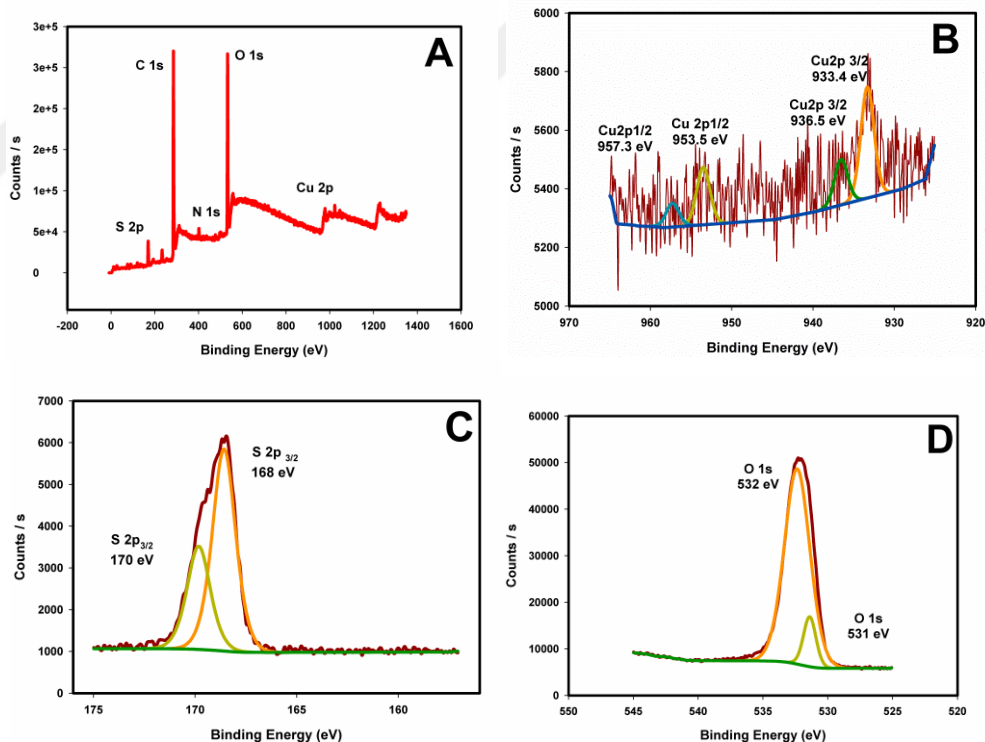


Figure 3.35 XPS spectra of poly(cresolred_{ox})/GC electrode represent A) survey spectrum, B) S 2p C) O 1s and D) C1s spectra peaks.

XPS of CuPc/poly(cresolred)/GC and CuPc/poly(cresolred_{ox})/GC electrodes were performed. The survey XPS spectrums were confirmed the Cu, S, N, O and C atoms in the composite structures (Figure 3.36 A and 3.37 A). According to the results of the investigation, it was observed that the S 2p atom structure changed after the over-oxidation of the polymer structure, as detailed above.

The CuPc/poly(cresolred) and CuPc/poly(cresolred_{ox}) of XPS spectras (Figure 3.36 B and 3.37B) show that the Cu 2p atom has two peaks at 933 eV and 953 eV. According to the literature, these energy levels represent Cu 2p_{3/2} and Cu 2p_{1/2} structures, respectively (Huang et al., 2021).

Futuremore two satalite peaks at 937 eV and 957 eV and main peaks indicating that the copper atoms in CuPc film were in Cu (II) form and Cu-N bonding in the structure. The 2p_{3/2} signal of Cu (II) in the center of the CuPc structure is seen in the 936.5 Ev binding energy (Liu et al., 2022).



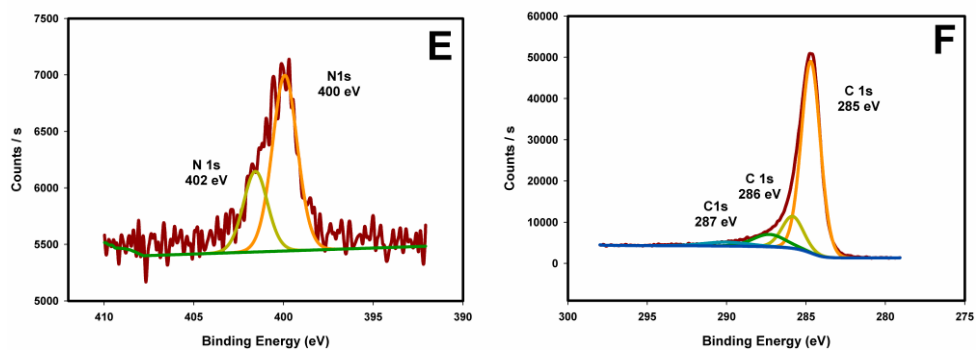


Figure 3.36 XPS spectra of CuPc/poly(cresolred)/GC electrode represent A) survey spectrum, B) Cu 2p, C) S 2p, D) O 1s, E) N1s and F) C 1s spectrums.

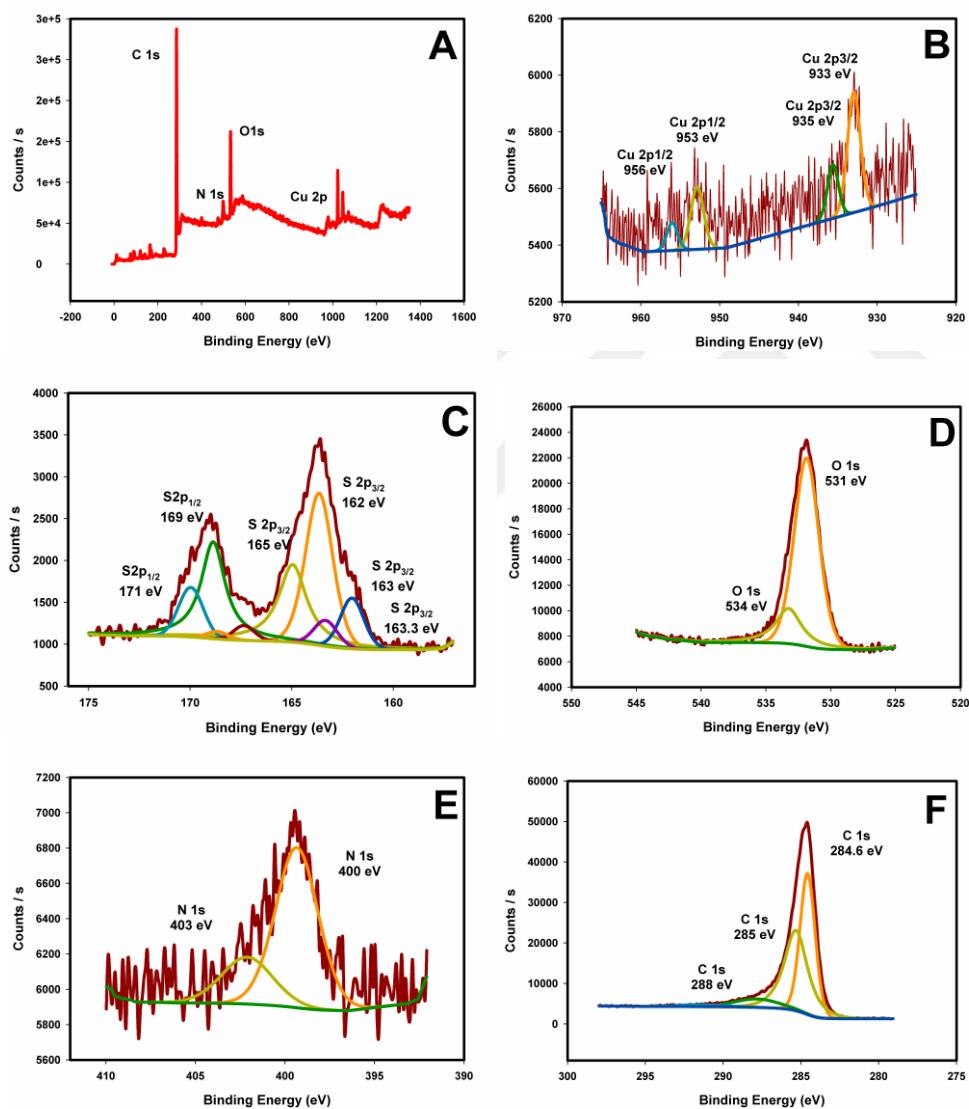


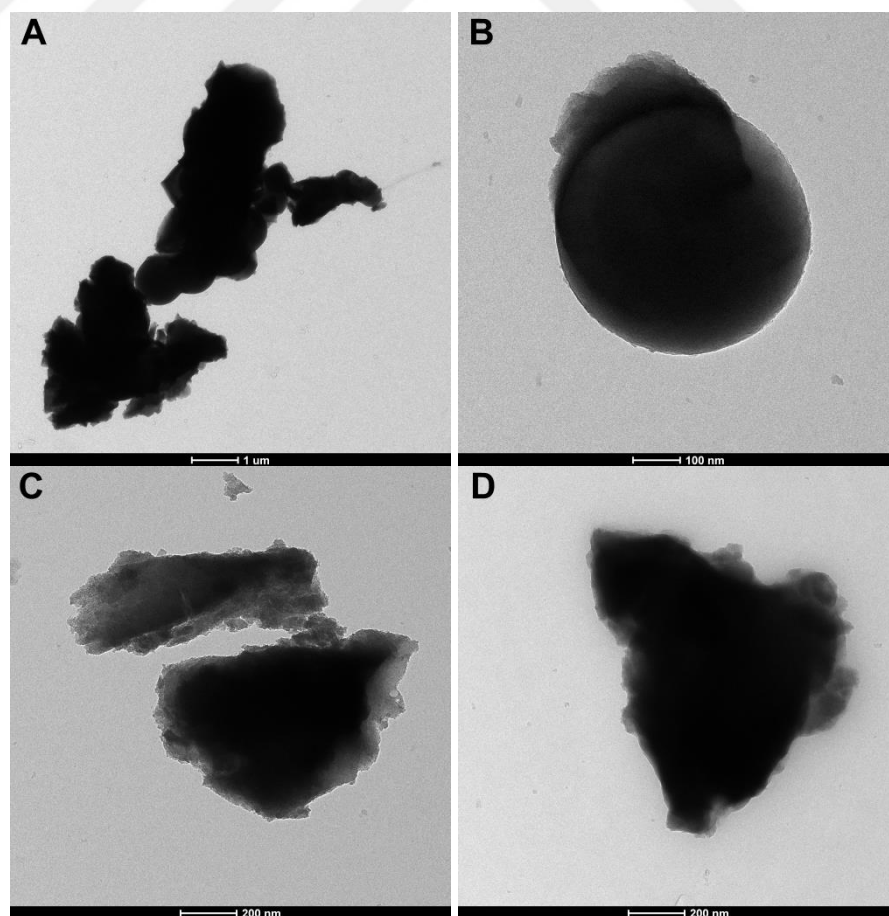
Figure 3.37 XPS spectra of CuPc/poly(cresolredox)/GC electrode represent A) survey spectrum, B) Cu 2p, C) S 2p, D) O 1s, E) N1s and F) C 1s spectrums.

While the O 1s atom is in the form of C-O (531 eV) and S-O (532 eV) in CuPc/Poly(cresolred)/GC electrode, it is found in the form of C-O (531 eV) and C=O (534 eV) in CuPc/Poly(cresolredox)/GC electrode.

N 1s atom is in C-N (400 eV) and N-O (402 eV) structure in CuPc/Poly(cresolred)/GC and CuPc/Poly(cresolredox)/GC electrodes, C 1S atom is in C-C (285 eV), C-N (286 eV) and C=O (288 eV) structures, but the C=O count value was higher in the CuPc/Poly(cresolred_{ox})/GC electrode modified with the over-oxidized polymer. Thus, it is seen that the -COO groups in the polymer structure increase the activity after the over-oxidation process (Ulubay Karabiberoğlu and Dursun, 2017).

3.1.7 TEM characterization of MCM/TiO₂ composite material

The TEM images performed in the surface characterization study of the MCM-TiO₂ material are shown in Figure 3.38. Gains knowledge about the surface morphology of materials synthesized by TEM imaging. In the SEM imaging results, it was observed that the MCM material formed homogeneous and spherical geometry. After the synthesis of MCM material with TiO₂ material by sol-gel method, it is seen that TiO₂ nanoparticles are deposited on MCM spheroids. TEM images compatible with literature data were obtained (Bo et al., 2013 and Liang et al., 2008).



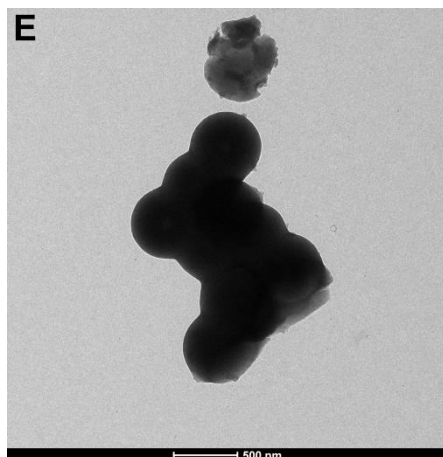


Figure 3. 38 TEM images of the TiO_2 -MCM composite material

3.1.8 Electrochemical characterization of modified electrodes by EIS

Electrochemical impedance spectroscopy (EIS) was used to evaluate the surface kinetics of the modified electrodes prepared for the studies. As is known, the EIS curve consists of two parts, semicircular for high frequencies and linear for low frequencies. The semicircular part involves electrochemical reactions involving electron transfer, and the diameter of the semicircle equals the electron transfer resistance R_{ct} . The linear function represents the diffusion process.

3.1.8.1 EIS chemical analysis of Cu and Au modified PPAP/GC electrodes

The electrochemical impedance spectroscopy (EIS) studies were carried out for Bare GCE, PPAP/GCE, Au/PPAP, Cu/PPAP, Au/Cu/PPAP/GCE, and Cu/Au/PPAP/GCE in containing $5 \text{ mmol L}^{-1} (\text{Fe}(\text{CN})_6)^{3-/4-}$ $1 \text{ mol L}^{-1} \text{ KNO}_3$ solution with frequencies ranging from 0.05 to 75,000 Hz.

The obtained EIS data were arranged with an $R(C(RW))$ circuit, and each value was shown in Table 3.1. In Figure 3.39, it was seen that the bare GC electrode has a significant charge transfer resistance of 650. The R_{ct} value for bare GCE is higher than the R_{ct} values obtained for other modified electrodes. This low R_{ct} value (103Ω) for Cu/Au/PPAP/GCE indicates relatively fast charge transfer compared to all replaced electrodes.

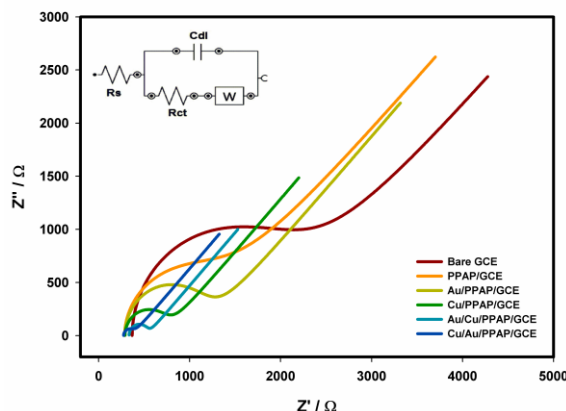


Figure 3. 39 The Nyquist plots of the bare and modified electrodes. The frequencies range from 0.05 to 75000 Hz at the formal potential.

Table 3.1 The R_s , R_{ct} , C_{dl} and W values of bare and modified electrodes.

	R_s (Ω)	R_{ct} (Ω)	C_{dl} (mF)	W (mMho)
Bare GCE	338	650	1.11	1.06
PPAP/GCE	286	971	2.42	1.55
Au/PPAP/GCE	288	865	4.69	1.58
Cu/PPAP/GCE	289	439	6.01	1.68
Au/Cu/PPAP/GCE	334	198	3.61	1.26
Cu/Au/PPAP/GCE	274	103	10.1	1.32

3.1.8.2 EIS chemical analysis of MCM/TiO₂ composite material

The resistance values obtained in the R (C(RW)) circuit design and electrode measurements in the EIS analysis of the GC electrode modified with MCM/TiO₂ composite material are shown in Table 3.2.

According to the results obtained, the circuit formed was found to be suitable for the R (C(RW)) circuit design. The $R_{ct}(\Omega)$ value obtained with the bare GCE electrode was read as 650 Ω for the bare GCE, and 203 Ω for the MCM-TiO₂/GCE modified electrode resistance value. Large semicircle as 290 ohm of R_{ct} value was obtained for bare GCE, indicating that there was a high electron transfer resistance. However, after MCM-TiO₂ composite material modification, a smaller semicircle which means small electron transfer resistance was obtained.

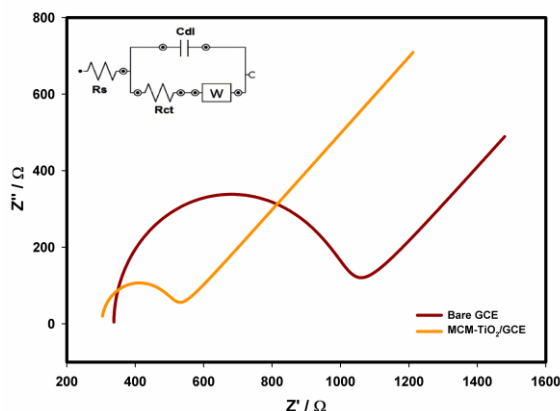


Figure 3. 40 The Nyquist plots of the bare and MCM/TiO₂ composite material modified electrodes. The frequencies range from 0.05 to 75000 Hz at the formal potential.

Table 3.2 The Rs, Rct, Cdl and W values of bare and MCM/TiO₂ composite material modified electrodes.

	Rs (Ω)	Rct (Ω)	Cdl (mF)	W(mMho)
Bare GCE	338	650	1.11	1.06
MCM-TiO₂/GCE	302	203	1.55	1.26

3.1.8.3 EIS chemical analysis of CuPc, Cresol red modified GC electrode

Figure 3.41 illustrates the electrochemical impedance spectroscopy (EIS) results of bare GCE, Poly(cresolred)/GCE, Poly(cresolred_{ox})/GCE, CuPc/Poly(Cresolred)/GCE and CuPc/Poly(cresolred_{ox})/GCE in the presence of 5 mmol L⁻¹ (Fe(CN)₆)^{3-/4-} containing 0.1 mol L⁻¹ KNO₃ solution at varying frequencies range 0.05 to 75,000 Hz.

EIS data were fitted with an R (C(RW)) equivalent circuit and values were shown in Table 3.3. it is clearly seen in Figure 3.41 that GC electrode shows a large charge transfer resistance of about 658 ohm. The Rct value for the bare GCE is higher than the Rct values obtained for other modified electrodes. The lowest Rct value (76 Ω) for the CuPc/CrRed_{ox}/GCE implies the relatively fast charge transfer compared to the CrRed/GCE (173 Ω), CrRed_{ox}/GCE (98 Ω) and bare GCE (658 Ω). These results indicated that the suitable electron transfer conditions could be proved by CuPc/CrRed_{ox}/GCE surface (Figure 3.41).

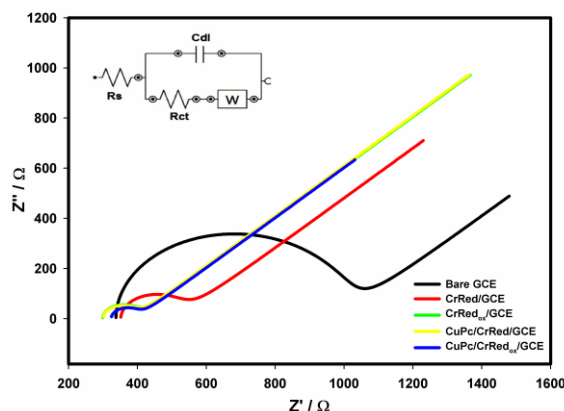


Figure 3. 41 The Nyquist plots of the bare, CrRed/GCE, CrRed_{ox}/GCE, CuPc/CrRed/GCE and CuPc/ CrRed_{ox}/GCE modified electrodes. The frequencies range from 0.05 to 75000 Hz at the formal potential.

Table 3. 3 The Rs, Rct, Cdl and W values of bare and modified electrodes.

	Rs (Ω)	Rct (Ω)	Cdl (mF)	W(mMho)
Bare GCE	337	658	1.11	1.06
CrRed/GCE	352	173	5.12	1.26
CrRed _{ox} /GCE	304	98	3.79	1.30
CuPc/CrRed/GCE	301	93	3.91	1.39
CuPc/CrRed_{ox}/GCE	324	76	3.97	1.41

3.2 Electrochemical and Electroanalytical Applications of Developed Electrodes

In this thesis, developed and characterized metal/metal oxide particles modified polymer film or composite electrodes were used for electrocatalytic and photocatalytic reduction of carbon dioxide in alkaline and methanol containing solutions by CV, CA and rotating disk electrode techniques(RDE). To obtain the best electrocatalytic and photocatalytic conditions, the effect of the electrode surface, type of polymer, type of supporting electrolyte, CO₂ feeding time, adjustment for the light time, etc., on their reduction behaviors were evaluated by use of various electrode types, which were prepared different metal/metal oxide nanoparticles and monomer concentration, different volume of composite material suspension. For electroanalytical applications, the voltammetric detection of antimony were studied in detail by CV and differential pulse anodic stripping voltammetric technique on poly(cresol Red), poly(CresolRed_{ox}), CuPc/poly(cresolRed) and CuPc/poly(CresolRed_{ox}) modified GC electrodes. The

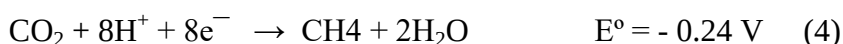
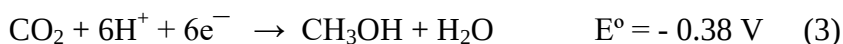
optimum developed electrode was tested for antimony detection in PET bottles samples. The studies were given in order of below.

3.2.1 Electrocatalytic behavior of carbondioxide

3.2.1.1 Investigation of electrochemical reduction of carbondioxide with cyclic voltammetry

Electrochemical reduction of carbon dioxide requires high overvoltage and the electrochemical reduction of carbon dioxide generally takes place at highly negative potentials on different electrodes and it competes with H₂ evolution reaction (Kaneco et al.,1998).

The species formed by the reduction of carbon dioxide were shown in Equation 1-5. These reactions are valid for normal hydrogen electrode (NHE) in aqueous solution at pH 7, temperature of 25°C and pressure of 1 atm (Kaneco et al.,1998):



The main compounds formed in the acidic environment in the reduction reactions are formic acid, methanol and oxalic acid. The Pourbaix diagram for a carbon dioxide is shown in Figure 3.42 (Konig et al., 2019).

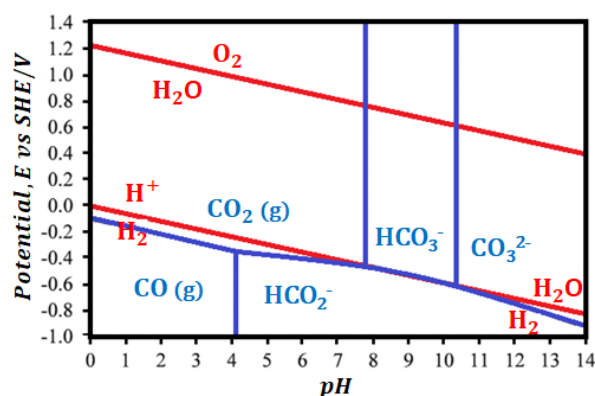


Figure 3. 42 Pourbaix diagram for a carbon dioxide (Konig et al., 2019)

Studies have been carried out on using various metal electrodes to reduce CO_2 by electrochemical methods in water and non-water environments (Sriram Mosali et al., 2019). Gattrell et al. reduced CO_2 to hydrocarbons in an aqueous medium using a Cu electrode (Gattrell et al., 2006). Hori et al., on the other hand, found that deactivation of copper occurred in their studies where they provided a reduction to hydrocarbon species by using Cu cathode. On top of that, many studies have reported that the copper electrode is "poisoned" and "deactivated" in 10-30 minutes due to CO_2 saturation (Hori et al., 2005).

Organic aprotic solvents are more effective than water in dissolving CO_2 . Many studies have investigated the electrochemical reduction of CO_2 with different metal electrodes using organic solvents instead of water (Vasileff et al., 2018). The most widely used solvents is methanol, which provides a better dissolution medium to CO_2 than water at low temperatures (Kaneco et al., 1999). In light of these data, this thesis aims to present a mechanism for the electrochemical reduction of carbon dioxide in different concentrations of sodium perchlorate and methanol solutions with a glassy carbon electrode modified with nano metallic Cu and Au-modified conductive polymers.

