

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**NANOHYBRID PHOTOCATALYTIC FILTER PRODUCTION VIA
ELECTROPHORETIC DEPOSITION**



M.Sc. THESIS

Onur AGMA

Department of Nano-Science and Nano-Engineering

Nano-Science and Nano-Engineering Programme

Thesis Advisor: Assist. Prof. Dr. Ali KILIC

AUGUST, 2016

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**ELEKTROFORETİK DEPOZİSYON YÖNTEMİYLE NANO HİBRİT
FOTOKATALİTİK FİLTRE ÜRETİMİ**

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To my family,



FOREWORD

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ABBREVIATIONS

AC	: Activated Carbon
Ag ,Ag(NO₃)	: Silver, Silver nitrate
ANOM	: Analysis of Means
ANOVA	: Analysis of Variance
BET	: Brunauer-Emmett-Teller
BRI	: Building Related Illness
CB	: Conduction Band
CHCl₃	: Chloroform
CNTs	: Carbon Nanotubes
CO-CO₂	: Carbon oxide, Carbon dioxide
DC	: Direct Current
DMF	: Dimethylformamide
EPD	: Electrophoretic Deposition
HEPA	: High Efficiency Particulate Arresting
IAQ	: Indoor Air Quality
LED	: Light Emitting Diode
MCS	: Multiple Chemical Sensitivity
MFC	: Mass Flow Controller
MS	: Mass Spectrometry
NaBH₄	: Sodium borohydride
NFs	: Nanofibers
NO_x	: Nitrogen oxides
NPs	: Nano Particles
NTP	: Non-thermal plasma
OP	: Orthophthalic polyester
PCO	: Photocatalytic Oxidation
PCB	: Printed Circuit Board
PDMS	: Polydimethylsiloxane
PERC	: Tetrachloroethylene
PP	: Polypropylene
SEM	: Scanning Electron Microscopy
SBS	: Sick Building Syndrome
SiC	: Silicon carbide
TCE	: Trichloroethylene
TiO₂	: Titanium dioxide
TPU	: Thermoplastic polyurethane
TTIP	: Titanium tetraisopropoxide
UV	: Ultraviolet
Uv-Vis	: Ultraviolet-visible Spectroscopy
VB	: Valance Band
VOCs	: Volatile Organic Compounds
WHO	: World Health Organization
XRD	: X-ray Diffraction



SYMBOLS

C	: Concentration of contaminant at time t
C₀	: Initial concentration
e⁻	: Electron
E	: Applied voltage
eV	: Electron volt
g/l	: Gram per liter
h⁺	: Hole
l/min	: Liter per min
mW/cm²	: Milliwatt per centimeter square
OH⁻	: Hydroxyl radical
pH	: Power of Hydrogen
ppm	: Parts per million
sec	: Second
t	: Time
η	: Efficiency
λ	: Wavelength



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NANOHYBRID PHOTOCATALYTIC FILTER PRODUCTION VIA ELECTROPHORETIC DEPOSITION

SUMMARY

Air pollution is one of the most serious problems that threatens human life on the globe. Hundreds of cities suffer from the pollution with exceeded air pollution threshold values. Hence, the pollution is counted to be one of the major reasons behind lung cancer, asthma, cardiovascular diseases and etc. Not only outdoor air pollution but also the condition in indoor environments is critical since indoor air quality additionally affects quality of human's life and comfort. Time in daily lives, which is spent in indoor environment such as houses, offices, shopping malls and vehicles increases day by day.

Particulate matter, dusts, viruses, bacteria, carbon oxides, nitrogen oxides and volatile organic compounds are among the contaminants in the indoor environment. Volatile organic compounds (VOCs) such as ethanol, toluene, benzene are major effective chemical contaminants that people breathe. They are emitted from different sources, established buildings, new and renovated buildings, school, new car interiors, carpets, floor coverings, wood-based panel and furniture, solid woods, paints, cleaning products, unflued gas heaters and electric ovens, office equipments. VOCs causes health problems in a short period such as headache, fatigue, tiredness and nausea. In a long period the effect might be more serious than these problems.

There are several traditional methods to remove VOCs in indoor air, however these methods are based on adsorption process from gaseous phase to solid phase. This requires frequent cleaning or periodical exchange of the filter, otherwise the adsorbed filters are going to get heavy and require replacement frequently.

Photocatalytic oxidation (PCO) is comparatively a novel and promising method for the improvement of indoor air quality since the contaminants can be removed from the indoor and oxidize the water vapour and carbon dioxide (CO₂) which are not harmful for human health by using a combination of semiconductor catalysts and light energy.