The electrochemical behavior of bare GCE, PANI/GCE, Cu/PANI/GCE, Au/PANI/GCE, Au-Cu/PANI/GCE and Cu-Au/PANI/GCE were examined by CV in 0.1 M KHCO_3 solution saturated with N_2 and CO_2 in 0.1 M KHCO_3 solution (Figure 3.43 A and B), respectively. In the absence of CO_2 , the hydrogen evolution was appeared at different potential on different electrodes. The largest working potential window was obtained with the Cu/PANI/GCE in the absence of both CO_2 . On the other hand, in the presence of CO_2 , a small reduction wave was appeared at -1.7 V for all electrodes in the 0.1 M KHCO_3 + CO_2 saturated solution. The higher wave current was obtained for Cu-Au/PANI and Au-Cu/PANI modified GCE electrodes as 3.97 μA and 2.86 μA . The obtained reduction potential and current of CO_2 were detailed at Table 3.4.

Table 3. 4 Voltammetric behavior of bare GCE and PANI/GCE modified electrodes in 0.1 M KHCO_3 supporting electrolyte and CO_2 saturated 0.1 M KHCO_3 medium

Modified Electrodes	Supporting electrolyte (0.1 M KHCO_3)		CO_2 saturated 0.1 M KHCO_3	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PANI/GCE	-	-	-	-
Cu/PANI/GCE	-	-	-1.7	0.78
Au/PANI/GCE	-	-	-	-
Cu/Au/PANI/GCE	-	-	-1.6	3.97
Au/Cu/PANI/GCE	-	-	-1.6	2.86

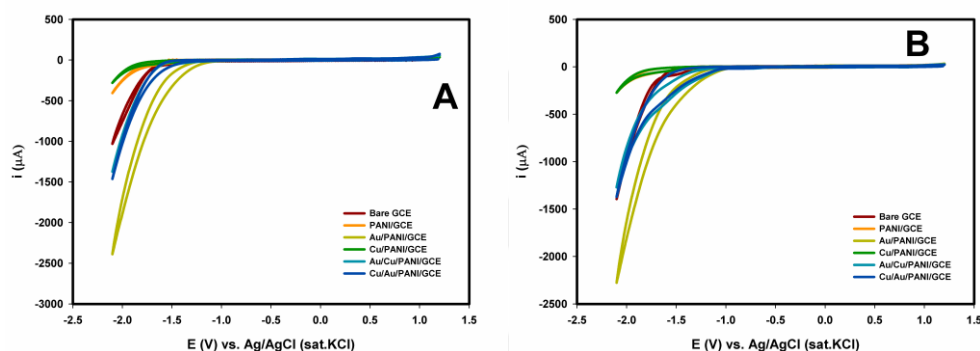


Figure 3. 43 Cyclic voltammograms of bare GCE and PANI modified GC electrodes in A) supporting electrolyte (0.1 M KHCO_3) B) CO_2 saturated 0.1 M KHCO_3 .

In order to examine the effect of the conductive polymer type on the reduction of CO_2 , the GC electrode was modified with PPAP instead of PANI polymer. For this purpose, modified electrodes were prepared by the cyclic voltammetry method, as detailed in the above sections.

The electrochemical behaviors of CO_2 in 0.1 M KHCO_3 solution was studied on bare GCE, PPAP/GCE, Cu/PPAP/GCE, Au/PPAP/GCE, Au-Cu/PPAP/GCE and Cu-Au/PPAP/GCE by CV with 0.05 V.s^{-1} (Figure 3.44B). During the direction of cathodic potential scan for in N_2 saturated 0.1 M KHCO_3 solution, there was no any reduction peak to expect hydrogen evolution reaction.

In the presence of saturated CO_2 , a reduction peak was observed at -1.3 V with a $9.75 \mu\text{A}$ peak current, -1.4 V with a $0.772 \mu\text{A}$ peak current, -1.457 V with a $8.59 \mu\text{A}$ peak current and -1.5 V with a $29.62 \mu\text{A}$ peak current at bare GCE, PPAP/GCE, Cu/PPAP/GCE, Au/PPAP/GCE, Au-Cu/PPAP/GCE and Cu-Au/PPAP/GCE, respectively. The potential and current values of bare and

modified electrodes were listed in the Table 3.5. The best electrocatalytic activity for CO_2 reduction was obtained on Cu-Au/PANI/GCE. A great peak current increasing was achieved with Cu-Au/PANI/GCE that was about 38.4 times higher than Au/PPAP/GCE and 3.4 times more higher than Au-Cu/PPAP/GCE and 3.0 times higher than Cu/PPAP/GCE.

Table 3.5 Voltammetric behavior of bare GCE and PPAP/GCE modified electrodes in 0.1 M KHCO_3 supporting electrolyte and CO_2 saturated 0.1 M KHCO_3 medium

Modified Electrodes	Supporting electrolyte (0.1 M KHCO_3)		CO_2 saturated 0.1 M KHCO_3	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PPAP/GCE	-	-	-	-
Cu/PPAP/GCE	-	-	-1.3	9.75
Au/PPAP/GCE	-	-	-1.4	0.77
Cu/Au/PPAP/GCE	-	-	-1.5	29.62
Au/Cu/PPAP/GCE	-	-	-1.5	8.59

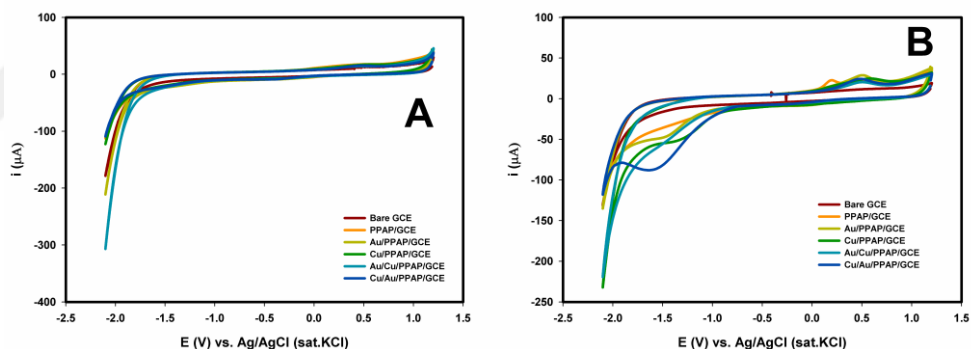


Figure 3.44 Cyclic voltammograms of bare GCE and PPAP modified GC electrodes in A) 0.1 M KHCO_3 B) CO_2 saturated 0.1 M KHCO_3 .

In the previous studies have shown that Cu particles containing modified electrodes are highly sensitive to the electrochemical reduction of CO_2 (Gattrel et al., 2006, Aydin et al., 2002 and Kane Co et al., 1998). The results we obtained in our thesis study confirmed the previous studies.

With the purpose of detail the studies and to observe the effect of KHCO_3 concentration, the reduction of CO_2 with plain, PANI and PPAP modified GC electrode by saturating 0.5 M KHCO_3 medium with CO_2 was investigated. The voltammetric behavior of bare GCE and all PANI modified GC electrodes was studied in the absence and presence of saturated CO_2 in 0.5 M KHCO_3 and there

was no any electrocatalytic activity for CO_2 reduction as in the previous study. Voltammograms for the study were shown in Figure 3.45.

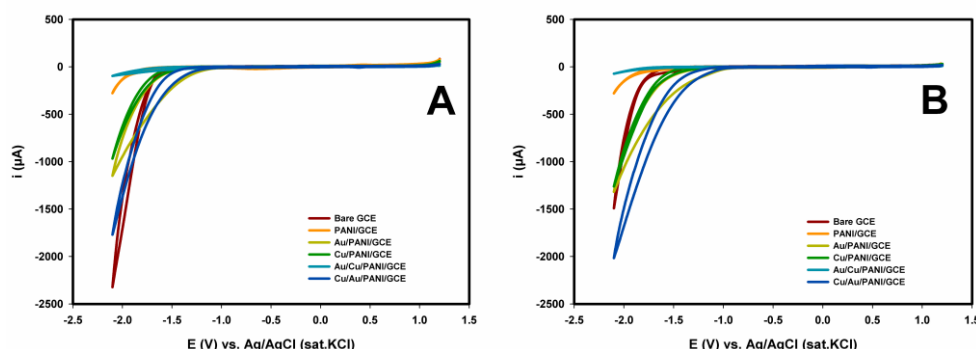


Figure 3. 45 Cyclic voltammograms of bare GCE and PANI modified GC electrodes in A) Supporting electrolyte (0.5 M KHCO_3) B) CO_2 saturated 0.5 M KHCO_3 .

To improve the electrocatalytic activity of composite electrodes toward the reduction of CO_2 , the electrochemical reduction of CO_2 was investigated in 0.5 M KHCO_3 solution at all PPAP/GC electrodes to see the effect of electrolyte concentration on CO_2 reduction (Figure 3.46 B).

The CO_2 reduction peak was appeared at -1.4 V with a 95.27 μA peak current, -1.5 V with a 5.88 μA peak current, -1.3 V with a 43.33 μA peak current and -1.7 V with a 111,42 μA peak current at bare GCE, PPAP/GCE, Cu/PPAP/GCE, Au/PPAP/GCE, Au-Cu/PPAP/GCE and Cu-Au/PPAP/GCE, respectively (Figure 3.46).

The peak currents were improved in presence of 0.5 M KHCO_3 on all PPAP/GC electrodes compare with 0.1 M KHCO_3 medium. The highest peak current was also obtained on Cu-Au/PPAP/GCE. The obtained data were given in Table 3.6.

Table 3.6 Voltammetric behavior of bare GCE and PPAP/GCE modified electrodes in 0.5 M KHCO_3 supporting electrolyte and CO_2 saturated 0.5 M KHCO_3 medium

Modified Electrodes	Supporting electrolyte (0.5 M KHCO_3)		CO_2 saturated 0.5 M KHCO_3	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PPAP/GCE	-	-	-1.4	1.60
Cu/PPAP/GCE	-	-	-1.5	85.27
Au/PPAP/GCE	-	-	-1.5	5.88
Cu/Au/PPAP/GCE	-	-	-1.7	111.42
Au/Cu/PPAP/GCE	-	-	-1.3	43.33

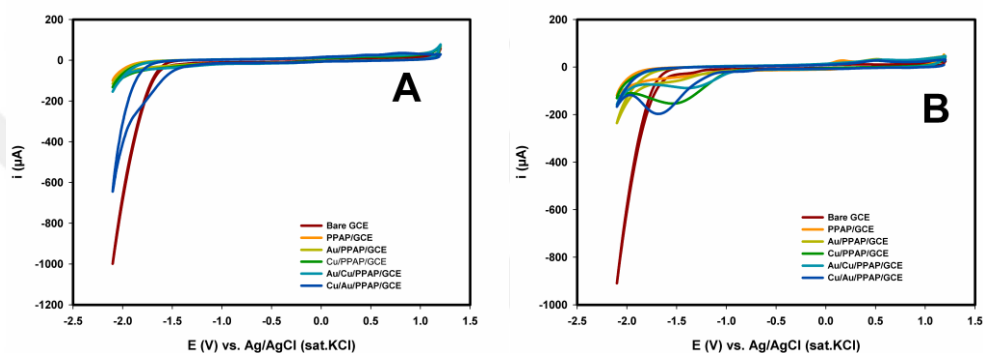


Figure 3. 46 Cyclic voltammograms of bare GCE and PPAP modified GC electrodes in A) supporting electrolyte (0.5 M KHCO_3) B) CO_2 saturated 0.5 M KHCO_3 .

Organic aprotic solvents have been preferred more than water in studies for the reduction of CO_2 . Especially since methanol can dissolve approximately five times more CO_2 than water at ambient temperature, many studies have been carried out in methanol media (Jitaru 2007). Due to the positive effect of methanol on the solubility of CO_2 , reduction studies of CO_2 were investigated in 0.1 M KHCO_3 + 0.1 M methanol medium.

As detailed above, studies were repeated with Bare GCE, PANI and PPAP modified electrodes. Bare GCE and PANI modified electrodes did not respond to the reduction of CO_2 in 0.1 M KHCO_3 + 0.1 M methanol electrolyte medium. Voltamograms of the study are given in Figure 3.47.

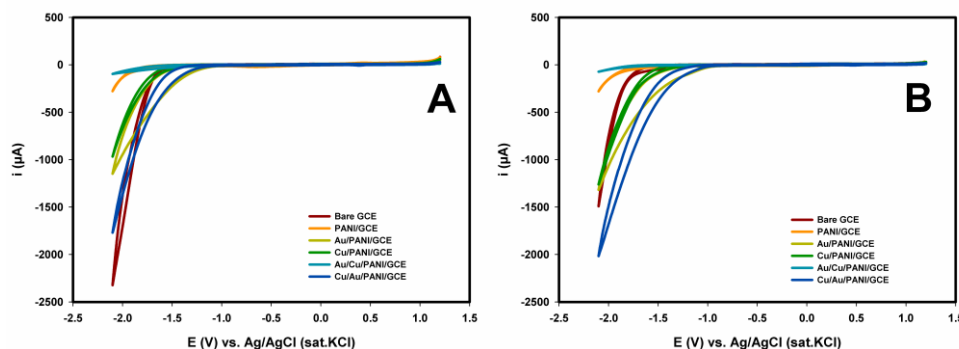


Figure 3. 47 Cyclic voltammograms of bare GCE and PANI modified GC electrodes in A) Supporting electrolyte (0.1 M KHCO_3 + 0.1 M methanol KHCO_3) B) CO_2 saturated in 0.1 M KHCO_3 + 0.1 M methanol

Positive responses to CO_2 reduction were obtained with metal particles modified PPAP film electrodes in 0.1 M KHCO_3 + 0.1 M Methanol medium as detailed above. As expected, the presence of methanol in 0.1 M KHCO_3 solution it was provided 4.2 times more higher peak current at Cu-Au/PPAP/GCE compare with previous studies at Cu-Au/PPAP/GCE in 0.1M KHCO_3 solution. Current-potential values obtained in 0.1 M KHCO_3 + 0.1 M methanol medium are given in Table 3.7 and voltammograms were given in Figure 3.48.

Table 3. 7 Voltammetric behavior of bare GCE and PPAP/GCE modified electrodes in 0.1 M KHCO_3 + 0.1 M methanol supporting electrolyte and CO_2 saturated 0.1 M KHCO_3 + 0.1 M methanol medium

Modified Electrodes	Supporting electrolyte (0.1 M KHCO_3 + 0.1 M methanol)		CO_2 saturated 0.1 M KHCO_3 + 0.1 M methanol	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PPAP/GCE	-	-	-1.5	4.74
Cu/PPAP/GCE	-	-	-1.3	43.49
Au/PPAP/GCE	-	-	-1.4	3.50
Cu/Au/PPAP/GCE	-	-	-1.3	124.80
Au/Cu/PPAP/GCE	-	-	-1.3	34.40

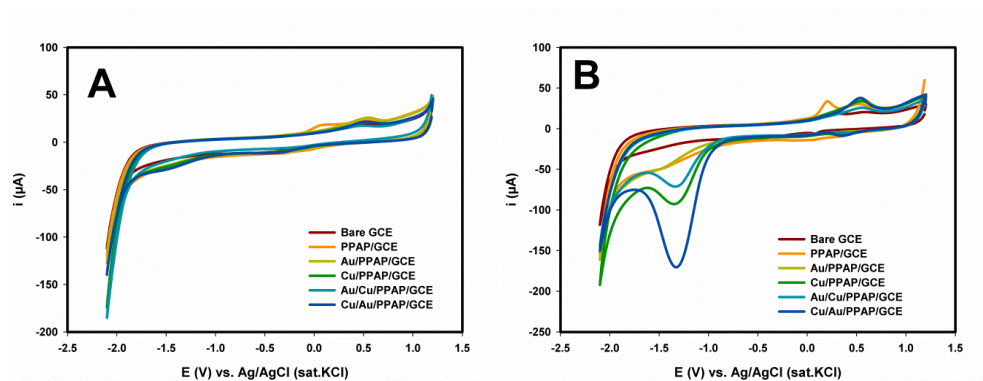


Figure 3. 48 Cyclic voltammograms of bare GCE and PPAP modified GC electrodes comparison towards A) N_2 and B) CO_2 in 0.1 M $KHCO_3$ + 0.1 M methanol

Bare GCE and PANI modified electrodes did not respond to the reduction of CO_2 in 0.5 M $KHCO_3$ + 0.5 M methanol electrolyte medium. Voltammograms of the study were shown in Figure 3.49.

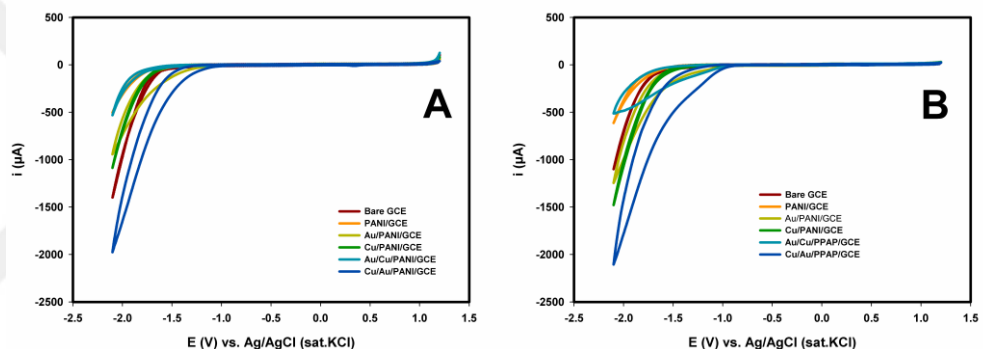


Figure 3. 49 Cyclic voltammograms of bare GCE and PANI modified GC electrodes in A) 0.5 M $KHCO_3$ + 0.5 M methanol B) CO_2 saturated 0.5 M $KHCO_3$ + 0.5 M methanol medium

The electrochemical reduction of CO_2 was also examined in the presence of investigated in 0.5 M $KHCO_3$ + 0.5 M methanol mixture electrolyte solution at all electrodes (Figure 3.50 B). The CO_2 reduction peak was appeared at -1.4 V with a 57.81 μA peak current, -1.5 V with a 9.25 μA peak current, -1.4 V with a 67.29 μA peak current and -1.3 V with a 198.36 μA peak current at bare GCE, PPAP/GCE, Cu/PPAP/GCE, Au/PPAP/GCE, Au-Cu/PPAP/GCE and Cu-Au/PPAP/GCE, respectively (Figure 3.50B). The peak currents were improved in presence of 0.5 M $KHCO_3$ + 0.5 M methanol mixture electrolyte solution on all electrodes compare with the 0.1 M $KHCO_3$ concentration. The highest peak current was also obtained on Cu-Au/PPAP/GCE. The obtained data were given in Table 3.8.

Table 3.8 Voltammetric behavior of bare GCE and PPAP/GCE modified electrodes in 0.5 M KHCO_3 + 0.5 M methanol supporting electrolyte and CO_2 saturated 0.5 M KHCO_3 + 0.5 M methanol medium

Modified Electrodes	Supporting electrolyte (0.5 M KHCO_3 + 0.5 M methanol)		CO_2 saturated 0.5 M KHCO_3 + 0.5 M methanol	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PPAP/GCE	-	-	-1.4	2.00
Cu/PPAP/GCE	-	-	-1.4	57.81
Au/PPAP/GCE	-	-	-1.5	9.25
Cu/Au/PPAP/GCE	-	-	-1.3	198.36
Au/Cu/PPAP/GCE	-	-	-1.4	67.29

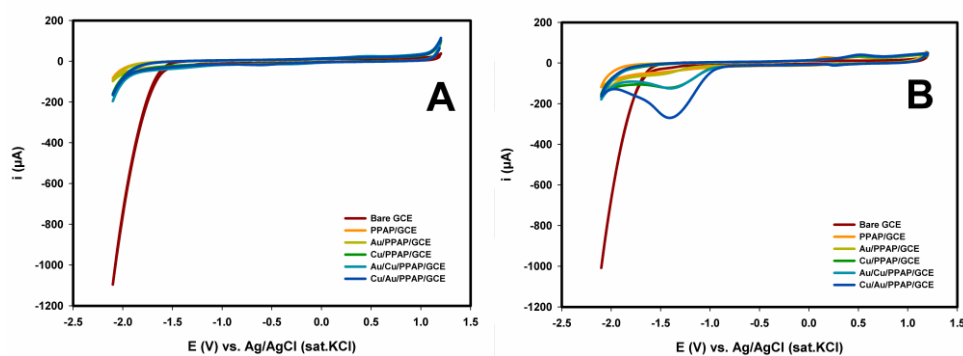


Figure 3.50 Cyclic voltammograms of bare GCE and PPAP modified GC electrodes in A) 0.5 M KHCO_3 + 0.5 M methanol B) CO_2 saturated 0.5 M KHCO_3 + 0.5 M methanol

Although methanol is one of the most suitable media for the dissolution of CO_2 , type of electrolyte (preferably NaClO_4) have been extensively investigated in the electrochemical reduction of CO_2 in many studies. (Konig et al., 2019, Kaneco et al. 2006, Aydın and Köleli, 2004). For this reason, The electrochemical reduction of CO_2 was studied in NaClO_4 + methanol medium.

In order to investigate the effect of NaClO_4 + Methanol supporting electrolyte medium on the electrochemical reduction of CO_2 , the CV studies were carried out with bare GCE, PANI and PPAP modified GC electrodes in 0.8 M NaClO_4 + 2 M Methanol medium. Similar to previous studies, there was no response to CO_2 reduction on bare GCE and PANI modified electrodes except Au and Au-Cu nanoparticles modified electrodes (Table 3.9 and Figure 3.51).

Table 3.9 Voltammetric behavior of bare GCE and PANI/GCE modified electrodes in 0.8 M NaClO₄ + 2 M methanol supporting electrolyte and CO₂ saturated 0.8 M NaClO₄ + 2 M methanol medium

Modified Electrodes	Supporting electrolyte (0.8 M NaClO ₄ + 2.0 M methanol)		CO ₂ saturated 0.8 M NaClO ₄ + 2.0 M methanol	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PANI/GCE	-	-	-	-
Cu/PANI/GCE	-	-	-	-
Au/PANI /GCE	-	-	-1.1	1.44
Cu/Au/PANI /GCE	-	-	-	-
Au/Cu/PANI /GCE	-	-	-1.6	2.62

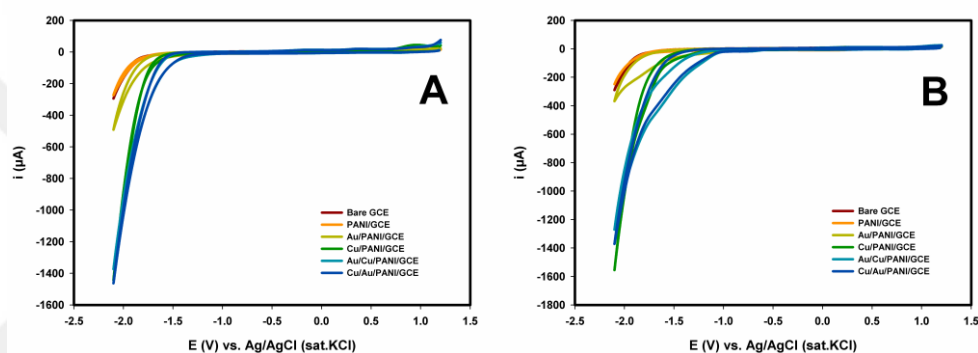


Figure 3. 51 Cyclic voltammograms of bare GCE and PANI modified GC electrodes A) 0.8 M NaClO₄ + 2 M methanol B) CO₂ saturated 0.8 M NaClO₄ + 2 M methanol

In studies with PPAP modified GC electrodes, electrocatalytic reduction of CO₂ was observed at all metal particles modified PPAP/GCE. The reduction peak was monitored at -1.5 V with a 90.64 μA peak current, -1.5 V with a 31.68 μA peak current, -1.5 V with a 75.34 a peak current and -1.4 V with a 210.76 μA peak current at bare GCE, PPAP/GCE, Cu/PPAP/GCE, Au/PPAP/GCE, Au-Cu/PPAP/GCE and Cu-Au/PPAP/GCE, respectively (Figure 3.52B). The highest peak current was also obtained on Cu-Au/PPAP/GCE. The obtained data were given in Table 3.10.

Table 3. 10 Voltammetric behavior of bare GCE and PPAP/GCE modified electrodes in 0.8 M NaClO₄ + 2 M methanol supporting electrolyte and CO₂ saturated 0.8 M NaClO₄ + 2 M methanol medium

Modified Electrodes	Supporting electrolyte (0.8 M NaClO ₄ + 2.0 M methanol)		CO ₂ saturated 0.8 M NaClO ₄ + 2.0 M methanol	
	E (V)	i (μA)	E (V)	i (μA)
Bare/GCE	-	-	-	-
PPAP/GCE	-	-	-1.3	7.46
Cu/PPAP/GCE	-	-	-1.5	90.64
Au/PPAP/GCE	-	-	-1.5	31.68
Cu/Au/PPAP/GCE	-	-	-1.4	210.76
Au/Cu/PPAP/GCE	-	-	-1.5	75.34

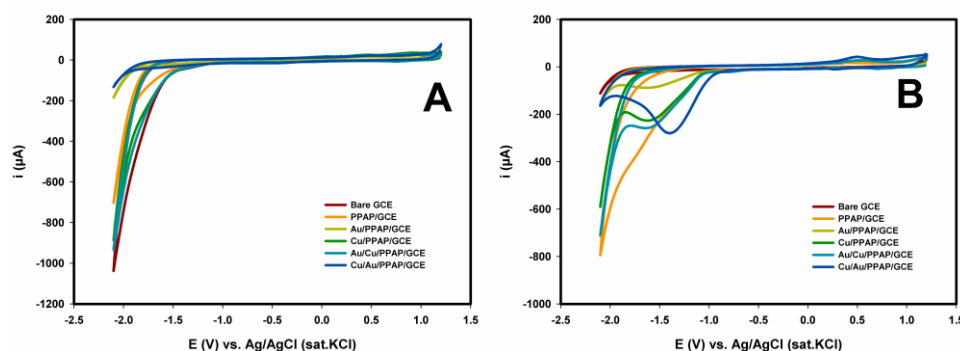


Figure 3. 52 Cyclic voltammograms of bare GCE and PPAP modified GC electrodes in A) Supporting electrolyte (0.8 M NaClO₄+ 2.0 M methanol) B) CO₂ saturated in 0.8 M NaClO₄+ 2.0 M methanol

3.2.1.2 Optimization studies for electrochemical reduction of CO₂ studies

Optimization of NaClO₄ and Methanol concentration for electrolyte solution

The effect of the supporting electrolyte concentration on the electrochemical reduction of CO₂ was investigated by varying the NaClO₄ concentrations (0.01-1.0 mol L⁻¹) in the presence of constant concentration of methanol as 2 M and then with different methanol concentrations at the optimum NaClO₄ concentration (Figure 3.53 and Figure 3.54). The voltammetric studies were performed at the modified electrodes prepared with the optimum concentration and cycle numbers of each component as detailed above.

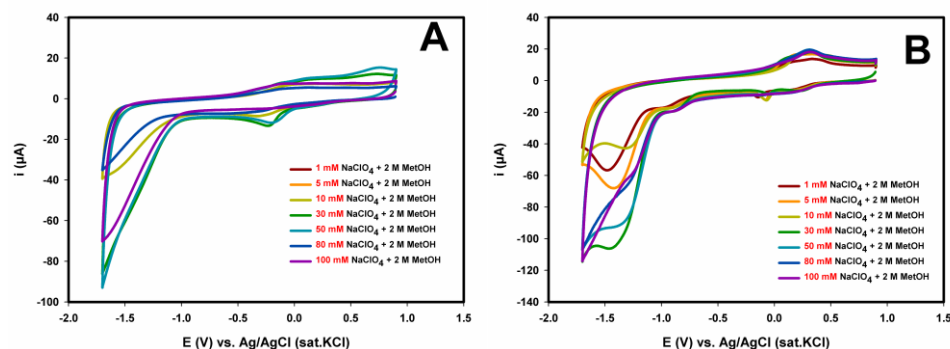


Figure 3. 53 Cyclic voltammograms of the effect of NaClO_4 concentration in 2 M methanol on A) Supporting electrolyte B) CO_2 saturated supporting electrolyte at $\text{Cu}/\text{Au}/\text{PPAP}/\text{GCE}$

The voltammograms shown in Figure 3.53 depending on NaClO_4 concentration with constant concentration of methanol as 2 mol L^{-1} . The peak current values were given in Table 3.20. Figure 3.54 has two maximum peak current as $52.98 \mu\text{A}$ for 0.5 M and $68.55 \mu\text{A}$ for 0.8 M NaClO_4 the current values was decreased after the 0.5 mol L^{-1} up to 0.8 mol L^{-1} by increasing concentration of NaClO_4 . The highest peak current for CO_2 reduction was obtained in the presence of 0.8 mol L^{-1} $\text{NaClO}_4 + 2.0 \text{ mol L}^{-1}$ methanol (Table 3.11). Thus, 0.8 mol L^{-1} was chosen as the optimum NaClO_4 concentration for future studies.

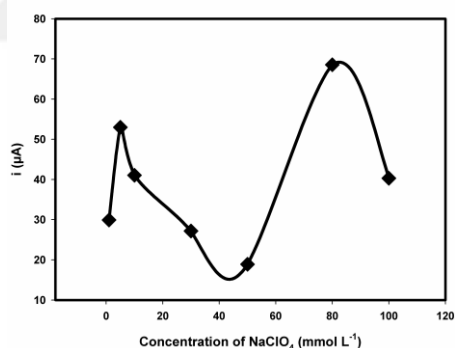
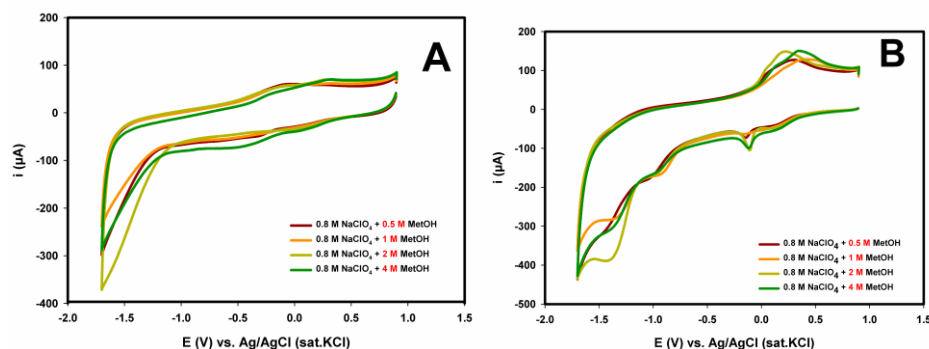


Figure 3. 54 Effect of NaClO_4 concentration on electrochemical reduction of CO_2 with $\text{Cu}/\text{Au}/\text{PPAP}/\text{GCE}$ in 2 M Methanol

Table 3. 11 The effect of NaClO₄ concentration in 2 M methanol on A) supporting electrolyte B) CO₂ saturated supporting electrolyte

NaClO ₄ concentration (mol L ⁻¹)	Supporting electrolyte		CO ₂ Saturated supporting electrolyte	
	E (V)	i (μA)	E (V)	i (μA)
0.01	-	-	-1.5	29.92
0.05	-	-	-1.4	52.98
0.1	-	-	-1.5	41.05
0.3	-	-	-1.3	27.18
0.5	-	-	-1.5	18.90
0.8	-	-	-1.7	68.55
1.0	-	-	-1.6	40.30

In order to examine the effect of methanol concentration on the electrochemical reduction of CO₂, voltammetric studies were carried out by varying the methanol concentrations (0.01-0.8 mol L⁻¹) in the presence of constant concentration of NaClO₄ solutions as 0.8 mol L⁻¹ (Figure 3.55).

Figure 3. 55 Cyclic voltammograms of the effect of methanol concentration in 0.8 M NaClO₄ on A) supporting electrolyte B) CO₂ saturated supporting electrolyte at Cu/Au/PPAP/GCE

The highest reduction peak current of CO₂ was obtained as 91.5 μA at -1.4 V in the presence of 2 mol L⁻¹ methanol + 0.8 NaClO₄ mol L⁻¹. For this reason, the 2 mol L⁻¹ methanol concentration was chosen as the optimum concentration for future studies. The peak potential and current values obtained in the absence and presence of CO₂ were shown in Table 3.12. Figure 3.56 shows the current values according to increasing concentration of methanol.

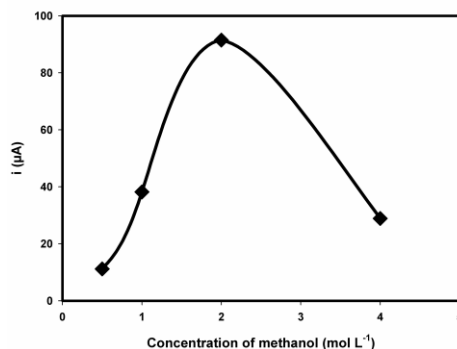


Figure 3. 56 Effect of metanol concentration on electrochemical reduction of CO₂ with Cu/Au/PPAP/GCE in 0.8 M NaClO₄

Table 3. 12 The effect of methanol concentration in 0.8 M NaClO₄ on A) supporting electrolyte B) CO₂ saturated supporting

Metanol concentration (mmol L ⁻¹)	Supporting elelctrolyte		CO ₂ Saturated supporting elelctrolyte	
	E (V)	i (μA)	E (V)	i (μA)
0.5	-	-	-1.4	11.20
1	-	-	-1.3	38.20
2	-	-	-1.4	91.50
4	-	-	-1.3	28.90

Optimization of p-(aminophenol) concentration and cycle number for preparation of PPAP polymer on GCE

The effects of p-aminophenol concentration and number of electropolymerization cycles on the GC electrode surface for the electrochemical reduction of CO₂ were investigated (Figure 3.57 B and 3.58, Table 3.16). The monomer concentration was 0.5, 1.0, 5.0 and 10 mmol L⁻¹. The higher peak current for CO₂ reduction was observed on Cu-Au/PPAP/GCE which was prepared with 5.0 mmol L⁻¹ p-aminophenol concentration. Therefore the optimum monomer concentration for future studies was choosen as 5.0 mmol L⁻¹ of p-aminophenol. The cycle number of CV was studied in range from 5.0 to 30 for 5.0 mmol L⁻¹ p-aminophenol at 50 V s⁻¹ scan rate. The best electrocatalytic activity was obtained on Cu-Au/PPAP/GCE which was prepared 15 cycles number in presence of 5.0 mmol L⁻¹ of p-aminophenol (Figure 3.57 B and 3.58; Table 3.13)

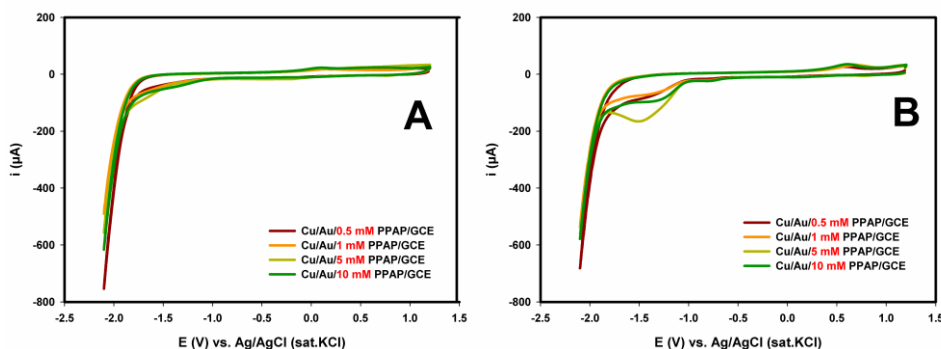


Figure 3. 57 Cyclic voltammograms of the effect of p-aminophenol concentration on A) 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte B) CO₂ saturated 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE with 50 V s⁻¹

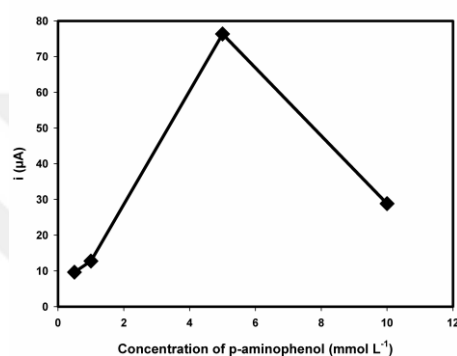


Figure 3. 58 Effect of p-aminophenol concentration on electrochemical reduction of CO₂ with Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M Methanol

Table 3. 13 The effect of p-aminophenol concentration on CO₂ reduction with Cu/Au/PPAP/GC electrodes in 0.8 M NaClO₄ + 2 M methanol.

p-aminophenol concentration (mmol L ⁻¹)	Supporting electrolyte		CO ₂ Saturated supporting electrolyte	
	E (V)	i (μA)	E (m)	i (μA)
0.5	-	-	-1.4	9.66
1	-	-	-1.3	12.76
5	-	-	-1.5	76.35
10	-	-	-1.3	28.85

According to results were given at Table 3.13 and Figure 3.57, 5 mmol L⁻¹ concentration of p-aminophenol and 15 cycle number of electropolymerization were chosen optimum values for future studies. Figure 3.59 and Figure 3.60 show the effect of p-aminophenol polymerization cycle number on current.

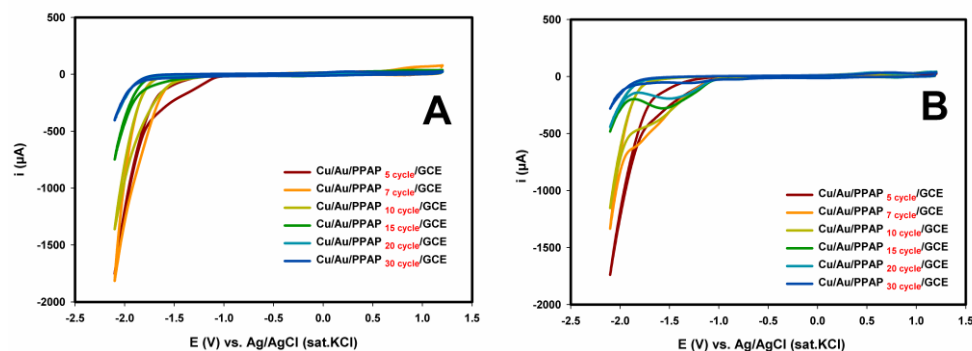


Figure 3. 59 Cyclic voltammograms of the effect of p-aminophenol cycle number on A) 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte B) CO₂ saturated 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE with 50 V s⁻¹

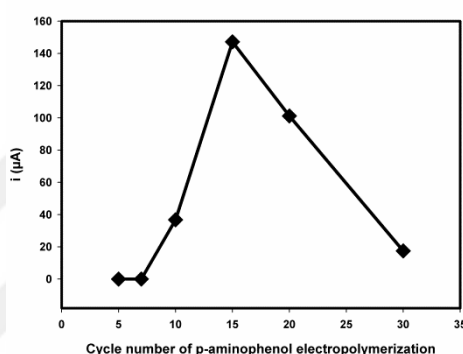


Figure 3. 60 The effect of p-aminophenol cycle number on electrochemical reduction of CO₂ with Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M Methanol

Table 3. 14 The effect of p-aminophenol cycle number on CO₂ reduction with Cu/Au/PPAP/GC electrodes in 0.8 M NaClO₄ + 2 M methanol

p-aminophenol cycle number	Supporting electrolyte		CO ₂ Saturated supporting electrolyte	
	E (V)	i (μA)	E (V)	i (μA)
5	-	-	-	-
7	-	-	-	-
10	-	-	-1.6	36.78
15	-	-	-1.5	147.15
20	-	-	-1.5	101.2
30	-	-	-1.3	17.47

Optimization of CuSO₄ concentration for preparation of Cu nanoparticles on Au/PPAP/GCE

The effect of copper sulfate concentration to prepare the Cu metal/metal oxide particles on the electrochemical reduction of CO₂ was studied in the presence of 0.1, 0.3, 0.5, 1, 3 and 5.0 mmol L⁻¹ CuSO₄ concentrations at

Cu/Au/PPAP/GCE (Figure 3.61) for 30 minutes CO_2 feeding in NaClO_4 + methanol solution. A reduction peak was observed for all copper sulfate concentrations at different potential and in varied current values (Table 3.15).

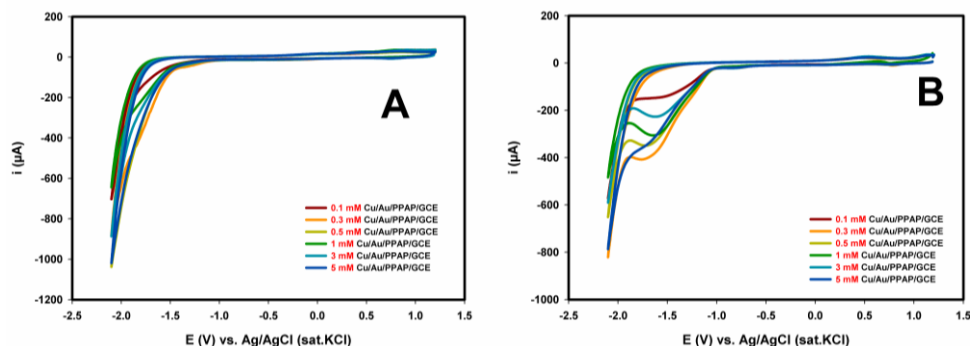


Figure 3. 61 Cyclic voltammograms of the effect of CuSO_4 concentration on A) 0.8 M NaClO_4 + 2 M Methanol supporting electrolyte B) CO_2 saturated 0.8 M NaClO_4 + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE.

The higher peak current for CO_2 reduction was obtained in the presence of 1.0 mmol L^{-1} copper sulfate used for preparing the Cu/Au/PPAP/GCE (Figure 3.61). The peak current of CO_2 reduction was decreased more than the 3.0 mmol L^{-1} CuSO_4 concentration used for preparing Cu/Au/PPAP/GCE, due to the deactivation of bimetallic properties of Cu-Au particles on PPAP/GCE (Figure 3.62 and Table 3.15). As a result, 1.0 mmol L^{-1} copper sulfate concentration was preferred as the optimum concentration for further studies.

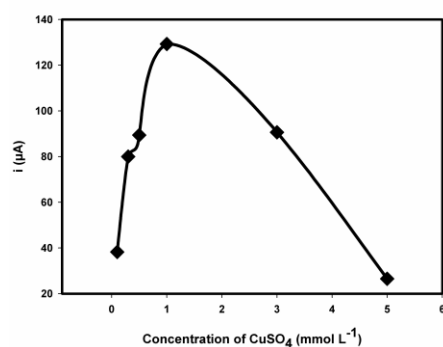


Figure 3. 62 Effect of CuSO_4 concentration on electrochemical reduction of CO_2 at Cu/Au/PPAP/GCE in 0.8 M NaClO_4 + 2 M methanol

Table 3. 15 The effect of CuSO_4 concentration on CO_2 reduction at Cu/Au/PPAP/GC electrode in 0.8 M NaClO_4 + 2 M methanol

CuSO_4 concentration (mmol L^{-1})	Supporting electrolyte		CO_2 saturated supporting electrolyte	
	E (V)	i (μA)	E (V)	i (μA)
0.1	-	-	-1.5	38.24
0.3	-	-	-1.6	88.01
0.5	-	-	-1.6	89.38
1.0	-	-	-1.6	129.24
3.0	-	-	-1.5	90.64
5.0	-	-	-1.6	34.13

Optimization of Cu nanoparticles cycle number for preparation Cu/Au/PPAP/GCE

The cycle number effect of Cu particles formation at the Au/PAPGCE on CO_2 reduction was studied in range of 3-15 cycles. The electrochemical behavior prepared Cu/Au/PPAP/GCE's were examined in the absence and presence of CO_2 (Figure 3.63). A reduction peak for CO_2 was observed for all Cu deposited on Au/PPAP/GCE for all cycles number at different potential with varied current values (Table 3.16). The higher reduction peak current of CO_2 was appeared for 10 cycles number for Cu deposition on Au/PPAP/GCE. Therefore 10 cycles number for Cu electrochemical deposition on Au/PPAP/GCE was chosen for future studies (Figure 3.64).

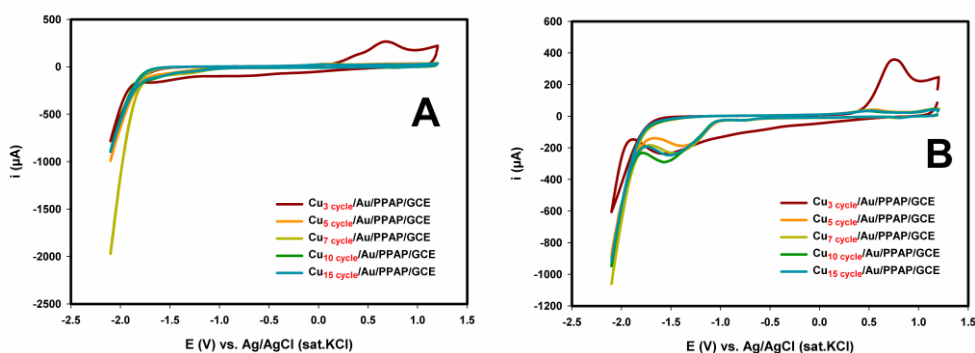


Figure 3. 63 Cyclic voltammograms of the effect of cycle number of CuSO_4 on A) 0.8 M NaClO_4 + 2 M Methanol supporting electrolyte B) CO_2 saturated 0.8 M NaClO_4 + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE.

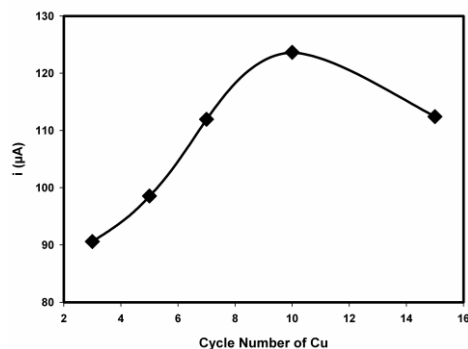


Figure 3. 64 Effect of Cu electrochemical deposition of cycle number on electrochemical reduction of CO₂ with Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M methanol

Table 3. 16 The effect of Cu cycle number on CO₂ reduction at Cu/Au/PPAP/GC electrodes in 0.8 M NaClO₄ + 2 M methanol

Cu cycle number	Supporting electrolyte		CO ₂ saturated supporting electrolyte	
	E (V)	i (μA)	E (V)	i (μA)
3	-	-	-1.6	90.61
5	-	-	-1.3	98.57
7	-	-	-1.4	111.96
10	-	-	-1.5	123.65
15	-	-	-1.5	112.43

Optimization of HAuCl₄ concentration for preparation of Au nanoparticles on Cu/Au/PPAP/GCE

The effect of HAuCl₄ concentration to prepare the Au particles on the on the CO₂ reduction was examined in the presence of 0.1, 0.3, 0.5, 1, 3 and 5 mmol L⁻¹ HAuCl₄ solution at Cu/Au/PPAP/GCE for 30 minutes CO₂ feeding in NaClO₄ + methanol solution (Figure 3.65). A reduction peak was observed for all HAuCl₄ concentrations at different potential and in varied current values (Table 3.17).

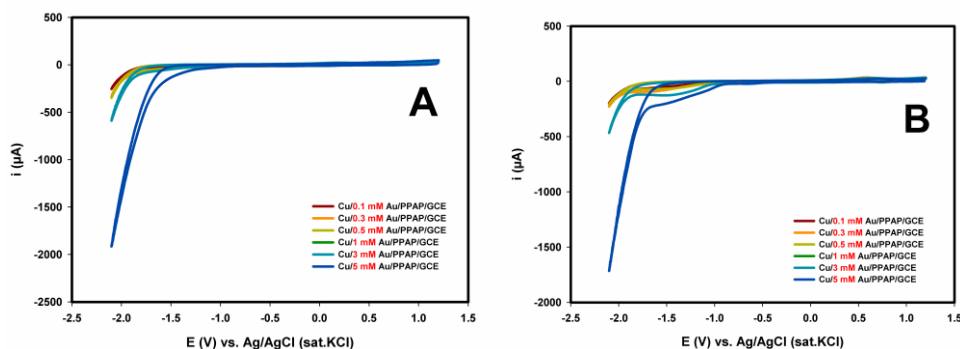


Figure 3. 65 Cyclic voltammograms of the effect of HAuCl₄ concentration on A) 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte B) CO₂ saturated 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE.

The highest peak current for CO₂ reduction was obtained in the presence of 1.0 mmol L⁻¹ HAuCl₄ to prepare the Cu/Au/PPAP/GCE (Figure 3.66). The peak current of CO₂ reduction was decreased more than the 1.0 mmol L⁻¹ CuSO₄ concentration to prepare Cu/Au/PPAP/GCE. As a result, 1.0 mmol L⁻¹ HAuCl₄ concentration was preferred as the optimum concentration for further studies.

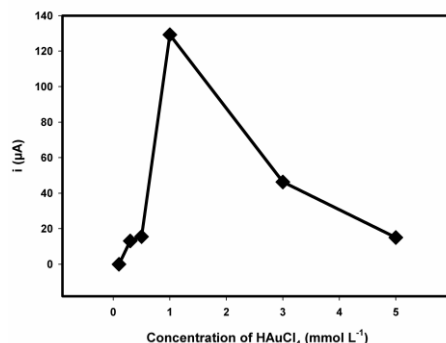


Figure 3. 66 Effect of HAuCl₄ concentration on electrochemical reduction of CO₂ at Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M Methanol

Table 3. 17 The effect of HAuCl₄ concentration on CO₂ reduction at Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M methanol

HAuCl ₄ concentration (mmol L ⁻¹)	supporting elelctrolyte		CO ₂ Saturated	
	E (V)	i (μA)	E (V)	i (μA)
0,1	-	-	-	-
0,3	-	-	-1.6	13.11
0,5	-	-	-1.5	15.54
1	-	-	-1.5	90.64
3	-	-	-1.4	46.33
5			-1.4	15.04

Optimization of Au nanoparticles cycle number for preparation Cu/Au/PPAP/GCE

As similar as Cu nanoparticle cycle number study, optimization study was performed to Au nanoparticles formation on PPAP/GCE surface (then modified with Cu) by varying the cycle number from 3-15 (Figure 3.67). It was observed that the height of reduction peak current of CO₂ was increased by increasing of the number of cycles until 10 cycles (Table 3.18). The highest peak current value was obtained with 10 cycles (Figure 3.68).

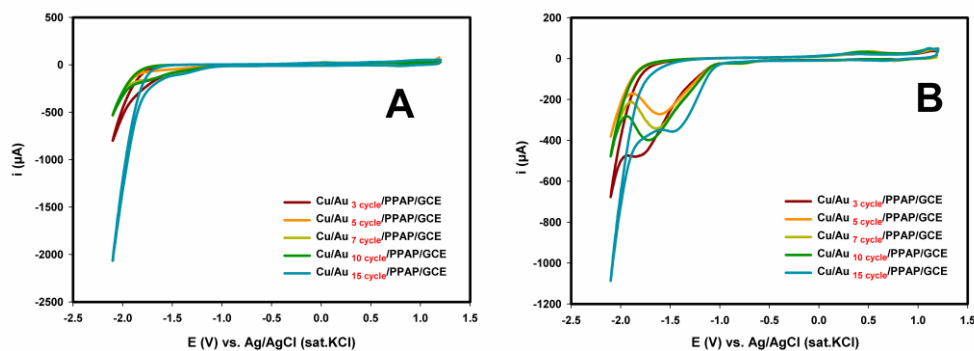


Figure 3. 67 Cyclic voltammograms of the effect of cycle number of Au on A) 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte B) CO₂ saturated 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE.

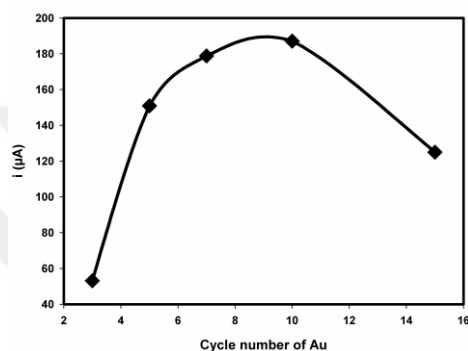


Figure 3. 68 Effect of Au cycle number on electrochemical reduction of CO₂ at Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M Methanol

Table 3. 18 The effect of Cu cycle number on CO₂ reduction at Cu/Au/PPAP/GC electrodes in 0.8 M NaClO₄ + 2 M Methanol environment.

Au cycle number	Supporting electrolyte		CO ₂ Saturated	
	E (V)	i (μA)	E (V)	i (μA)
3	-	-	-1.8	53.13
5	-	-	-1.6	150.92
7	-	-	-1.6	178.84
10	-	-	-1.7	187.11
15	-	-	-1.4	125.01

Optimization of CO₂ Feeding Time

The effect of CO₂ feeding time on electrochemical reduction of CO₂ was also performed with 5, 10, 20, 30 and 45 minutes at Cu/Au/PPAP/GCE in the presence of 0.8 M NaClO₄ + 2 M methanol (Figure 3. 69). A highest CO₂ reduction peak current was obtained for 30 minutes feeding time compare the others (Figure 3.70 and Table 1. 19).

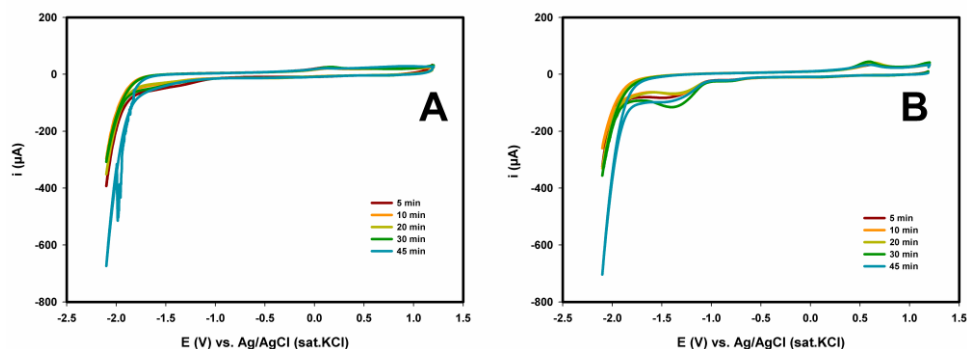


Figure 3. 69 Cyclic voltammograms of the effect of CO₂ feeding time on A) 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte B) CO₂ saturated 0.8 M NaClO₄ + 2 M Methanol supporting electrolyte at Cu/Au/PPAP/GCE.

As expected and detailed, increasing the CO₂ feeding time causes CO₂ deactivation in the solution and the current values decrease after 30 minutes of feeding (Table 3.18 and Figure 3. 70). For this reason, 30 minutes of feeding time was chosen as the optimum time for further studies.

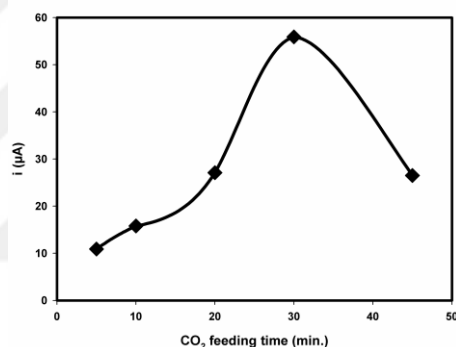


Figure 3. 70 Effect of CO₂ feeding time on electrochemical reduction of CO₂ at Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M methanol

Table 3. 19 The effect of CO₂ feeding time on CO₂ reduction with optimum Cu/Au/PPAP/GC electrode in 0.8 M NaClO₄ + 2 M methanol

CO ₂ feeding time (min.)	Supporting electrolyte		CO ₂ Saturated	
	E (V)	I (μA)	E (V)	I (μA)
5	-	-	-1.4	20.90
10	-	-	-1.3	25.80
20	-	-	-1.3	27.10
30	-	-	-1.4	55.90
45	-	-	-1.3	26.50

As a result, the optimum electrode and optimum working environment developed for the electrochemical reduction of CO₂ in the optimization studies were obtained, as indicated in Table 3.20.

Table 3. 20 The optimum conditions for electrochemical behavior of CO₂ on Cu/Au/PPAP/GCE

Experimental parameter	Optimum conditions
poly (aminophenol) concentration	5 mmol L ⁻¹
Cycle number of poly (aminophenol) electropolymerization	30 cycle
Au concentration	1 mmol L ⁻¹
Cycle number of Au electropolymerization	10 cycle
Cu concentration	1 mmol L ⁻¹
Cycle number of Cu electropolymerization	10 cycle
CO ₂ feeding time	30 min

3.2.1.4 Investigation of carbon dioxide reduction with rotating disk electrode

The CO₂ reduction kinetics were studied on Cu/Au/PPAP/GCE in 0.8 M NaClO₄ + 2 M methanol and a stable current density-potential curves for CO₂ reduction were obtained (Figure 3.71).

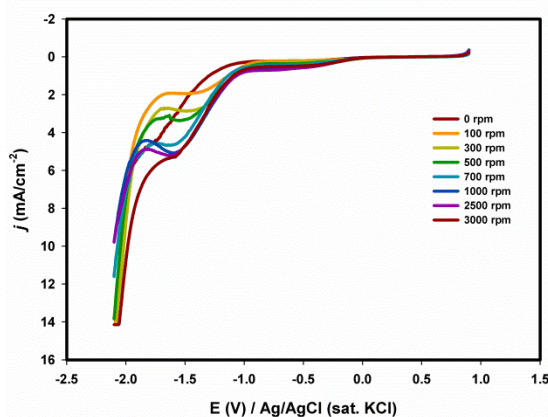


Figure 3. 71 Rotating disk electrode voltammetry results for CO₂ reduction on Cu/Au/PPAP/GCE in CO₂ saturated 0.8 M NaClO₄ + 2 M methanol

As seen in Figure 3.71, the CO₂ reduction current density at different potentials varies linearly with $\omega^{-1/2}$. The number of electrons was estimated from the slope of the Koutecki – Levich (KL) plots for the oxygen reaction mechanism. K-L graphs can be expressed with the following equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

Where, j is the measured current density, j_k is kinetic current density, ω is the rotation rate of the electrode and B is the Levich slope. The theoretical value can be explained by Equation :

$$B = 0.62nFC_{(CO_2)}D_{CO_2}^{2/3}\gamma^{-1/6} \quad (2)$$

Where, n is the number of electrons transferred for per carbon dioxide molecule, F is Faraday constant (96500 C mol^{-1}), $C_{(CO_2)}$ is the concentration of carbon dioxide (0.06 mol L^{-1} in $\text{NaClO}_4 + \text{Methanol}$), D_{CO_2} is the diffusion coefficient of carbon dioxide ($4.54 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), γ is the kinematic viscosity of the solution ($7.37 \times 10^{-3} \text{ cm}^2/\text{s}$) that measured by Ostwald viscometer.

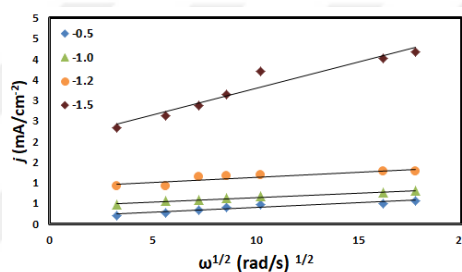


Figure 3.72 K-L plots for CO_2 reduction at different potentials on Cu/Au/PPAP/GCE in CO_2 saturated 0.8 M $\text{NaClO}_4 + 2$ M methanol

The number of electrons transferred per oxygen molecule in carbon dioxide reduction at the CuPc/Poly(Cresolred_{ox})/GCE electrode, was calculated as 1.9 from the slope of the K–L plots over the whole range of potentials (Figure 3.72). This value indicates that molecular carbon dioxide was reduced at the almost two-electron pathway to produce HCOOH .

3.2.2 Photocatalytic Reduction of Carbon Dioxide at Modified Electrodes

The photoelectrochemical reduction of CO_2 was studied in detail on carbon paste modified with MCM- TiO_2 composite and MnO_2 - TiO_2 modified GC electrodes without and with illumination of the electrode surface. In the following sections, the modifications of the electrodes used to determine and increase the photocatalytic efficiency of CO_2 , the selection of the appropriate supporting electrolyte, and optimization studies are given.

3.2.2.1 Experimental studies of the photocatalytic reduction of CO₂

Studies with carbon paste electrode

To examine the photoelectrocatalytic behavior of CO₂, firstly, studies were carried out with the carbon paste electrode; its preparation was detailed in the above sections. Since high current values were obtained in 0.8 M NaClO₄ + 2 M methanol supporting electrolyte in the electrochemical reduction of CO₂, the studies were started with this supporting electrolyte. The electrochemical and photoelectrochemical behavior of 10% MCM-TiO₂ + 30% Nujol + 60% graphite carbon paste electrode without and with illumination of the electrode surface by UV light were investigated in supporting electrolyte (0.8 M NaClO₄ + 2 M methanol) and CO₂ saturated 0.8 M NaClO₄ + 2 M methanol (Figure 3.73). Almost the same voltammograms were obtained for all conditions. The observed reduction peak at about -1.4 V and small oxidation peak at -1.1 V could be related with composite electrode material. There was no any new peak for CO₂ reduction in CO₂ saturated solution in both without and with illumination of the electrode surface by UV light. Therefore the prepared composite electrode will not be used for future studies.

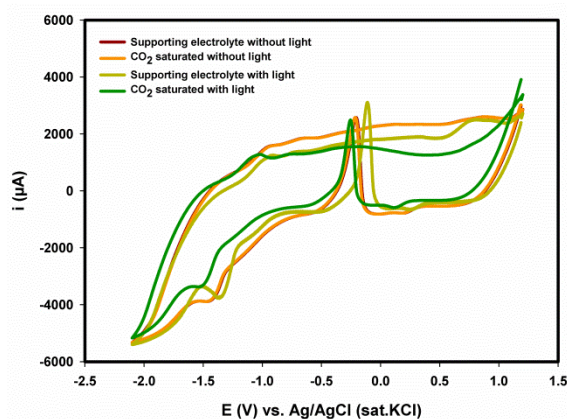


Figure 3. 73 Voltammetric behaviors of 10% MCM-TiO₂ + 30% Nujol + 60% graphite composite electrode in 0.8 M NaClO₄ + 2 M methanol supporting electrolyte and CO₂ saturated 0.8 M NaClO₄ + 2 M methanol without and with UV light

Studies with metal oxides modified GC electrode

When the literature studies were examined, it was seen that conductive metal oxides such as RuO₂, MnO₂, and CoO₂, together with TiO₂, gave effective results in the photocatalytic behavior of CO₂ (Bandi 1990 and Che Mat et al., 2019). For this reason, the composite material was prepared by combining MnO₂

metal oxides with TiO_2 . As detailed above, the working electrode was developed by dropping the prepared $\text{MnO}_2\text{-TiO}_2$ composite material onto the GC electrode surface. The electrochemical and photoelectrochemical behavior of $\text{MnO}_2\text{-TiO}_2$ modified GCE without and with illumination of the electrode surface by UV light were investigated in supporting electrolyte ($0.5 \text{ mol L}^{-1} \text{ KHCO}_3$) and CO_2 saturated $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ (Figure 3.74).

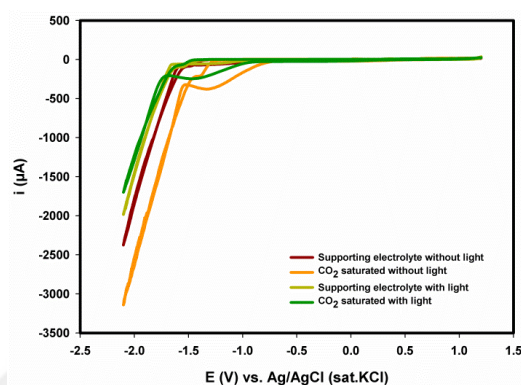


Figure 3. 74 Voltammetric behaviors of $\text{MnO}_2\text{-TiO}_2/\text{GCE}$ composite electrode in 0.5 M KHCO_3 supporting electrolyte and CO_2 saturated 0.5 M KHCO_3 without and with UV light

In the $\text{MnO}_2\text{-TiO}_2/\text{GC}$ electrode studies, there was no any reduction or oxidation peak for both without and with illumination of the electrode surface in the presence of $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$, while a reduction peak was observed for both without and with illumination of the electrode surface in the presence of CO_2 saturated $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ medium. In the absence of light, the reduction peak current value was $124.82 \mu\text{A}$ at -1.3 V . On the other hand, the peak potential was shifted to -1.4 V and peak current decreased as $90.4 \mu\text{A}$ by lighting of the electrode surface (Figure 3.74). However, studies with $\text{MnO}_2\text{-TiO}_2$ electrodes were not continued due to the decrease in current values in the presence of light and the decrease in catalytic efficiency by shifting the potential to more negative value.

Studies with MCM-TiO_2 composite material modified GC electrode

It has been explained in the above sections that syntheses were carried out using 4-aminophenol, catechol, and resorcinol as initiators for MCM synthesis. To investigate the photoelectrochemical behavior of CO_2 , MCM and TiO_2 composite material was suspended in DMF. $20 \mu\text{L}$ of each MCM-TiO_2 suspension was dropped onto the GC electrode surface and dried in an oven at 70°C . The prepared electrodes were used for electrocatalytic and photoelectrocatalytic reduction of

CO₂ without and with illumination of electrode surface by UV light in CO₂ saturated 0.5 mol L⁻¹ KHCO₃ supporting electrolyte solution. The obtained CVs were given in Figure 3.75 and Figure 3.76, respectively. A poor electrocatalytic and photoelectrocatalytic activities towards CO₂ reduction were observed on catechol-MCM-TiO₂ and 4-aminophenol-MCM-TiO₂ on GCE surfaces. The hydrogen evolution was appeared at different potentials depending on experimental conditions. Therefore, the catechol-MCM-TiO₂ and the 4-aminophenol-MCM-TiO₂ on GCE surfaces will not use in future studies.

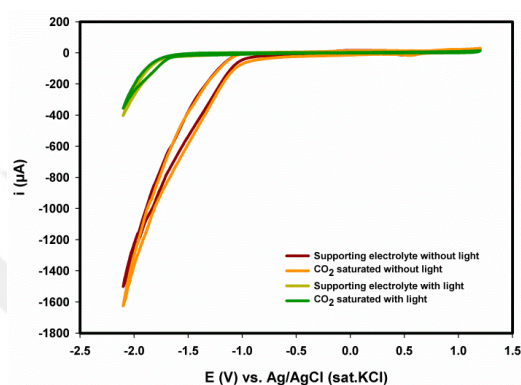


Figure 3. 75 Voltammetric behaviors of catechol-MCM-TiO₂/GCE composite electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ without and with UV light

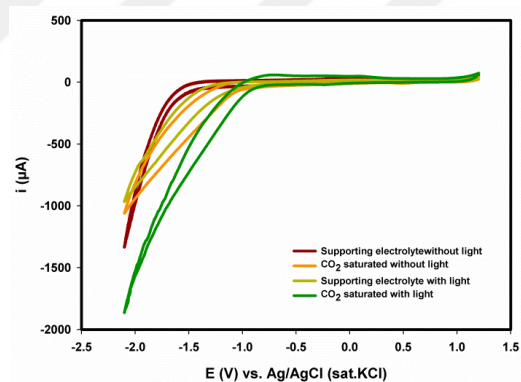


Figure 3. 76 Voltammetric behaviors of 4-aminophenol-MCM-TiO₂/GCE composite electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ without and with UV light

As detailed in the above studies, it has been observed that conductive polymers contribute positively effect on the electrochemical reduction of CO₂. For this reason, to prepare physically stable electrode surface, in the first step, a PPAP film was formed on the GCE surface by electrochemical polymerization of 4-aminophenol with 3 cycles and then 20 μL of MCM-TiO₂ composite + DMF suspension was dropped onto the PPAP/GCE surface, and the electrode was dried in an oven at 70°C. The electrochemical and photoelectrochemical behavior of MCM-TiO₂/PPAP/GCE without and with illumination of the electrode surface by

UV light were investigated in supporting electrolyte ($0.5 \text{ mol L}^{-1} \text{ KHCO}_3$) and CO_2 saturated $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$. A reduction peak was appeared at about -1.5 V in the absence of CO_2 and with and without surface illumination by UV light. Almost same potentials a reduction peak was observed for CO_2 saturated $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ solution and without surface illumination by UV light (Figure 3.77). The evaluated peak currents and potentials were given in Table 3.21.

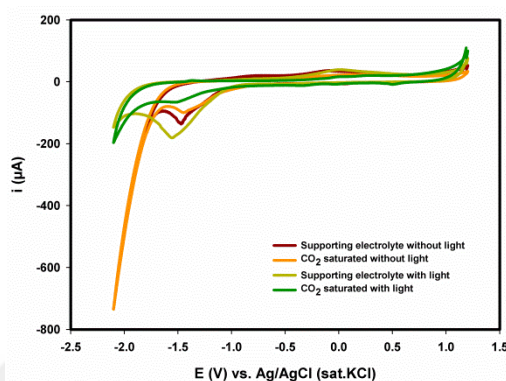


Figure 3. 77 Voltammetric behaviors of $20 \mu\text{L}$ MCM- $\text{TiO}_2/3$ cyc PPAP/GCE composite electrode in 0.5 M KHCO_3 supporting electrolyte and CO_2 saturated 0.5 M KHCO_3 without and with UV light

Table 3. 21 Electrochemical and photoelectrochemical behaviour of MCM- $\text{TiO}_2/\text{PPAP}/\text{GCE}$ in electrode in 0.5 M KHCO_3 supporting electrolyte and CO_2 saturated 0.5 M KHCO_3 absence and presence of UV light

	Absence of UV light		Presence of UV light	
	E (V)	i (μA)	E (V)	i (μA)
Supporting electrolyte	-1.5	62.35	-1.6	113.05
CO_2 Saturated	-1.4	34.66	-1.5	13.93

Continuing studies were not continued with $20 \mu\text{L}$ MCM- $\text{TiO}_2/3$ cyc PPAP/GCE, because a higher peak current was obtained in the absence of CO_2 in both without and with electrode surface illumination conditions.

Since promising results could not be obtained in the investigation of different modified electrodes, the photoelectrochemical behavior of CO_2 was investigated in $0.5 \text{ mol L}^{-1} \text{ KHCO}_3$ solution with GC electrode modified with $20 \mu\text{L}$ of MCM- TiO_2 suspension prepared which the componenet of the MCM in MCM- TiO_2 composite synthesized with resorcinol initiator (Figure 3.78).

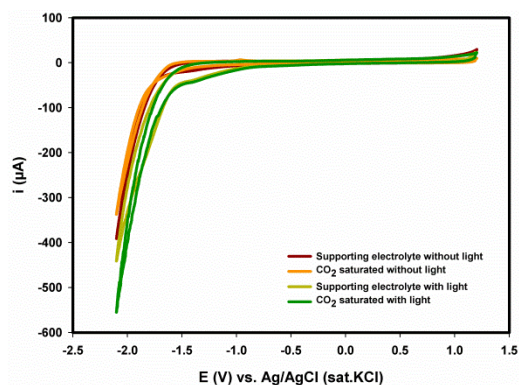


Figure 3. 78 Voltammetric behaviors of resorcinol-MCM-TiO₂/GCE composite electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ without and with UV light

As seen in Figure 3.78, no reduction peaks were observed in supporting electrolyte (absence of CO₂) at 20 μ L MCM-TiO₂/GC electrode in the presence of light and without light. When the supporting electrolyte was saturated with CO₂, a reduction peak was appeared at -1.3 V with 1.04 μ A peak current in the absence light on the electrode surface. On the other hand, the peak current was improved as 1.62 μ A by illumination of the electrode surface with UV light. The evaluated data were given in Table 3.22. The obtained results showed that the photoelectrocatalytic activity was observed for CO₂ reduction on MCM-TiO₂/GC electrode by illumination of the electrode surface with UV light.

Table 3. 22 Electrochemical and photoelectrochemical behaviour of 20 μ L MCM-TiO₂/GCE in electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ absence and presence of UV light

	Absence of UV light		Presence of UV light	
	E (V)	i (μ A)	E (V)	i (μ A)
Supporting electrolyte	-	-	-	-
CO₂ Saturated	-1.3	1.04	-1.5	1.62

For the following study, the amount of MCM-TiO₂ was changed as 10 μ L instead of 20 μ L, and then the electrochemical and photoelectrochemical behavior of the MCM-TiO₂/GCE was studied in the absence and presence of CO₂ (Figure 3.79, Table 3.23). There was no any reduction peak in supporting electrolyte (absence of CO₂) at 10 μ L MCM-TiO₂/GCE without and with illumination of 10 μ L MCM-TiO₂/GCE surface by UV light. When the supporting electrolyte was saturated with CO₂, a reduction peak was formed at -1.5 V with 5.89 μ A in the absence light and -1.4 V with 12.89 μ A with light on MCM-TiO₂/GCE.

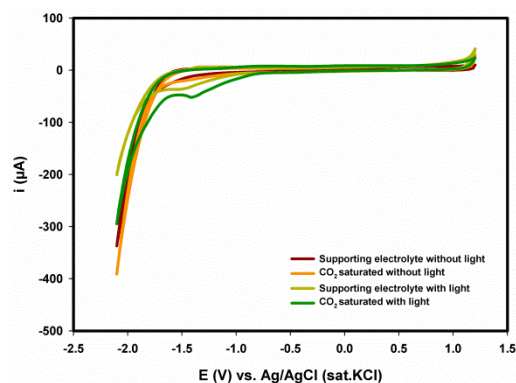


Figure 3. 79 Voltammetric behaviors of 10 μ L MCM-TiO₂/GCE composite electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ without and with UV light

The obtained results were given in Table 3.26. In the case of composite electrode prepared with 10 μ L MCM-TiO₂, the electrocatalytic and photoelectrocatalytic activity was improved by decreasing the amount of MCM-TiO₂ on GCE surface due to offer a thin film of 10 μ L MCM-TiO₂ then 20 μ L MCM-TiO₂ covered GCE surface. Therefore, 10 μ L MCM-TiO₂ composite will be used for future studies.

Table 3. 23 Electrochemical and photoelectrochemical behaviour of 10 μ L MCM-TiO₂/GCE in electrode in 0.5 M KHCO₃ supporting electrolyte and CO₂ saturated 0.5 M KHCO₃ absence and presence of UV light

	Absence of UV light		Presence of UV light	
	E (V)	i (μ A)	E (V)	i (μ A)
Supporting electrolyte	-	-	-	-
CO ₂ Saturated	-1.5	5.89	-1.4	12.89

3.2.2.2 Optimization studies for photocatalytic reduction of CO₂ studies

Optimization of KHCO₃ concentration

To increase the photoelectrocatalytic activity of MCM-TiO₂ /GCE surface on CO₂ reduction, the supporting electrolyte (KHCO₃) concentration was varied in the range from 0.01 to 0.70 mol L⁻¹ KHCO₃. The voltammograms were recorded without or with illumination by UV light of MCM-TiO₂ /GCE surface in the absence and presence of CO₂ saturated KHCO₃ solutions (Figure 3.87A, B,C and D). From the studies, the best result in terms of current value was obtained at a potential of -1.17 V with 6.99 μ A in 0.1 mol L⁻¹ KHCO₃ medium (Table 3.24 and 3.25 and Figure 3.80).

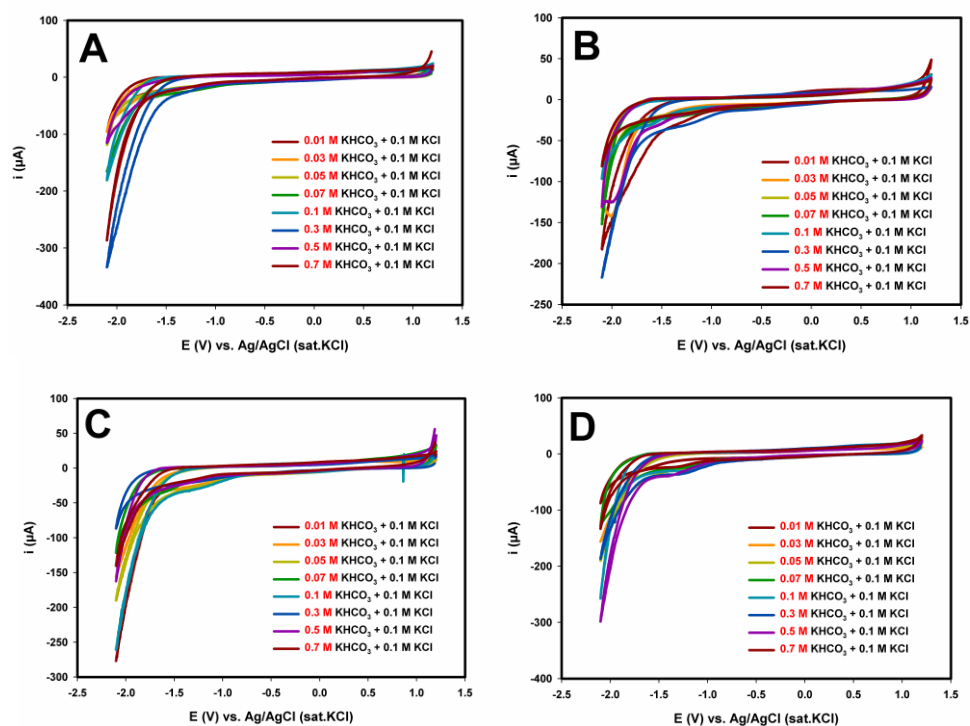


Figure 3.80 The effect of KHCO_3 concentration on electrochemical and photoelectrochemical behavior of A) supporting electrolyte without light, B) supporting electrolyte with light, C) CO_2 saturated supporting electrolyte without light, and D) CO_2 saturated supporting electrolyte with UV light, respectively.

Table 3.24 The effect of KHCO_3 concentration on electrochemical and photoelectrochemical behavior of CO_2 saturated supporting electrolyte without UV light

Concentration of KHCO_3 (mol L^{-1})	Supporting electrolyte		CO_2 saturated supporting electrolyte	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
0.01	-1.2	0.24	-1.2	0.53
0.03	-1.2	0.42	-1.3	0.75
0.05	-1.2	0.46	-1.2	1.24
0.07	-1.2	0.94	-1.6	1.38
0.1	-1.2	0.99	-1.2	2.10
0.3	-1.4	0.68	-1.2	1.45
0.5	-1.2	0.53	-1.3	0.87
0.7	-1.3	0.39	-1.3	0.41

Table 3. 25 The effect of KHCO_3 concentration on electrochemical and photoelectrochemical behavior of CO_2 saturated supporting electrolyte with UV light

Concentration of KHCO_3 (mol L^{-1})	Supporting electrolyte		CO_2 saturated supporting electrolyte	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
0.01	-1.3	0.57	-1.6	1.38
0.03	-1.5	1.41	-1.7	2.60
0.05	-1.3	1.41	-1.7	3.09
0.07	-1.2	1.94	-1.2	3.74
0.1	-1.6	2.82	-1.2	6.99
0.3	-1.2	2.04	-1.2	6.08
0.5	-1.5	1.26	-1.4	4.37
0.7	-1.3	0.78	-1.3	2.83

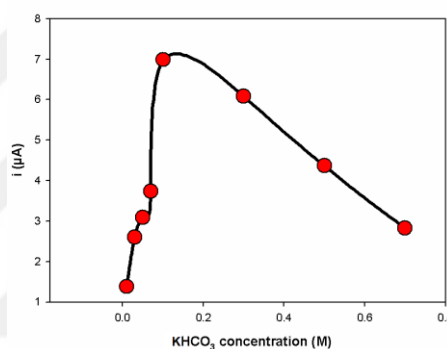


Figure 3. 81 The effect of KHCO_3 concentration on photoelectrochemical behavior of CO_2 .

Optimization of CO_2 feeding time

In another study conducted to increase the current values obtained in the photoelectrochemical reduction of CO_2 , the optimization of the CO_2 saturation time was investigated. For this purpose, experimental studies were carried out with different CO_2 saturation times from 5.0 to 50 minutes. The optimum CO_2 feeding time was found as 30 minutes (Table 3.26 and 3.27) due to the highest peak current observed as $6.78 \mu\text{A}$ and $12.05 \mu\text{A}$ in both without or with illumination by UV light of MCM-TiO_2 /GCE surface respectively (Figure 3.82 and Figure 3.83).

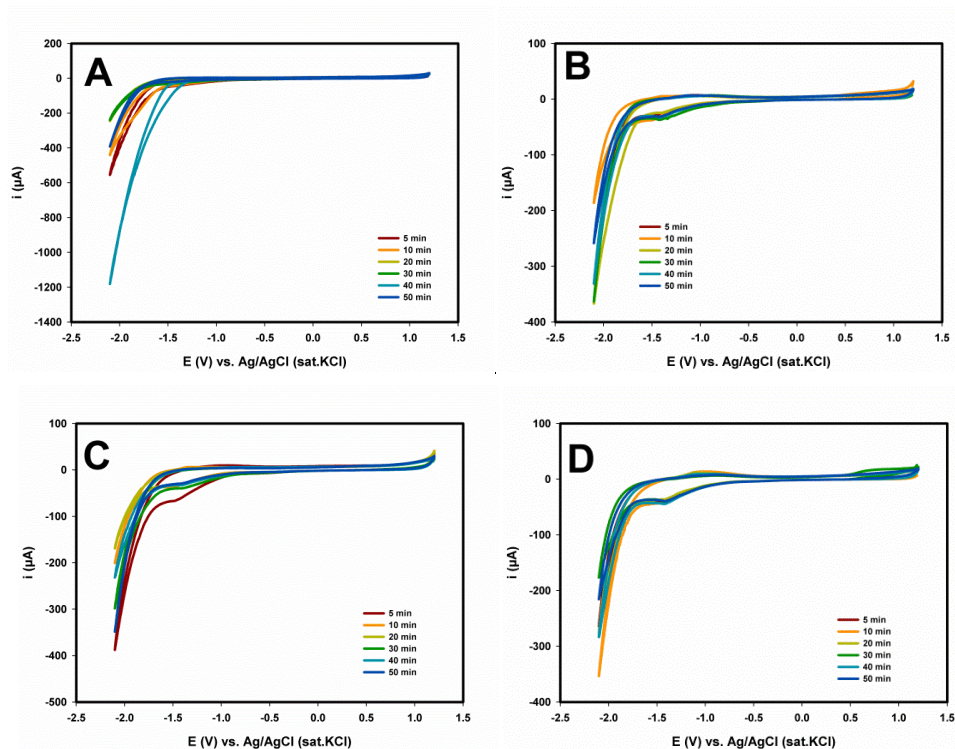


Figure 3.82 The effect of CO₂ feeding time on electrochemical and photoelectrochemical reduction of CO₂ in A) and B) supporting electrolyte without and with light, respectively, C) and D) CO₂ saturated supporting electrolyte without and with light, respectively.

Table 3.26 The effect of CO₂ feeding time on electrochemical and photoelectrochemical behavior of CO₂ saturated supporting electrolyte without UV light

CO ₂ feeding time (min)	Supporting electrolyte		CO ₂ saturated supporting electrolyte	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
5	-	-	-1.4	3.18
10	-	-	-1.4	4.19
20	-1.4	1.08	-1.4	4.56
30	-1.4	1.54	-1.4	6.78
40	-1.4	0.94	-1.4	5.90
50	-1.4	0.38	-1.4	5.12

Table 3.27 The effect of CO₂ feeding time on electrochemical and photoelectrochemical behavior of CO₂ saturated supporting electrolyte with UV light

CO ₂ feeding time (min)	Supporting electrolyte		CO ₂ saturated supporting electrolyte	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
5	-1.4	2.47	-1.4	6.02
10	-1.4	4.97	-1.4	8.17
20	-1.4	5.25	-1.4	9.95
30	-1.4	9.08	-1.4	12.05
40	-1.4	7.76	-1.4	11.53
50	-1.4	5.40	-1.4	10.70

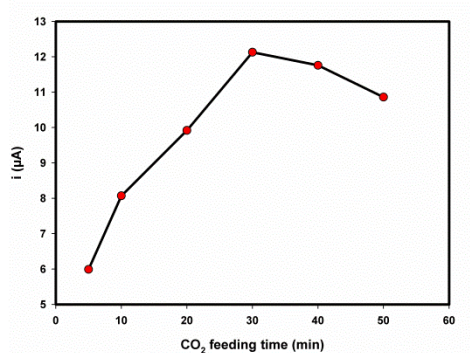


Figure 3. 83 The effect of CO₂ feeding time on photoelectrochemical behavior of CO₂ reduction with UV light.

Optimization of the effect of the UV light time given on the electrode surface before the measurement

The effect of UV light duration given on the electrode surface before the measurement was investigated in optimization studies. For this purpose, 10 μL of MCM-TiO₂/GCE was immersed in 0.1 M KHCO₃ supporting electrolyte saturated with CO₂ and UV light was illuminated on the electrode surface for 5, 10, 15, 20, 25 and 30 minutes before each measurement. The photoelectrochemical behavior of CO₂ was investigated by stopping the illumination of MCM-TiO₂/GCE with UV light. It was observed that the highest peak current was 1.77 μA at -1.7 V for 10 minutes illumination. Obtained voltammograms were shown in Figure 3.84 and Figure 3.85, and potentials and currents were given in Table 3.28.

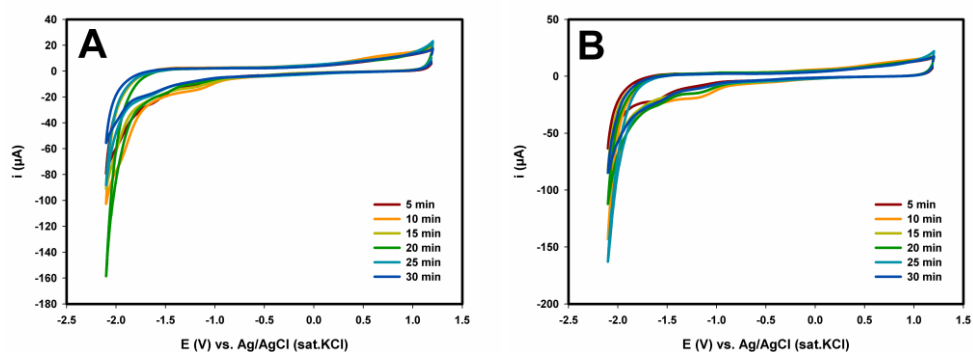


Figure 3. 84 The effect of UV light time given on the electrode surface before the measurement on electrochemical and photoelectrochemical behavior of A) supporting electrolyte without light, B) supporting electrolyte with light, C) CO₂ saturated supporting electrolyte without light, and D) CO₂ saturated supporting electrolyte with UV light, respectively.

Table 3. 28 The effect of UV light time given on the electrode surface before the measurement on electrochemical and photoelectrochemical behavior of with UV light

	Supporting electrolyte		CO ₂ saturated supporting electrolyte	
UV light duration (min)	Potential (V)	Current (μA)	Potential (V)	Current (μA)
5	-1.6	0.81	-1.6	2.37
10	-1.2	1.77	1.2	3.25
15	-1.2	0.78	1.2	2.33
20	-1.6	0.58	1.2	2.04
25	-1.6	0.47	-1.6	1.01
30	-1.6	0.40	-1.6	0.44

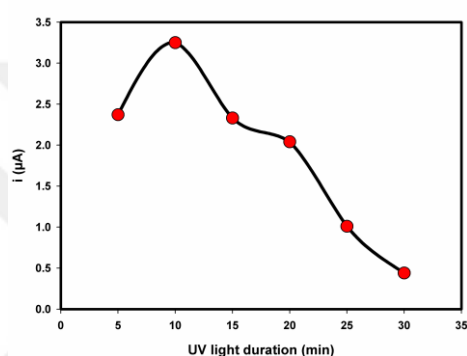


Figure 3. 85 The effect of UV light time given before measurement on photoelectrochemical behavior of CO₂.

As a result, the optimum conditions for the photoelectrochemical reduction of CO₂ were summarized in Table 3.29.

Table 3. 29 The optimum conditions for electrochemical behavior of CO₂

Experimental parameter	Optimum conditions
KHCO ₃ concentration	0.1 mol L ⁻¹
CO ₂ feeding time	5 min
UV light time given on the electrode before measurement	10 min

The electrochemical and photoelectrochemical behavior of CO₂ were investigated at MCM-TiO₂/GCE in 0.1 M KHCO₃ supporting electrolyte at optimum conditions. The obtained voltammograms and current potential values were shown in Figure 3. 86 and in Table 3. 30, respectively.

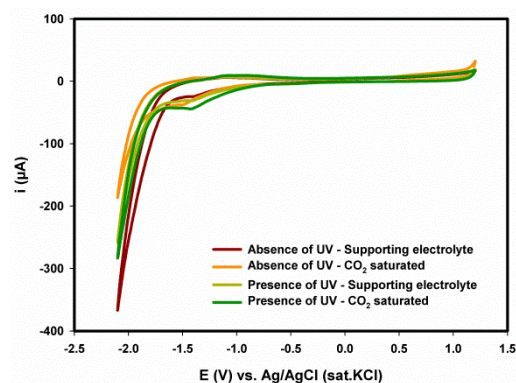


Figure 3. 86 The behavior of optimum conditions on electrochemical and photoelectrochemical reduction of CO₂ absence and presence of UV light

Table 3. 30 The behavior of optimum conditions on electrochemical and photoelectrochemical reduction of CO₂ absence and presence of UV light

	Supporting electrolyte		CO ₂ saturated supporting electrolyte	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
Absence of UV light	-1.4	2.42	-1.4	5.43
Presence of UV light	-1.5	5.18	-1.4	11.61

According to the results obtained under optimum conditions, the photoelectrochemical reduction peak current of CO₂ increased from 5.18 μA to 11.61 μA with the effect of light. When the voltammograms obtained under optimum experimental conditions with and without illumination of MCM-TiO₂/GCE were compared, it was determined that the photoelectrochemical CO₂ reduction peak current increased approximately 2.24 times compared to the electrochemical reduction. According to this result, it was determined that the MCM-TiO₂/GCE showed a high photoelectrocatalytic activity towards CO₂ reduction in 0.1 M KHCO₃ medium.

3.2.3 Voltammetric Determination of Antimony

In this part of the thesis, the development of new electrode and a method to detection of antimony by voltammetric techniques were aimed. For this purpose, CV and anodic stripping voltammetry were used to develop antimony-sensitive modified electrodes. After optimization studies with the developed modified electrode, the detection of antimony in PET bottle samples was carried out under optimum conditions. The studies were performed in the following sections in detailed.

3.2.3.1 Electrochemical Behavior of Antimony at Modified GC Electrodes

Modification of the GC electrode surface with conductive polymers has been studied. For this purpose, poly(cresolred) conductive polymer film covered GCE was prepared for the determination of antimony since it contains (-) charged functional group $-\text{SO}_3^-$ and electron-rich oxygen atom (Chen et al., 2005).

The electrochemical polymerization of cresol red monomer with CV and the over-oxidation procedure on poly(Cresol red) were used to prepare and then the polymer film electrodes of both poly(Cresol red) and poly(Cresol red_{ox}) were modified with CuPc by CV as explained in section 2.3.6 and 2.3.7.

The electrochemical behavior of on bare GCE, by poly(cresolred)/GCE and poly(Cresolred_{ox})/GCE was investigated in the absence and presence of 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl solution by DPASV (Figure 3.87)

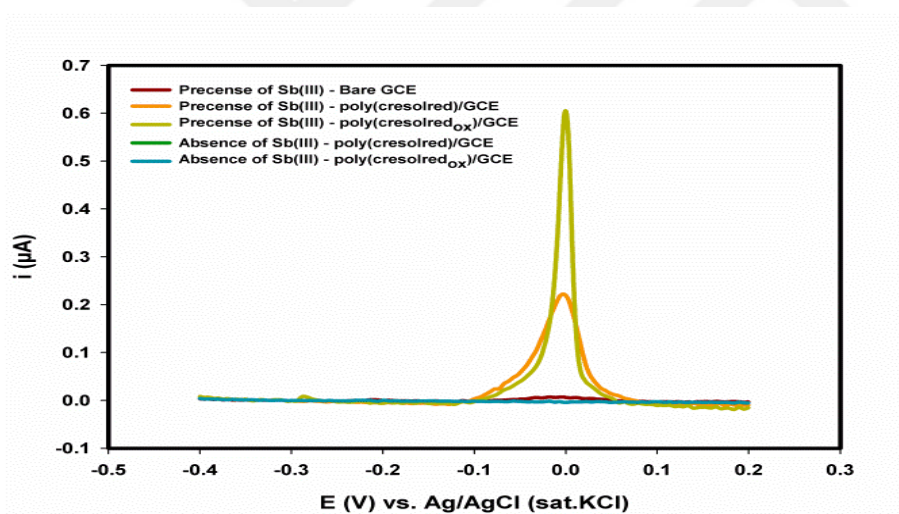


Figure 3. 87 ASV voltammograms of absence and presence of Antimony (III) for Bare GCE, poly(cresolred)/GCE and poly(cresolred_{ox})/GCE modified electrodes in 0.1 M HCl, at -0.4 V deposition potential, for 100 sec.

Although, there were not observe any reduction and oxidation peak in the absence of Antimony (III) in 0.1 M HCl for all electrodes (Figure 3.88 A), an oxidation peak in the presence of 0.01 mmolL⁻¹ Antimony (III) was appeared at -0.01 V with 2.31μA and 5.99 μA on poly(cresolred)/GCE and poly(Cresolred_{ox})/GCE respectively Figure 3.88 B and Table 3.31). As can be seen from the results, the over-oxidation of poly(cresolred) polymer was provided activity of the poly(cresolred)/GCE for electrochemical behaviour of Antimony (III).

Table 3.31 DPASV data of 0.01 mmol L⁻¹ Antimony (III) obtained with polymer film electrodes

Modified Electrode	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
Bare GCE	-	-	-	-
Poly(cresolred)/GCE	-	-	-0.02	0.231
Poly(cresolred _{ox})/GCE	-	-	-0.02	5.99

To improve the electrochemical activity of both poly(cresolred)/GCE and poly(cresolred_{ox})/GCE on Antimony (III), the polymer films were modified with Cu metal particles and CuPc. The Cu particles were deposited on the polymer film surface by CV with 10 cycles current potential scan from 0.1 mmol L⁻¹ Cu(II) in 0.1 mol L⁻¹ HCl solution. The CuPc modifications were carried out by dropping the 0.035 mmol L⁻¹ of 2 mg CuPc + 2 mL DMF suspension on poly(cresolred_{ox})/GCE. The electrochemical behaviour of the new modified polymer film electrodes were examined in the absence and presence of 0.01mmol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl (Figure 3.88) by DPASV, and the potentials and current values were represented in Table 3.32. Although antimony oxidation was observed close potentials about at -0.03 V at all electrodes, the highest peak current was obtained as 8.91 μA on electrochemically deposited CuPc on poly(cresolred_{ox})/GCE (denote as CuPc/poly(cresolred_{ox})/GCE) compare with other modified poly(cresolred_{ox})/GCE. Therefore, CuPc/poly(cresolred_{ox})/GCE was used as working electrode for future studies.

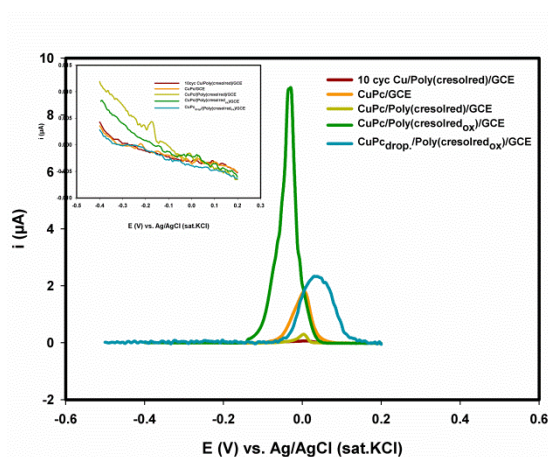


Figure 3.88 ASV voltammograms of presence of Antimony (III) for Cu/Poly(cresolred)/GCE, CuPc/GCE, CuPc/Poly(cresolred)/GCE, CuPc/Poly(cresolred_{ox})/GCE and CuPc_{drop}/Poly(cresolred_{ox})/GCE, respectively in M HCl, inset: 0.1 M HCl supporting electrolyte solution

Table 3.32 DPASV data of 0.01 mmol L⁻¹ Antimony (III) obtained with different modified electrodes

Modified Electrode	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
Cu/Poly(cresolred)/GCE	-	-	-0.01	0.07
CuPc/GCE	-	-	-0.03	3.35
CuPc/Poly(cresolred)/GCE	-	-	-0.03	0.31
CuPc/Poly(cresolred _{ox})/GCE	-	-	-0.03	8.91
CuPc _{drop} /Poly(cresolred _{ox})/GCE	-	-	-0.03	2.32

3.3.3.2 Optimization studies for voltammetric determination of antimony

To provide the optimum parameters of Antimony (III) detection on CuPc/poly(cresolred_{ox})/GCE, the significant variables that could be assumed as monomer concentration, polymerization cycle numbers, NaOH concentration, over-oxidation potential and time of Poly(cresolred), CuPc concentration, CuPc deposition potential and time. The optimum conditions for ASPV detection were obtained by monitoring the peak current while varying each parameter mentioned above. The detailed studies were explained followed section.

Optimization of cresolred monomer concentration and cycle number of electropolymerization

To obtain the optimum cresol red concentration, CuPc/Poly(cresolred_{ox})/GCE was prepared by varying the monomer concentration from 0.01 mmol L⁻¹ to 10 mmol L⁻¹ with accompanying deposition of 15 cycles number. The prepared each Poly(cresolred) film electrode was over-oxidized in NaOH solution and then 0.035 mmol L⁻¹ + 0.1 mol L⁻¹ H₂SO₄ CuPc was deposited on the polymer film modified electrode surface -0.1 V potential for 100 sec. The final obtained electrode was used for DPASV behaviour of 0.01 mmol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl medium (Figure 3.89 and Table 3.33).

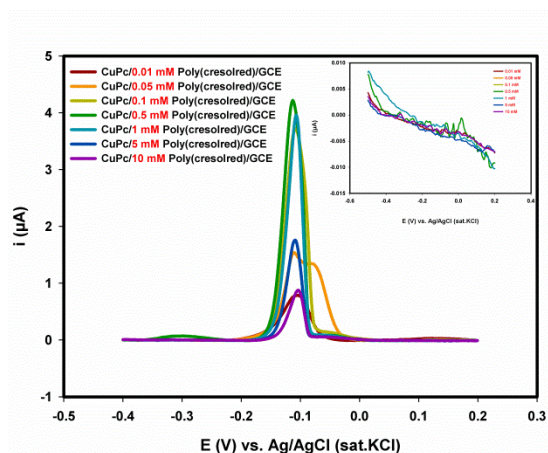


Figure 3. 89 The effect of the cresol red monomer concentration on 0.01 mmol L⁻¹ Antimony (III) ⁺ in 0.1 M HCl, inset: absence of Antimony (III)

Table 3. 33 The effect of the cresol red monomer on peak height of Antimony (III)

Cresolred monomer concentrations (mmol L ⁻¹)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
0.01	-	-	-0.11	0.79
0.05	-	-	-0.11	1.55
0.1	-	-	-0.11	3.73
0.5	-	-	-0.11	4.18
5	-	-	-0.11	3.96
10	-	-	-0.11	1.76

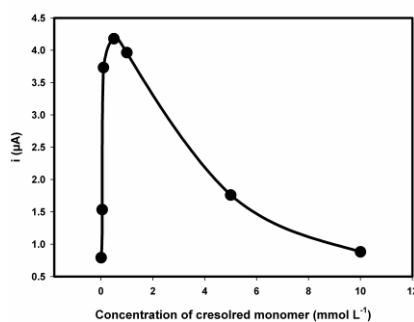


Figure 3. 90 The effect of the cresol red monomer concentration on Antimony (III) in 0.1 M HCl

As seen in Table 3.33, since the highest peak current for Antimony (III) was observed as 4.178 μA at -0.12 V on CuPc/poly(cresolred_{ox})/GCE which was the polymer component prepared from 0.5 mmol L⁻¹ cresol red. The future studies will be performed with the electrode.

After the monomer concentration optimization, the electrochemical polymerization of cresol red was carried out depending of cycle number in the range from 5 to 40 cycles and the prepared polymer film electrodes were over-

oxidized in the presence of NaOH at 0.1 V for 100 sec. Finally, CuPc was deposited on the electrode surface from 0.035 mmol L⁻¹ + 0.1 mol L⁻¹ H₂SO₄. CuPc was deposited on the polymer film modified electrode surface -0.1 V potential for 100 sec. and then the electrochemical behaviour of prepared electrodes were investigated by DPASV for 0.01 mmol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl medium (Figure 3.91 and Table 3.34). It was clearly seen in Figure 3.98 that the peak potential of antimony was not changed whereas the maximum peak current as 8.908 μ A was obtained for 30 consecutive scans deposition procedure of polycresol red optimum electrode surface.

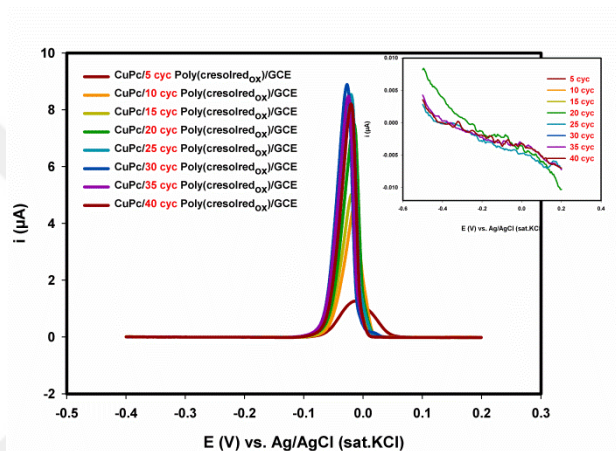


Figure 3. 91 The effect of the cycle number of cresol red polymerization on 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl, inset: absence of Antimony (III)

Table 3. 34 The DPASV data obtained for 0.01 mmolL⁻¹ Antimony (III) by changing the cycle number of electropolymerization of cresol red monomer

Cycle number of Cresolred monomer	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μ A)	Peak Potential (V)	Peak Current (μ A)
5	-	-	-0.01	1.28
10	-	-	-0.01	4.52
15	-	-	-0.01	4.98
20	-	-	-0.01	7.47
25	-	-	-0.01	8.50
30	-	-	-0.01	8.91
35	-	-	-0.01	8.32
40	-	-	-0.01	8.14

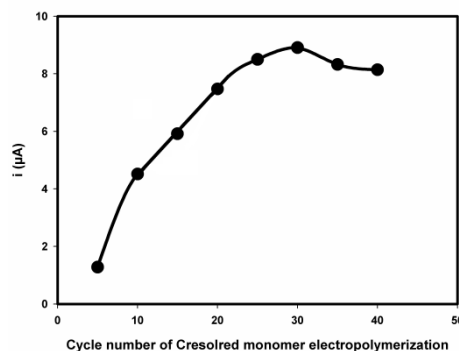


Figure 3.92 The effect of the cycle number of electropolymerization of cresol red monomer on DPASV antimony oxidation

Optimization of NaOH concentration, over-oxidation potential and time

After obtaining optimum values for the concentration and cycle number of cresol red monomer, optimization studies of the second step of the modified electrode preparation, the over-oxidation step, was carried out. First, the concentration of NaOH, the over-oxidation medium, and then optimization studies for the over-oxidation potential and time were carried out. The effect of NaOH concentration in the concentration range from 0.1 mol L⁻¹ to 0.3 mol L⁻¹ on over-oxidizing of poly(cresol red) was studied by monitoring the DPASV peak current of 0.01 mmol L⁻¹ Antimony (III) at optimum electrode (Figure 3.100). The data obtained from the NaOH concentration optimized studies shown that, the heights peak current for antimony was obtained on CuPc/Poly(cresolred_{ox})/GCE which was prepared in the presence of 0.2 M NaOH solution for over-oxidation of poly(cresol red) (Figure 3.93).

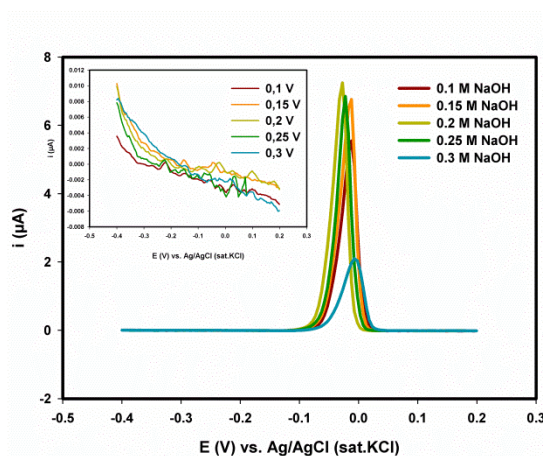


Figure 3.93 The effect of the NaOH concentration for over-oxidation of poly(cresol red) on 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl, inset: absence of Antimony (III)

Table 3. 35 The effect of the NaOH concentration on voltametric determination of Antimony (III) ⁺

Cresolred monomer concentrations (mmol L ⁻¹)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Peak Potential (V)	Peak Current (μA)
0.10	-	-	-0.01	5.55
0.15	-	-	-0.01	6.77
0.20	-	-	-0.01	7.25
0.25	-	-	-0.01	6.86
0.30	-	-	-0.01	2.11

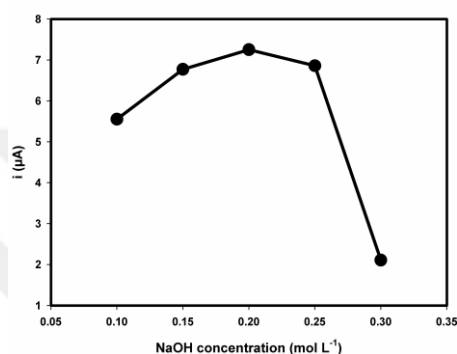


Figure 3. 94 The effect of the NaOH concentration on Antimony (III) in 0.1 M HCl

Since the highest current value for the NaOH concentration was obtained with 0.2 mol L⁻¹, this concentration was continued to be over-oxidized. Over-oxidation potential was also examined as further studies, respectively. For this purpose, a modified electrode was prepared by performing over-oxidation at 0.5, 0.6, 0.7, 0.8 and 0.9 V potentials.

Then, CuPc was deposited on the each modified electrode surface from 0.035 mmol L⁻¹ CuPc 0.1 mol L⁻¹ HCl at -0.1 V constant potential for 100 s and finally the DPASV behaviour of the prepared electrodes was examined in the presence of 0.01 mmol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl medium (Figure 3.102, Figure 3.103 and Table 3.41).

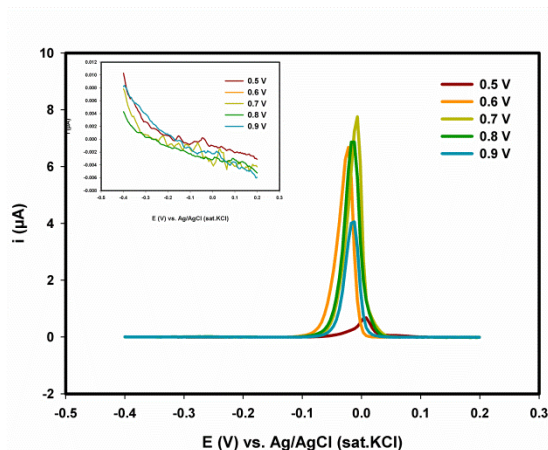


Figure 3. 95 The effect of the potential for over-oxidation of poly(cresol red) on 0.01 mmol L^{-1} Antimony (III) in 0.1 M HCl , inset: absence of Antimony (III)

Table 3. 36 The effect of the potential for over-oxidation on voltametric determination of Antimony (III)

Potential for over-oxidation (V)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
0.5	-	-	-0.01	0.61
0.6	-	-	-0.01	6.68
0.7	-	-	-0.01	7.59
0.8	-	-	-0.01	6.87
0.9	-	-	-0.01	4.06

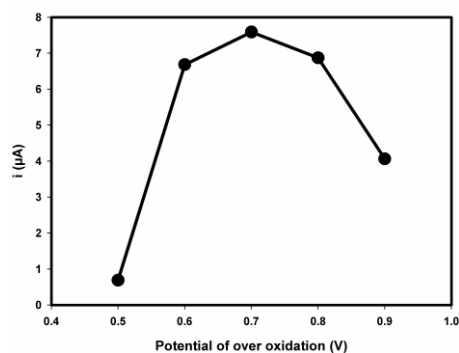


Figure 3. 96 The effect of the potential for over-oxidation on Antimony (III) in 0.1 M HCl

The over-oxidation potential on the poly(cresol red) component at CuPc/Poly(cresolred_{ox})/GCE was indicated that the best potential was 0.70 V since highest peak current for antimony as $7.589 \mu\text{A}$. To obtain the best over-oxidation time, the poly(cresol red)/ GCE electrode was prepared by varying the over-oxidation time from 30 to 175 seconds. Then, CuPc was deposited on each modified electrode surface $0.035 \text{ mmol L}^{-1}$ CuPc 0.1 mol L^{-1} HCl at -0.1 V constant potential for 100 s. Finally, the DPASV behaviour of the prepared

CuPc/Poly(cresolred_{ox})/GCE was studied in the presence of 0.01 mmol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl medium (Figure 3.104, Figure 3.105 and Table 3.42). The over-oxidation time studies indicate that, the highest peak current for antimony was obtained on CuPc/Poly(cresolredox)/GCE which was prepared by the 100s over-oxidation time of poly(cresol red)/GC.

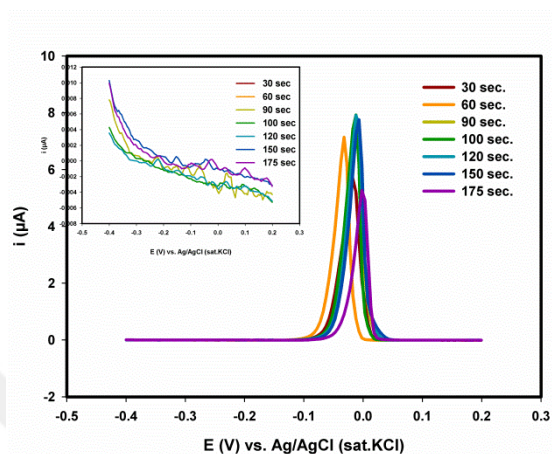


Figure 3. 97 The effect of the duration for over-oxidation of poly(cresol red) on 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl, inset: absence of Antimony (III)

Table 3. 37 The effect of the duration for over-oxidation on voltametric determination of Antimony (III)

Potential for over-oxidation (V)	Absence of Antimony (III)		Presence of Antimony (III)	
	Peak Potential (V)	Peak Current (μA)	Peak Potential (V)	Peak Current (μA)
30	-	-	-0.01	5.68
60	-	-	-0.01	7.15
90	-	-	-0.01	7.64
100	-	-	-0.01	7.93
120	-	-	-0.01	7.91
150	-	-	-0.01	7.76
175	-	-	-0.01	5.27

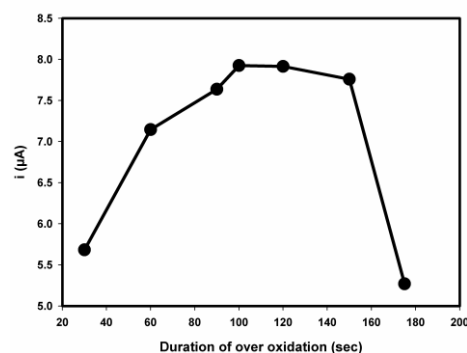


Figure 3. 98 The effect of the duration for over-oxidation on Antimony (III) ⁺ in 0.1 M HCl

In the over-oxidation concentration, potential, and time optimization studies, the optimum NaOH concentration was 0.2 mol L^{-1} , the optimum over-oxidation potential was 0.70 V , and the time was 100 seconds. For this reason, the ongoing optimization studies were continued with these optimum conditions.

Optimization of CuPc concentration, CuPc deposition potential and time

To optimize the other CuPc component of CuPc/Poly(cresolred_{ox})/GCE, its concentration, deposition potential, and time on Poly(cresolred_{ox})/GCE studies were performed. To obtain the optimum concentration of CuPc, the electrochemical deposition of CuPc on Poly(cresolred_{ox})/GCE was carried out from $2.5 \text{ } \mu\text{mol L}^{-1}$ to $25 \text{ } \mu\text{mol L}^{-1}$ CuPc containing 0.1 M HCl . Then, 0.01 mmol L^{-1} Antimony (III) response was investigated in $0.1 \text{ mol L}^{-1} \text{ HCl}$ medium with the prepared CuPc/Poly(cresolred_{ox})/GCE (Figure 3.106, Figure 3.107 and Table 3.43).

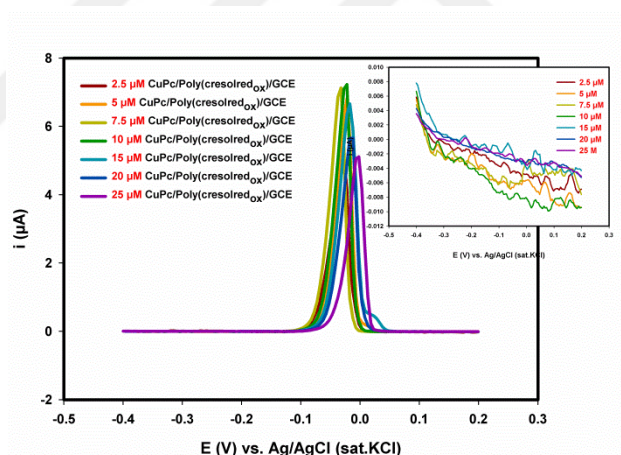


Figure 3. 99 The effect of the concentration of CuPc on 0.01 mmol L^{-1} Antimony (III) in 0.1 M HCl , inset: absence of Antimony (III) .

Table 3. 38 The effect of the concentration of CuPc on voltametric determination of Antimony (III)

CuPc Concentration ($\mu\text{mol L}^{-1}$)	Absence of Antimony (III)		Presence of S Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
2.5	-	-	-0.12	5.12
5	-	-	-0.12	6.82
7.5	-	-	-0.12	7.14
10	-	-	-0.12	7.24
15	-	-	-0.12	6.67
20	-	-	-0.12	5.66
25	-	-	-0.12	5.12

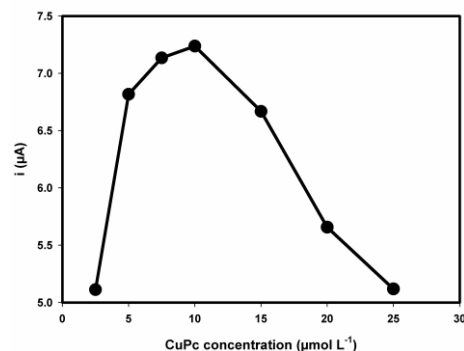


Figure 3.100 The effect of the concentration of CuPc on Antimony (III) in 0.1 M HCl

Since the highest peak current was monitored as $7.925 \mu\text{A}$ for $10 \mu\text{mol L}^{-1}$ in CuPc concentration. Thus, the $10 \mu\text{mol L}^{-1}$ CuPc was chosen as the optimum concentration for future studies. The following parameter investigated in CuPc optimization studies is the deposition potential. To find the optimum deposition potential, CuPc was deposited on the Poly(cresolred_{ox})/GCE from $10 \mu\text{mol L}^{-1}$ CuPc containing 0.1 mol L^{-1} HCl by varying the deposition potential from -0.25V to 0.00 V .

Finally, the DPASV behaviour of the prepared CuPc/Poly(cresolred_{ox})/GCE was studied in the presence of 0.01 mmol L^{-1} Antimony (III) in 0.1 mol L^{-1} HCl medium (Figure 3.108, Figure 3.109 and Table 3.44). The over-oxidation potential studies show that, the highest peak current for antimony was demonstrated at CuPc/Poly(cresolred_{ox})/GCE which was prepared by the electrochemical deposition at -0.1V on poly(cresolred_{ox})/GCE.

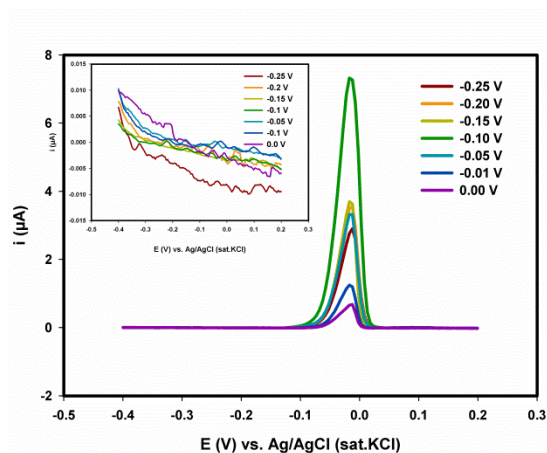


Figure 3.101 The effect of CuPc deposition potential on 0.01 mmol L^{-1} Antimony (III) in 0.1 M HCl , inset: absence of Antimony (III).

Table 3. 39 The effect of CuPc deposition potential on voltametric determination of Antimony (III)

CuPc deposition potential (V)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
-0.25	-	-	-0.12	2.20
-0.20	-	-	-0.12	3.27
-0.15	-	-	-0.12	3.71
-0.10	-	-	-0.12	7.33
-0.05	-	-	-0.12	3.33
-0.01	-	-	-0.12	1.26
0.00	-	-	-0.12	0.69

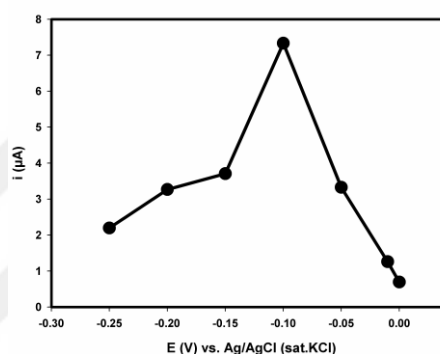


Figure 3. 102 The effect of CuPc deposition potential on Antimony (III) in 0.1 M HCl

For this reason; the CuPc deposition potential was choosed as -0.1V in for future studies. As the last study was electrochemical deposition time of CuPc from $10\mu\text{mol L}^{-1}$ CuPc containing 0.1 mol L^{-1} at 0.1V constant potential. The effect of CuPc deposition time on antimony oxidation peak current was studied in range of 3.0 -180 seconds. Then, Then the prepared electrode behaviour was investigated in the presence of 0.01 mmol L^{-1} Antimony (III) in 0.1 mol L^{-1} HCl medium (Figure 3.110, Figure 3.111 and Table 3.45).

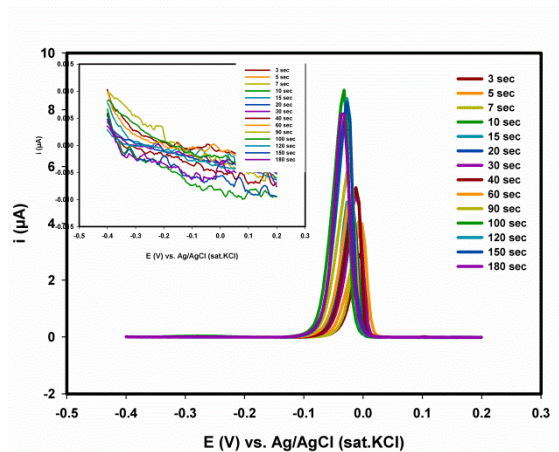


Figure 3. 103 The effect of CuPc deposition time on 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl, inset: absence of Antimony (III).

Table 3. 40 The effect of CuPc deposition time on voltametric determination of Antimony (III)

CuPc deposition time (sec.)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
3	-	-	-0.07	2.92
5	-	-	-0.02	4.00
7	-	-	-0.07	4.11
10	-	-	-0.02	4.57
15	-	-	-0.02	4.73
20	-	-	-0.02	4.76
30	-	-	-0.02	5.05
40	-	-	-0.02	5.26
60	-	-	-0.07	5.95
90	-	-	-0.02	6.09
100	-	-	-0.02	8.70
120	-	-	-0.02	8.41
150	-	-	-0.02	8.28
180	-	-	-0.02	7.87

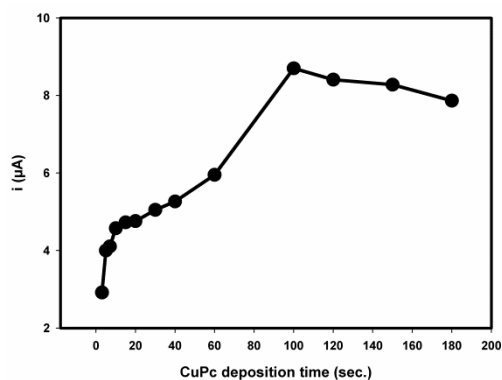


Figure 3. 104 The effect of CuPc deposition time on Antimony (III) in 0.1 M HCl

The best deposition time for CuPc on Poly(cresolred_{ox}) was obtained as 100 sec for antimony oxidation. For this reason, the optimum deposition time for CuPc was choosed as 100 s for future studies. As a result, in CuPc optimization studies, the CuPc concentration, deposition potential and time were found to be $10\mu\text{mol L}^{-1}$, -0.1 V , and 100 seconds respectively.

Optimization of amplitude, Antimony (III) deposition potential and time

In optimization studies, the amplitude effect on electrochemical oxidation of antimony in the presence of 0.01 mmol L^{-1} Antimony (III) in 0.1 M HCl solution at CuPc/Poly(cresolredox)/GCE was studied in range from 5 V 0 .to 75 V (Figure 3.112, Figure 3.113 and Table 3.46). The peak current was increased by increasing the amplitude potential until 55 V and then suddenly decreased to kept constant values in the following amplitude potentials, The highest peak current was obtained with 55 V amplitude potential, thus it was choosed as an optimum amplitude potential (Ulubay Karabiberoğlu and Dursun, 2017).

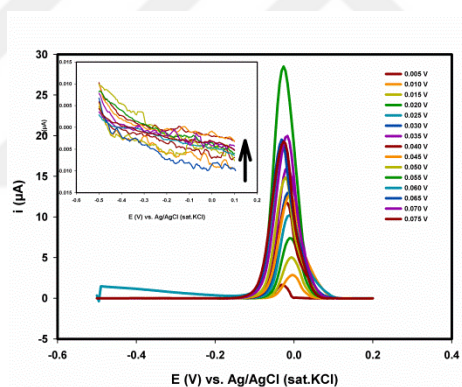


Figure 3. 105 The effect of amplitude on 0.01 mmol L^{-1} Antimony (III) in 0.1 M HCl , inset: absence of Antimony (III)

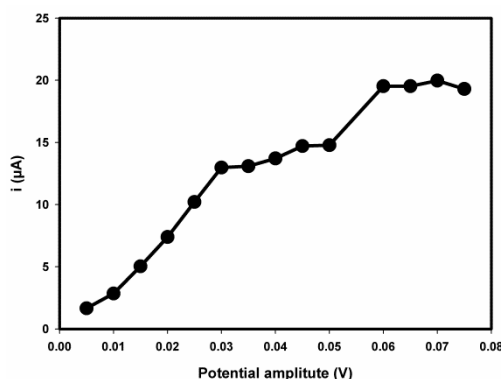


Figure 3. 106 The effect of amplitude on Antimony (III) ⁺ in 0.1 M HCl

To optimize the deposition potential of Antimony (III), the applied potential was changed from -0.65 V to -0.35 V (Figure 3.114 and 3.115; Table

3.46). The highest peak current was obtained by applying the -0.50 V constant deposition potential. It was used for future studies.

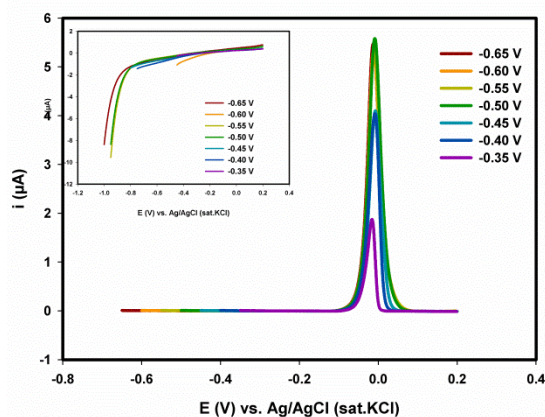


Figure 3. 107 The effect of deposition potential on 0.01 mmol L⁻¹ Antimony (III) ⁺ in 0.1 M HCl, inset: absence of Antimony (III).

Table 3. 41 The effect of deposition potential on voltametric determination of Antimony (III)

Antimony (III) deposition potential (V)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
-0.65	-	-	-0.11	5.10
-0.60	-	-	-0.11	5.34
-0.55	-	-	-0.11	5.36
-0.50	-	-	-0.07	5.52
-0.45	-	-	-0.07	4.10
-0.40	-	-	-0.07	4.02
-0.35	-	-	-0.07	1.86

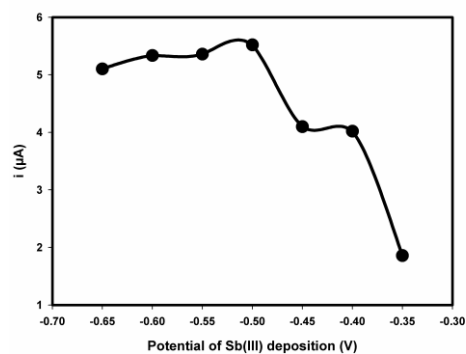


Figure 3. 108 The effect of deposition potential on Antimony (III) in 0.1 M HCl

The aftermost optimization study was performed for deposition time of 0.01 mmol L⁻¹ on CuPc/Poly(cresolred_{ox})/GCE between 3-300s (Figure 3.116 and

3.117; Table 3. 47). The peak current was almost constant after the 200s deposition time. The 300 s was chosen as the optimum deposition time.

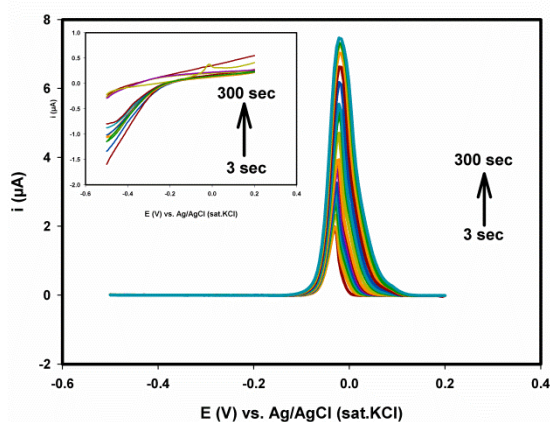


Figure 3. 109 The effect of deposition time on 0.01 mmol L⁻¹ Antimony (III) in 0.1 M HCl, inset: absence of Antimony (III)

Table 3. 42 The effect of deposition time on voltammetric determination of Antimony (III)

Antimony (III) deposition time (sec.)	Absence of Antimony (III)		Presence of Antimony (III)	
	Potential (V)	Current (μA)	Potential (V)	Current (μA)
3	-	-	-0.03	1.99
5	-	-	-0.03	1.93
7	-	-	-0.03	2.34
10	-	-	-0.03	2.65
15	-	-	-0.03	2.94
20	-	-	-0.03	3.26
25	-	-	-0.03	3.65
30	-	-	-0.03	3.89
40	-	-	-0.02	3.94
60	-	-	-0.02	4.71
90	-	-	-0.02	5.30
100	-	-	-0.02	5.55
120	-	-	-0.02	6.18
150	-	-	-0.02	6.63
180	-	-	-0.02	7.03
200	-	-	-0.02	7.24
250	-	-	-0.02	7.32
300	-	-	-0.02	7.47

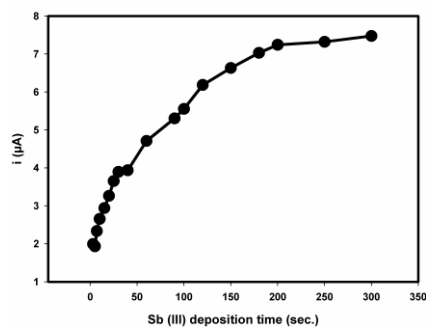


Figure 3.110 The effect of Antimony (III) deposition time on Antimony (III) in 0.1 M HCl

As a result, the optimum conditions the voltammetric determination of Antimony (III) were given in Table 3.49.

Table 3.43 The optimum conditions for voltammetric determination of Antimony (III)

Experimental parameter	Optimum conditions
Cresol red concentration	0.5 mmol L ⁻¹
Cycle number of cresolred electropolymerization	30 cycle
NaOH concentration	0.2 mol/L
Potential of over oxidation	0.7 V
Duration of over oxidation	100 sec
CuPc concentration	0.01 mmol L ⁻¹
Potential of CuPc deposition	-0.1 V
CuPc deposition time	100 sec
Potential amplitude	0.055 V
Potential of Antimony (III) deposition	-0.5 V
Antimony (III) deposition time	300 sec

3.2.3.2 Differential pulse anodic stripping voltammetric determination of antimony

The DPASV determination of Antimony (III) was performed with bare GCE, poly(cresolred)/GCE, poly(Cresolred_{ox})/GCE, CuPc/poly(Cresolred)/GCE, and CuPc/poly(Cresolred_{ox})/GCE under optimum operating conditions.

Figure 3.118 shows that differential pulse voltammograms of bare GCE in the absence and presence of increasing concentrations of Antimony (III).

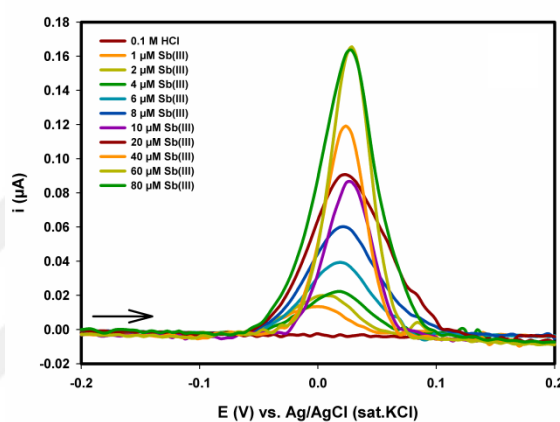


Figure 3. 111 DPASV voltammograms of various concentration of Antimony (III) at bare GCE in 0.1 mol L⁻¹ HCl.

The dynamic range of Antimony (III) on bare GCE is ranged from 1.0 $\mu\text{mol L}^{-1}$ to 80 $\mu\text{mol L}^{-1}$ (Figure 3.119-A). The expanded dynamic concentration range is the range in which there is a measurable response to the analyte but no increase in response at higher concentrations. Therefore, the linear range should be determined according to the regression coefficient (R^2). In case the linear range is extended to a subsequent upper concentration, the linearity limit is calculated by equation 1 given below (Nakiboğlu 2014);

$$\%s = \left| \left(\frac{y_i}{\hat{y}} - 1 \right) \right| \times 100 = \left| \left(\frac{y_i}{mx_i + b} - 1 \right) \right| \times 100 \quad (1)$$

In this equation, y_i is the measured value, $\hat{y}$ is the calculated value from the calibration equation. If $\%s \leq 5\%$, linearity is considered, but if $\%s \geq 5\%$, this concentration (y_i) is considered not included in the calibration linear.

Accordingly, when the %s calculation was performed for 1, 2 and 20 $\mu\text{mol L}^{-1}$ concentrations using the equation, the %s value were calculated as 8.4%, 2.5% and 0.1% respectively. Since the concentration of 1.0 $\mu\text{mol L}^{-1}$ Antimony (III) and %s is greater than 5.0, linearity is not achieved. For this reason, the linear range was accepted as 2.0 - 20 $\mu\text{mol L}^{-1}$ with equation $I_p = 0.0043C_{\text{Sb}} + 0.0059$ ($R^2 = 0.9950$) (Figure 3.119-B). The detection limit at bare GCE was calculated as $1.8 \times 10^{-7} \text{ mol L}^{-1}$ (3S/m) for Antimony (III). Relative standard deviation (RSD) was 4.52 % ($1 \times 10^{-6} \text{ mol L}^{-1}$, $n=5$) for bare GCE.

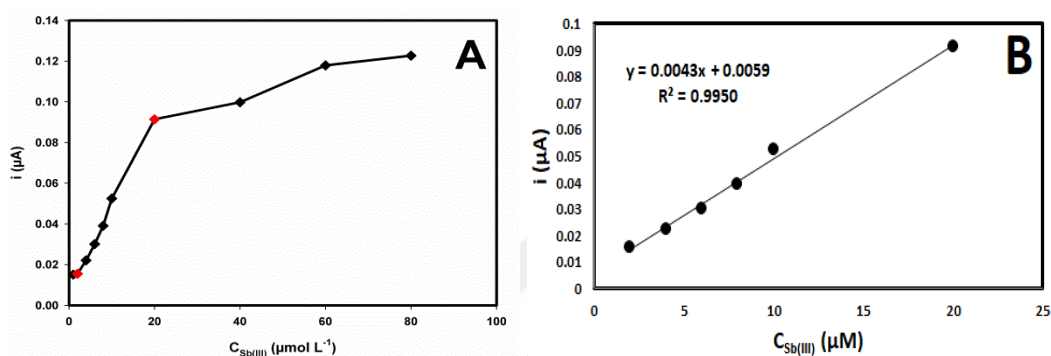


Figure 3. 112 A) The plot of peak current vs Antimony (III) concentration: 1, 2, 4, 6, 8, 10, 20, 40, 60 and 80 $\mu\text{mol L}^{-1}$ B) and linear calibration range with 2 – 20 $\mu\text{mol L}^{-1}$ Antimony (III) concentration in 0.1 mol L^{-1} HCl on bare GCE.

Figure 3.120 indicate DPASV response of Poly(cresolred)GC electrode in 0.1 mol L^{-1} HCl solution in the absence and presence of increasing concentrations Antimony (III).

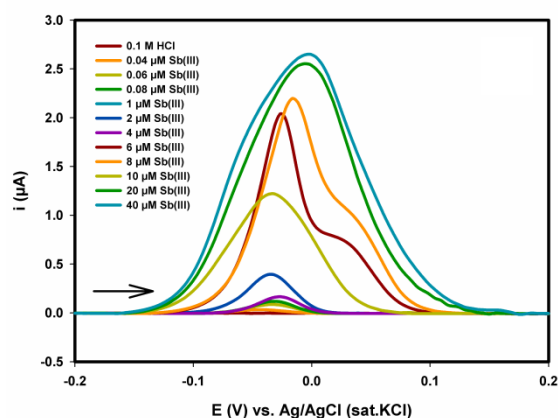


Figure 3. 113 DPASV voltammograms of various concentration of Antimony (III) at poly(cresolred)/GCE in 0.1 mol L^{-1} HCl.

Figure 3. 121-A shows the expanded dynamic range and Figure 3.121-B shows the linear range of Antimony (III) on Poly(cresolred)GCE. When the linearity of the calibration were calculated by the equation for 0.4, 0.6 and 10 $\mu\text{mol L}^{-1}$, the %s value were calculated as 8.10 %, 2.70 % and 0.96 %

respectively. Since the concentration of $0.4 \mu\text{mol L}^{-1}$ Antimony (III) and %s is greater than 5.0, the linear range was obtained in the concentration range of Antimony (III) between $0.6 - 10 \mu\text{mol L}^{-1}$ with the equation $I_p = 0.1814C_{\text{Sb}} - 0.0040$ ($R^2 = 0.9984$). The detection limit at Poly(cresolred)GC electrode was calculated as $1.41 \times 10^{-8} \text{ mol L}^{-1}$ (3S/m) for Antimony (III). Relative standard deviations (RSD) are 2.35 % ($6 \times 10^{-7} \text{ mol L}^{-1}$, $n=5$) for Poly(cresolred)GCE.

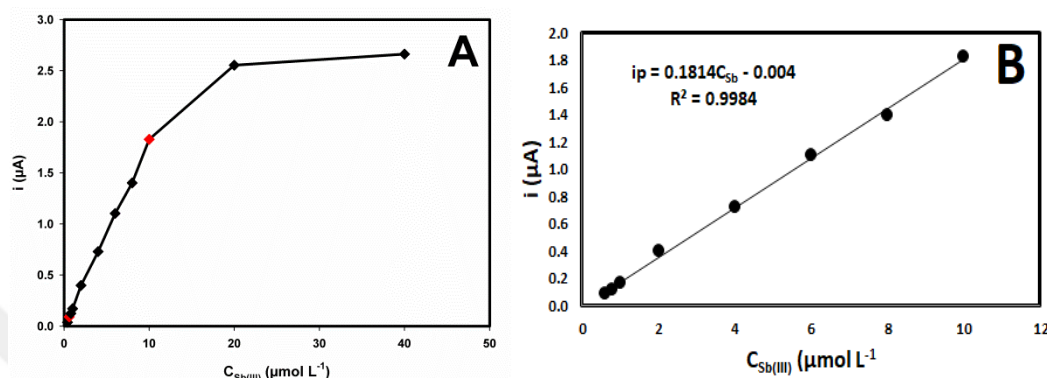


Figure 3.114 A) the plot of peak current vs Antimony (III) concentration: 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, 10, 20 and $40 \mu\text{mol L}^{-1}$ B) and linear calibration range with $0.6 - 10 \mu\text{mol L}^{-1}$ antimony (III) concentration in 0.1 mol L^{-1} HCl on poly(cresolred)/GCE.

Figure 3.122 represent the differential pulse anodic stripping voltammograms obtained on Poly(cresolred_{ox})GC electrode in 0.1 mol L^{-1} HCl solution in the absence and presence of increasing concentrations Antimony (III).

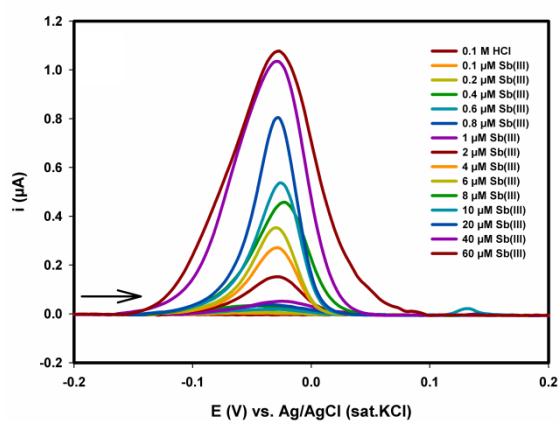


Figure 3.115 DPASV voltammograms of various concentration of Sb at Poly(cresolred_{ox})/GCE in 0.1 mol L^{-1} HCl.

Figure 3.123-A shows the expanded dynamic range and Figure 3.123-B shows the linear range of antimony (III) on Poly(cresolred_{ox})GCE. When the linearity of the calibration were calculated for 0.1, 0.2 and $10 \mu\text{mol L}^{-1}$, the %s value were calculated as 6.8 %, 3.8 % and 0.6 % respectively. Since the concentration of $0.1 \mu\text{mol L}^{-1}$ antimony (III) and %s is greater than 5.0, the linear

range was obtained in the concentration range of antimony (III) between 0.2 - 10 $\mu\text{mol L}^{-1}$ with the equation $I_p = 0.0492C_{\text{Sb}} + 0.0144$ ($R^2 = 0.9966$). The detection limit at Poly(cresolred_{ox})GC electrode was calculated as $2.94 \times 10^{-8} \text{ mol L}^{-1}$ (3S/m) for Antimony (III). Relative standard deviations (RSD) are 2.80 % ($2.8 \times 10^{-6} \text{ mol L}^{-1}$, $n=5$) for Poly(cresolred_{ox})GCE.

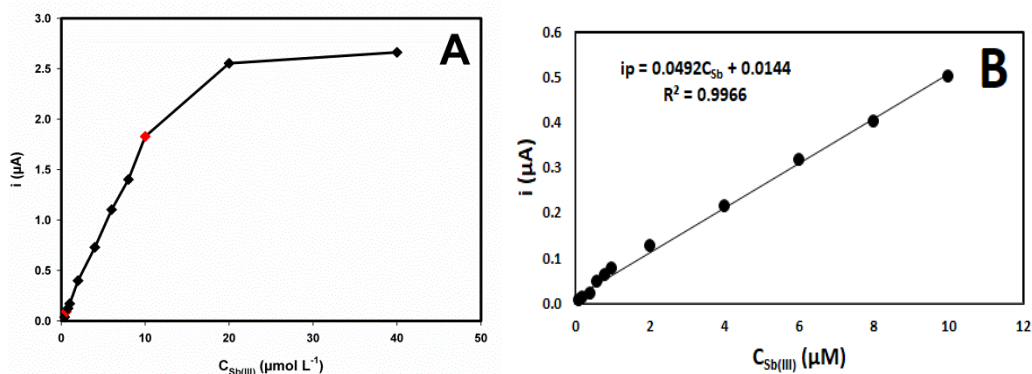


Figure 3. 116 A) The plot of peak current vs Antimony (III) concentration: 0.1, 0.2 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, 10, 20, 40 and 60 $\mu\text{mol L}^{-1}$ B) and linear calibration range with 0.2 – 10 $\mu\text{mol L}^{-1}$ Antimony (III) concentration in 0.1 mol L^{-1} HCl on Poly(cresolred_{ox}) GCE.

The DPASV Antimony (III) response with a CuPc/Poly(cresolred)GC electrode was dedicated in Figure 3.124.

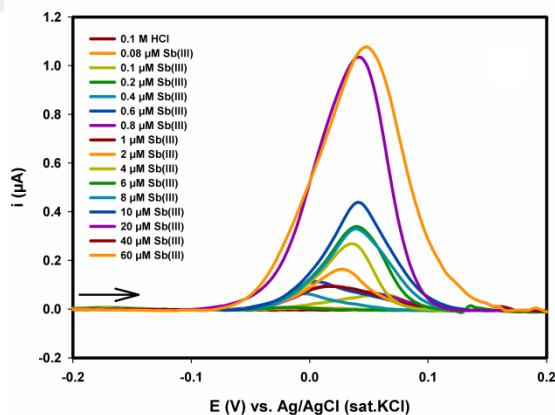


Figure 3. 117 DPASV voltammograms of various concentration of Sb at CuPc/Poly(cresolred_{ox})/GCE in 0.1 mol L^{-1} HCl.

Figure 3. 125-A shows the dynamic range and Figure 3.125-B shows the linear range of Antimony (III) on CuPc/Poly(cresolred)GCE. The first linear segment increases from 0.08 $\mu\text{mol L}^{-1}$ to 1 $\mu\text{mol L}^{-1}$. The %s values were calculated for 0.08 $\mu\text{mol L}^{-1}$ and 1 $\mu\text{mol L}^{-1}$ as 3.39 %, and 1.78 % respectively. The second linear segment increases from 2 $\mu\text{mol L}^{-1}$ to 20 $\mu\text{mol L}^{-1}$ and the %s values were calculated for 2 $\mu\text{mol L}^{-1}$ and 20 $\mu\text{mol L}^{-1}$ as 2.58 % and 1.14 %, respectively. Since the all %s were lower than 5.0 for all concentrations, the linear

ranges were obtained in the concentration range of Antimony (III) between 0.08 – 1.0 $\mu\text{mol L}^{-1}$ and with the equation $I_p = 0.1169C_{\text{Sb}} + 0.0465$ ($R^2 = 0.9925$) and for 2 $\mu\text{mol L}^{-1}$ to 20 $\mu\text{mol L}^{-1}$ concentration with the equation $I_p = 0.0511C_{\text{Sb}} + 0.0798$ ($R^2 = 0.9943$). The detection limit at CuPc/Poly(cresolred)GC electrode was calculated as $4.46 \times 10^{-8} \text{ mol L}^{-1}$ (3S/m) for Antimony (III). Relative standard deviations (RSD) are 3.40 % ($1 \times 10^{-7} \text{ mol L}^{-1}$, $n=5$) for Poly(cresolred)GCE.

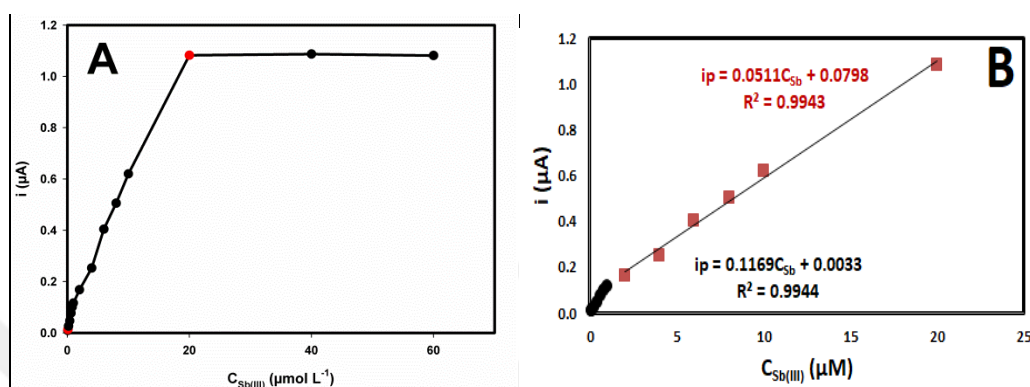


Figure 3.118 A) The plot of peak current vs Antimony (III) concentration: 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, 10, 20, 40 and 60 $\mu\text{mol L}^{-1}$ C) and linear calibration range with 0.08 – 1 $\mu\text{mol L}^{-1}$ and 2– 20 $\mu\text{mol L}^{-1}$ Antimony (III) concentration in 0.1 mol L^{-1} HCl on CuPc/Poly(cresolred_{ox}) GCE.

Figure 3.126 demonstrate DPASV response on CuPc/Poly(cresolred_{ox})GC electrode in the absence and presence of increasing concentrations of Antimony (III) in 0.1 M HCl solution.

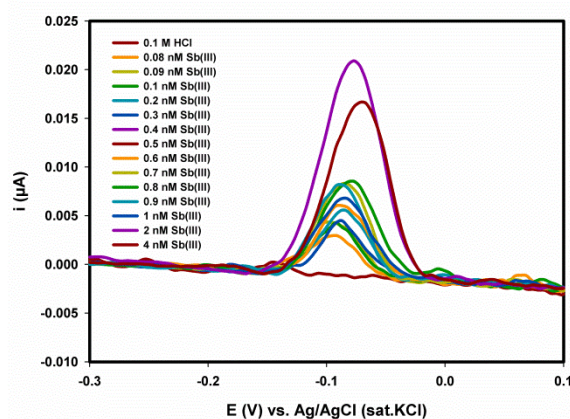


Figure 3.119 DPASV voltammograms of various concentration of Sb at CuPc/Poly(cresolred_{ox})/GCE in 0.1 mol L^{-1} HCl.

The expanded dynamic range of Antimony (III) on CuPc/Poly(cresolred_{ox})GCE was obtained in the concentration range from 0.08 nmol L^{-1} to 6.00 nmol L^{-1} (Figure 3.127-A). When the linearity of the calibration were calculated for 0.08 and 1 nmol L^{-1} , the %s value were calculated as 3.30 % and 2.60 % respectively. Since the concentration of 0.08 nmol L^{-1} and 6.00 nmol

L⁻¹ Antimony (III) %s is lower than 5.0, the linear range was obtained in the concentration range of Antimony (III) between 0.08 – 1 nmol L⁻¹ with the equation $i_p = 0.0527C_{Sb} + 0.0505$ ($R^2 = 0.9918$) (Figure 3.127-B). The detection limit at CuPc/Poly(cresolred_{ox})GC electrode was calculated as 1.18×10^{-11} mol L⁻¹ (3S/m) for antimony (III). Relative standard deviations (RSD) are 2.34% (9×10^{-11} mol L⁻¹, n=5) for CuPc/Poly(cresolred_{ox})GCE.

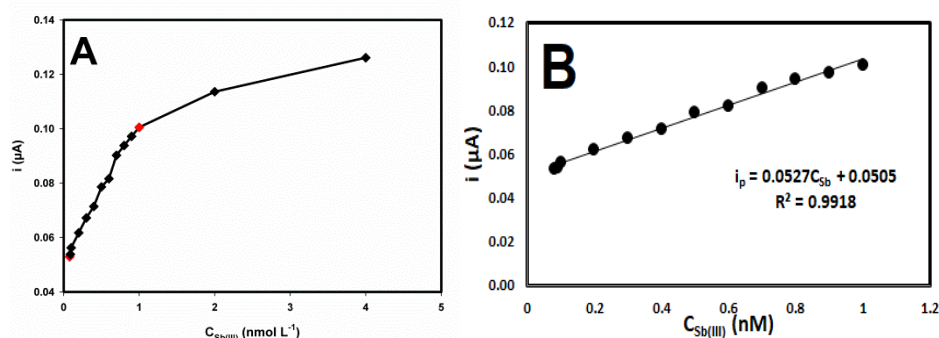


Figure 3.120 A) The plot of peak current vs antimony (III) concentration: 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 4 and 6 nmol L⁻¹ antimony (III) concentration in 0.1 mol L⁻¹ HCl on CuPc/Poly(cresolred_{ox}) GCE C) and linear calibration range with 0.08 – 1 nmol L⁻¹ antimony (III) concentration in 0.1 mol L⁻¹ HCl on CuPc/Poly(cresolred_{ox})/GCE.

Table 3.44 Analytical characteristics for determination of antimonu under optimum conditions

	Bare GCE	P(CrRed)/GCE	P(CrRed _{ox})/GCE
Calibration Equation^a	$i_p = 0.0043C_{Sb} + 0.0059$	$i_p = 0.1814C_{Sb} - 0.0040$	$i_p = 0.0492C_{Sb} + 0.0144$
Linear Range (mol L⁻¹)	$2 \times 10^{-6} - 2 \times 10^{-5}$	$6 \times 10^{-7} - 1 \times 10^{-5}$	$2 \times 10^{-7} - 1 \times 10^{-5}$
Dinamic Range (mol L⁻¹)	$1 \times 10^{-6} - 8 \times 10^{-5}$	$4 \times 10^{-7} - 4 \times 10^{-5}$	$1 \times 10^{-7} - 6 \times 10^{-5}$
Limit of detection (3S/m) (mol L⁻¹)	1.8×10^{-7}	1.41×10^{-8}	2.94×10^{-8}
R²	0.9950	0.9984	0.9966
%RDS (n=5)	4.52	2.35	2.80
	CuPc/P(CrRed)/GCE	CuPc/P(CrRed_{ox})/GCE	
Calibration Equation^a	$i_p = 0.1169C_{Sb} + 0.0465$	$i_p = 0.0527C_{Sb} + 0.0505$	
Lineer Range (mol L⁻¹)	$8 \times 10^{-8} - 1 \times 10^{-5}$	$8 \times 10^{-11} - 6 \times 10^{-5}$	
Dinamic Range (mol L⁻¹)	$8 \times 10^{-8} - 6 \times 10^{-5}$	$8 \times 10^{-11} - 6 \times 10^{-9}$	
Limit of detection (3S/m) (mol L⁻¹)	4.46×10^{-8}	1.18×10^{-11}	
R²	0.9925	0.9918	
%RDS (n=5)	3.40	2.34	

^a i_p is μA and concentration (C) is $\mu mol L^{-1}$

3.2.3.3 Interference Studies

One of the biggest challenges is performing measurements with high selectivity with modified electrodes developed to perform sensitive analysis. Before the determination of antimony from real samples, the interference effect

with some cations that may interfere was investigated. The molar effect of the investigated cations on the 1×10^{-10} mol L⁻¹ antimony response is given in Table 3.51.

Table 3. 45 Relative (%) change of the signal of Antimony (1×10^{-10} mol L⁻¹) in the presence of various interfering substances, n=3.

Interfering species	Molar ratio ((Interfering species)/(Antimony (III)))	Change on the analytical signal of Antimony (III) (%)
Cl ⁻	1	-0.23
	10	0.47
	100	1.86
	1000	3.49
SO ₄ ²⁻	1	0.47
	10	0.71
	100	4.03
	1000	6.40
NO ₃ ⁻	1	1.37
	10	0.68
	100	-0.91
	1000	-2.97
Na ⁺	1	1.32
	10	1.75
	100	3.07
	1000	3.51
K ⁺	1	1.37
	10	0.68
	100	-0.91
	1000	-2.97
Pb ²⁺	1	-0.97
	10	-1.70
	100	6.08
	1000	9.00
Ni ²⁺	1	2.00
	10	0.89
	100	0.22
	1000	-0.22
Cu ²⁺	1	-2.63
	10	-14.80
	100	-20.05
	1000	-27.68
As ³⁺	1	4.37
	10	-5.90
	100	-11.35
	1000	-15.50

The results showed that the Antimony (III) response showed the highest increase in the presence of Pb^{2+} , Cu^{2+} and As^{3+} , while the current values decreased due to negative effects in other cations.

3.2.3.4 Reproducibility, Repeatability of CuPc/Poly(Cresolred_{ox})/GCE

In addition to sensitivity; reproducibility, repeatability and stability are important parameters for applying modified electrodes to real samples. Five different electrodes that were fabricated independently under the same experimental conditions were used for examine reproducible preparation of CuPc/Poly(Cresolred_{ox})/GCE. The relative standard deviation (RSD) was calculated as % 3.55 for Antimony (III) peak current. The repeatability of CuPc/Poly(Cresolred_{ox})/GCE was studied by measuring the peak current of the 9×10^{-11} mol L⁻¹ Antimony (III) for DPASV in 0.1 mol L⁻¹ HCl solution for successive five measurements. The RSD was 1.07 % for Antimony (III)

Shelf life investigation of CuPc/Poly(Cresolred_{ox})/GCE modified electrode was studied. The prepared electrode measured 3×10^{-10} mol L⁻¹ Antimony (III) in 0.1 mol L⁻¹ HCl solution for five days. At the end of the third day, the measurement flow values continued at 92.4% of the initial value. At the end of 5 days, it was observed that this value decreased to 70.5%. As a result, the CuPc/Poly(Cresolred_{ox})/GCE-modified electrode has a shelf life of 3 days without significant variation in current values.

3.2.3.5 Electroanalysis of antimony in PET bottles

The applicability of CuPc/Poly(Cresolred_{ox})/GC electrode was studied to determine Antimony (III) in different brand PET bottle samples. PET bottle samples were prepared as detailed in the section above, and sample analysis was carried out using the standard addition method. Studies were carried out in 0.1 mol L⁻¹ HCl medium. 5 mL of sample solution was added to 5 mL of 0.1 mol L⁻¹ HCl solution, and Antimony (III) was added to the medium by the standard addition method. The voltammograms obtained for each PET bottle samples are given in Figure 3.128A, B and C.

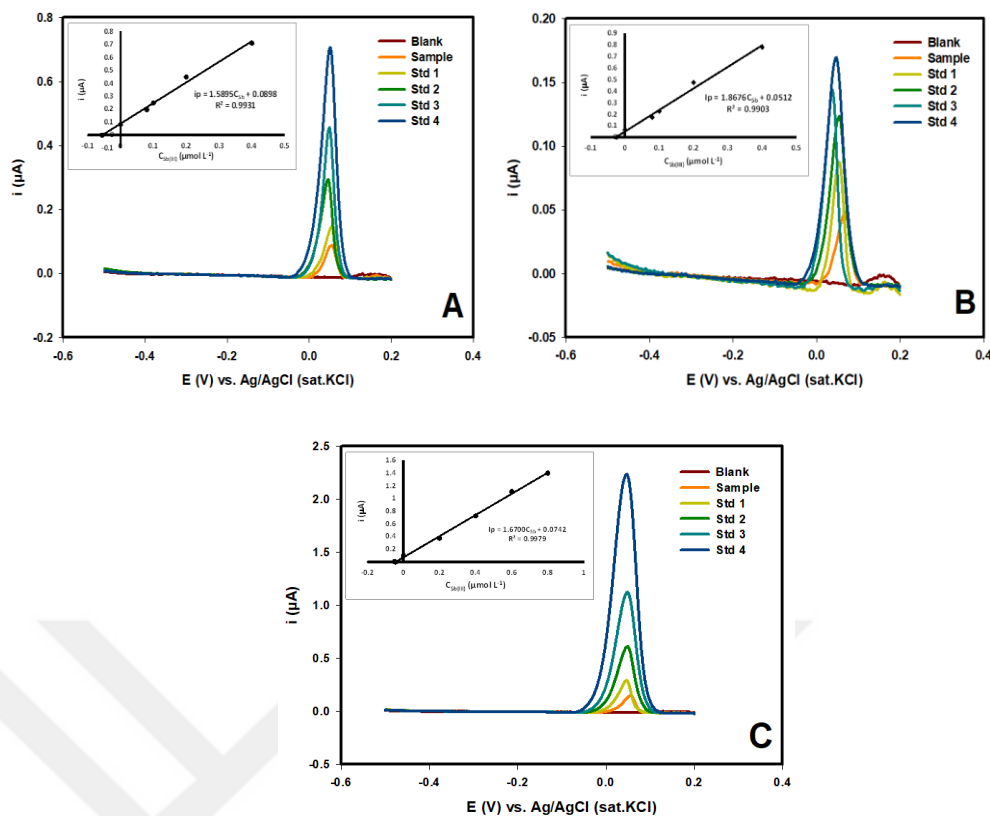


Figure 3. 121 Application of the standard addition method for antimony determination in PET bottle samples by DPASV at CuPc/Poly(Cresolred_{ox})/GCE, inset: Calibration curve of sample analysis.

The peak current increased with addition of antimony standard solutions into PET bottle samples. For PET Bottle Sample A the equation: $i_p = 1.5895C_{sb} + 0.0898$, $R^2=0.9931$, $n=3$, which by extrapolation indicated that the concentration of antimony in the PET Bottle Sample-A was 2.82 mg/kg PET bottle. For PET Bottle Sample B the equation: $i_p = 1.8676C_{sb} + 0.0512$, $R^2=0.9903$, $n=3$, which by extrapolation indicated that the concentration of antimony in the PET Bottle Sample-B was 1.20 mg/kg PET bottle. And then, for PET Bottle Sample C the equation: $i_p = 1.6700C_{\text{Antimony (III)}} + 0.0742$, $R^2=0.9979$, $n=3$, which by extrapolation indicated that the concentration of antimony in the PET Bottle Sample-C was 2.22 mg/kg PET bottle. The DPASV measurement results of PET bottle samples were compared to ICP-MS results, and the Antimony (III) amounts were relatively close. All equations, R^2 and concentration of antimony in the PET Bottle were given Table 3.52.

Table 3. 46 Equation, R^2 and concentration of Antimony (III) for each PET bottle samples

PET Bottle	Calibration Equation	R^2	Concentration of antimony (mg/kg)	ICP-MS results (mg/kg)
A	$ip = 1.5895C_{Sb} + 0.0898$	0.9931	2.82 ± 0.03	2.83 ± 0.03
B	$ip = 1.8676C_{Sb} + 0.0512$	0.9903	1.20 ± 0.02	1.16 ± 0.03
C	$Ip = 1.6700C_{Sb} + 0.0742$	0.9979	2.22 ± 0.03	2.34 ± 0.03

The recovery results for standard solid solutions of each PET bottle sample are summarized in Table 3.53 (n=3). Recovery values were in the range of 93%-109%. These recovery results show that there is no interference with the PET bottle samples under optimum experimental conditions.

Table 3. 47 Recovery results for each PET bottle samples

Samples	Antimony (III) added ($\mu\text{mol L}^{-1}$)	Antimony (III) expected ($\mu\text{mol L}^{-1}$)	Antimony (III) found ($\mu\text{mol L}^{-1}$)	Recovery (%)
A	0.00	-	-	-
	0.16	0.25	0.15	98
	0.26	0.45	0.28	108
	0.46	0.71	0.44	97
B	0.00	-	-	-
	0.16	0.23	0.12	93
	0.26	0.46	0.25	109
	0.46	0.78	0.42	98
C	0.00	-	-	-
	0.16	0.23	0.13	98
	0.26	0.50	0.26	103
	0.46	0.78	0.48	99

For plastics that come into contact with or will come into contact with food, European regulations set specific requirements for materials such as monomers, additives, and polymer production aids that can be used in these materials. Migration limits, called SML, have been determined for permissible substances after transport tests on plastic materials (Carneado et al., 2015). The SML value for Sb_2O_3 as an antimony source is specified as $40 \mu\text{g kg}^{-1}$ total Sb in PET and packaged food materials. (European Commission 2011). It was observed that the analysis results with real PET bottle samples matched the literature data and the results were below the SML limits.

4. CONCLUSIONS

4.1 Electrochemical and Photoelectrochemical Reduction of CO₂

Due to increasing fossil fuel consumption, natural processes, and industrial applications, the concentration of carbon dioxide in the atmosphere has grown rapidly in the last ten years. The increase in the CO₂ concentration in the atmosphere has had global reflections, such as the acidification of the oceans and seas and the increase in global surface temperatures. According to the statement made by the Intergovernmental Panel on Climate Change (IPCC) in 2019, it has been stated that reducing CO₂ emissions to zero level by 2050 to reduce global warming below 1.5°C, otherwise; otherwise be an unavoidable consequence of the global climate crisis (Buckingham et al., 2022). Therefore, it is clear that there is a need for measures to reduce CO₂ emissions and reduce the current CO₂ concentration

In the first part of this thesis, first of all, a new generation modified electrode preparation was studied to provide catalytic efficiency in the electrochemical reduction of CO₂ with different conductive polymers and various metal nanoparticles. For this purpose, poly(aniline) and poly(4-aminophenol) polymer films were used as catalysts on the glassy carbon electrode (GCE) surface in the reduction of Cu and Au metal nanoparticle CO₂. The modified GC electrodes were used directly for the electrochemical reduction of CO₂. To examine the performance of the developed modified electrode, the cyclic voltammetry technique and the bare and modified electrode behaviors were compared. The parameters in the prepared modified electrode, the supporting electrolyte (NaClO₄ + Methanol) concentration, the saturation time of CO₂, and the concentration and coating numbers of polymer and metal nanoparticles were investigated.

It was found that the Cu/Au/PPAP/GCE surface provided the best catalytic effect for the electrochemical reduction of carbon dioxide. It was observed that the solution concentration of the supporting electrode was supplied with 0.8 mol L⁻¹ NaClO₄ + 2 mol L⁻¹ Methanol. It was observed that the highest catalytic effect was obtained when Cu and Au metal nanoparticles were coated on the PPAP film GC electrode surface at a concentration of 0.1 mmol L⁻¹ for 10 cycles. It was

found that the measurements made after the CO_2 was saturated with the supporting electrolyte solution for 30 minutes provided the highest current values.

In the first part of the thesis, the photochemical reduction of CO_2 was also investigated. For this purpose, mesoporous carbon material (MCM) synthesis was carried out using resorcinol, catechol, and 4-aminophenol initiators. Synthesized MCM was combined with tetrabutyl titanate by sol-gel method to form a composite material with TiO_2 .

TiO_2 is an excellent photocatalyst, has long-term stability, offers low-cost preparation, and has an oxidizing power strong enough to be helpful for the decomposition of unwanted organic compounds.

TiO_2 is an excellent photocatalyst semiconductor with long-term stability and low cost, and it can assist in the decomposition of many organic compounds. In addition, the photocatalysis efficiency of TiO_2 is dependent only on UV radiation, which covers 5% of the visible region spectrum due to its expansive band gap energy (about 3.2 eV). For this reason, many studies have been carried out to expand the absorbance region of TiO_2 (Xu et al., 2014). One of these studies is the use of supporter catalysts.

In supporter catalysts, the catalytically active particle or material is dispersed on the nano- or mesoporous carbon, which can increase the exposed surface area. For this purpose, the most commonly used supporting catalyst carbon materials are carbon nanotubes (CNTs), nanofibers (CNFs), and regular or mesoporous carbon (OMC or MCM). In particular, in recent years, mesoporous carbon structures have been preferred in studies such as fuel cells and supercapacitors due to the coexistence of different grain sizes and therefore offering a larger surface area (Zhang et al., 2016).

The investigations were made on the feeding time of CO_2 to the environment and the duration of the UV light environment, which is the main feature of photochemical reactions, in the amount of MCM- TiO_2 used in the support electrolyte solution used. The examination results found that the highest catalytic effect on the photoelectrochemical reduction of CO_2 was a 10 μL drop from the MCM- TiO_2 suspension onto the GC electrode surface, 0.5 mol L^{-1} KHCO_3 saturated with CO_2 for 30 min. It was observed that it was obtained after 10 minutes of light was dropped on the electrode surface.

According to the results of SEM, XPS, and TEM detailed surface characterization investigations showed that mesoporous carbon material was successfully synthesized, MCM material and TiO_2 were successfully prepared by the sol-gel method, and the composite material was formed. As expected, no current changes were observed in the conditions saturated with N_2 and CO_2 , as scheduled in the electrochemical reduction studies in the UV light environment with the GCE electrode prepared with MCM- TiO_2 composite material.

In the examinations performed under UV light, it was observed that there were current changes in the conditions saturated with N_2 without CO_2 . It can be said that the TiO_2 on the TiO_2 -MCM composite GC electrode surface causes these changes. In the photochemical reduction study carried out under UV light after the support medium was saturated with CO_2 , it was observed that the current values increased due to the photochemical reduction of CO_2 on the TiO_2 material surface. As a result, it can be said that the photoelectrochemical reduction of CO_2 in the presence of TiO_2 , which also shows photocatalytic activity, is successfully carried out due to the increase in the current values obtained.

According to the results of the first part of the thesis, the electrochemical reduction of CO_2 can be performed using Cu and Au metal nanoparticles and a poly(4-aminophenol) film GC electrode. In addition, photochemical reduction of CO_2 can be achieved by preparing the MCM- TiO_2 modified GC electrode.

4.2 Analytical Application

One of the most important advantages of electrochemical studies is the development of chemically modified electrodes that provide selective and sensitive measurements for the analytes to be determined. Thus, sensitive and selective determination of the desired analyte can be made even in samples with complex matrix structures. Although different spectroscopic techniques are generally used for the sensitive and selective determination of different analytes, in recent years electrochemical techniques have been preferred because they are simple and portable measurement systems, allowing direct analysis at the sample source, repeatability, relative ease in sample preparation, fast in field applications and low analysis costs.

PET is a thermoplastic polymer used in plastic food and beverage packaging. It was recorded that approximately 583 billion PET bottles were produced worldwide in 2021. PET bottles are preferred because they are light, transparent, unbreakable and CO₂ impermeable (Filella 2020).

It has been reported in previous years that it contains antimony in the structure of polyethylene terephthalate (PET) and that it passes by diffusion under water contact conditions. (Ashby, 1988; Fordham et al., 1995; Thompson et al., 1997). In another study, Shotyk et al. stated that there is a significant amount of antimony in bottled water and the source of antimony is antimony trioxide (Sb₂O₃), which is used as a catalyst in the production of PET bottles. (Shotyk et al., 2006). While the antimony content of drinking water is at most 5.0 µg L⁻¹ according to European Union Standards, the World Health Organization is determined this limit as 20 µg L⁻¹ in 2011. (He et al., 2012). Keeping the World Health Organization limit value high can be attributed to the difficulty and cost of both antimony removal and antimony sensitization (Filella et al., 2002b). Since PET bottles are food contact materials such as drinking water, fruit juices and carbonated beverages, European Union (EU) restrictions have been introduced due to the possibility of antimony transfer from PET bottles to beverages by transport.

The development of modified electrodes has been investigated to selectively and sensitively detect antimony in real PET bottle samples. For this purpose, a Poly(cresolred) film GC electrode was prepared by electrochemical polymerization of cresol red monomer. Poly(Cresolred_{ox}) film GCE was prepared by over-oxidation with NaOH solution due to the high sensitivity and selectivity effect achieved by our team in the prepared modified electrode in previous studies (Ulubay Karabiberoğlu and Dursun, 2017). In addition to these electrodes, CuPc was deposited on the polymer film electrode surface. The electrochemical behavior of antimony was investigated with the prepared four modified electrodes. Electrochemical analyzes were carried out with the differential pulse anodic stripping voltammetry (DPASV) technique since it provides high selectivity and sensitivity detection in the determination of trace amounts of

analytes. In the electrochemical examinations, measurements were taken with each modified electrode.

When the optimum conditions for the determination of antimony on the prepared electrodes are examined, it is seen that the highest catalytic activities are observed when 0.5 mmol L^{-1} monomer concentration is coated as 30 cycles, when over-oxidation is done with 0.2 mol L^{-1} concentration NaOH for 100 seconds at 0.7 V potential, 0.01 mmol L^{-1} concentration is observed. It was found that CuPc was deposited on the polymer modified GC electrode at a potential of -0.1 V for 100 seconds.

Electrochemical behavior of antimony was investigated with Poly(cresolred)/GCE, Poly(cresolred_{ox})/GCE, CuPc/Poly(cresolred)/GCE and CuPc/Poly(cresolred_{ox})/GC modified electrodes prepared under optimum conditions. The current values for the bare GC electrode are linear in the concentration range of $1 \times 10^{-6} - 2 \times 10^{-5} \text{ mol L}^{-1}$ and the lower limit of detection was found to be $1.8 \times 10^{-7} \text{ mol L}^{-1}$ (3S/m). The current values for the Poly(cresolred)/GC electrode are linear in the concentration range of $4 \times 10^{-7} - 1 \times 10^{-5} \text{ mol L}^{-1}$ and the lower limit of detection was found to be $1.41 \times 10^{-8} \text{ mol L}^{-1}$ (3S/m). The current values for the Poly(cresolred_{ox})/GC electrode were linear between $1 \times 10^{-7} - 1 \times 10^{-5} \text{ mol L}^{-1}$ concentrations, and the limit of detection was obtained as $2.94 \times 10^{-8} \text{ mol L}^{-1}$ at even lower concentration as the expected effect of over-oxidation of the polymer. (3S/m). In the examination made with CuPc/Poly(cresolred)/GC electrode, the concentration range in which the current values are linear is $8 \times 10^{-8} - 2 \times 10^{-5} \text{ mol L}^{-1}$, and the limit of detection is $4.46 \times 10^{-8} \text{ mol L}^{-1}$ thanks to the catalytic efficiency provided by CuPc found (3S/m). In the examination performed with CuPc/Poly(cresolred_{ox})/GC electrode, the antimony concentration range with linear current values was found to be $8 \times 10^{-11} - 1 \times 10^{-5} \text{ mol L}^{-1}$. The limit of detection was calculated as $1.18 \times 10^{-11} \text{ mol L}^{-1}$ (3S/m). Therefore, antimony determination was made with CuPc/poly(cresolred_{ox})/GC electrode in real PET bottle samples.

As real PET bottle samples, four different brand PET bottle samples were prepared and antimony was determined by standard addition method with CuPc/Poly(cresolred_{ox})/GC electrode. According to the results of the examination,

0.003, 0.001, 0.001 and 0.002 μg Antimony (III)/g PET bottle amount of antimony was determined for four different samples, respectively. It was found that the obtained amounts were below the PET amount of 40 $\mu\text{g kg}^{-1}$ total Sb, which is the limit of transport and water penetration stated in the literature.

According to the analytical study results, sensitive and sensitive antimony determination can be performed in real PET bottle samples by using a CuPc-modified Poly(Cresolred_{ox})GC electrode.

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ÖZGEÇMİŞ

<i>Kişisel Bilgiler</i>	
Öğrenci Adı	Şebnem Gül İLARSLAN
TC Kimlik No	
Tel No	
e-mail	
<i>Eğitim Bilgileri</i>	
Lisans	Ege Üniversitesi Kimya Bölümü, 2006-2010
Yüksek Lisans	Fen Bilimleri Enstitüsü Analitik Kimya Bölümü, 2010-2012
YL Tez Adı	Selective separation of lithium and boron from geothermal water using ion-exchange-membrane filtration hybrid methods
<i>Doktora Tezine Bağlı Yayın ve Bildiriler</i>	
<i>Uluslararası Kongre Sunumları</i>	
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