In this study widely used titanium dioxide (TiO₂) was selected to produce photocatalytic air filters. Electrophoretic deposition was preferred to immobilize TiO₂ nanoparticles over polymeric and metallic substrates. TiO₂ as a wideband gap semiconductor was also modified to enhance its PC activity. It is still challenge to produce visible light activated catalysts. For that various configurations, such as silver doped TiO₂, silver decorated TiO₂ and silver coated TiO₂ nanoparticles were produced. Obtained particles were immobilized over metallic meshes via electrophoretic deposition. Finally their performance was evaluated in a custom made UV-LED based PCO reactor.

High efficiency particulate arresting (HEPA) type filters are already included in recent indoors but these filters only remove particulates and particles. Consequently,

PCO reactors must be developed and mounted in indoor gaseous pollutants. In this thesis, photocatalytic oxidation is capable at NF and metallic meshes based filters was designed and fabricated. As a fast and facile method electrophoretic deposition was used to coat TiO_2 on these substrates and their optimization, in the filter usage area use with LED for UV light and highly efficient air filtration system with use the PCO process.



ELEKTROFORETİK DEPOZİSYON YÖNTEMİYLE NANO HİBRİT FOTOKATALİTİK FİLTRE ÜRETİMİ

ÖZET

Günümüzde artan endüstrileşme, yüksek nüfus artışı ve kentselleşme ile birlikte insanlığı tehdit eden bir çok sorun ortaya çıkmıştır. Başta gelen sorunlardan biri de, insan yaşamının temeli olan su ve hava gibi doğal kaynakların kirlenmesidir. Özellikle iç ortam hava kalitesi, yani insanların çok büyük zamanlarını geçirdikleri ev, ofis, ulaşım araçları gibi kapalı ortamlar dış ortamdaki havaya göre daha düşük bir kaliteye sahiptir. İç ortam hava kalitesinin insanların sağlığını, çalışma verimliliğini ve yaşam konforunu doğrudan etkilediği raporlanmıştır.

İç ortamlardaki havanın, dış ortamdaki havadan daha az sirküle ve daha hareketsiz bir yapıya sahip olması ve tozlar, bakteriler, virüsler, karbon oksitler, nitrojen oksitler ve uçucu organik bileşikler gibi bir çok kirleticisi bulundurduğundan, dış ortam hava kalitesinden daha düşük olmasına neden olmaktadır. Bu kirleticilerden bazılarının insan sağlığı üstünde ciddi bir etkisi olmazken, bazıları ise ölümcül etkilere sahip kanserojen yapılara sahip olabilmektedir. Kısmen daha az etkisi olduğunu söyleyebileceğimiz uçucu organik bileşikler ise insanların özellikle iç ortamlarda soludukları kimyasal organik kirleticilerdir. Bu bilgiler ışığında, hava vasıtasıyla bulaşan hastalıkların önlenmesi, yukarıda bahsedilen zararlı etkileri azaltmak veya yoketmek için filtrasyon teknolojilerinde ciddi çalışmalar yapılmaktadır.

Kirleticiler arasında en yoğun olarak rastlanan uçucu organik bileşikler, özellikle yeni binalarda, okullarda, yeni araçlarda, halılarda, zemin kaplamalarında, odun temelli eşyalarda, boyalarda, gazlı ısıtıcılar veya fırınlarda, ofis ekipmanlarında yoğun olarak bulunmaktadır. İç ortamda yüksek konsantrasyona ulaşan uçucu organik bileşiklere uzun süre boyunca maruz kalınması sonucunda, insanlarda halsizlik, baş ağrısı, yorgunluk ve bulantı gibi birçok sağlık problemlerinin görülmesi söz konusu olabilir. Bu olumsuz etkilerinden ötürü, uçucu organik bileşiklerin uzaklaştırılması çok önemli bir çalışma konusu haline gelmiştir.

Bu kapsamda bir çok akademik çalışma yapılmakta olup çalışmalar kapsamında geliştirilen filtrelerin çok büyük bir yoğunluğu, gaz fazındaki uçucu organik bileşikleri absorpsiyon ve adsorpsiyon yöntemiyle, katı bir faza hapseden mekanizmalar geliştirilmiştir ve ticari olarak kullanılmaktadır. Örneğin, bunların en bilinenlerinden biri olan aktif karbonun, gazı yüzeyde tutarak çalışmasından ötürü çok sık yenilenmesi ve gaz depolanması sonucu ağırlaşan filtrelerin, kullanıldığı yerde, özellikle taşıtlarda, istenilen özelliği elde etmek için başka ek maliyetlere ve iş gücüne yol açmasına sebep olmaktadır.

Uçucu organik bileşikleri, katalizör ve kullanılan katalizöre göre seçilen ışık yardımıyla kısmen zararsız olan karbon dioksit ve su buharına dönüştüren fotokatalitik oksidasyon yöntemi, iç ortamdaki uçucu organik bileşiklerin temizlenmesi için etkili ve ümit vaat eden yöntemlerden biri olarak gözükmektedir.

UV ışığı altında aktifleşen titanyum dioksit (TiO_2); insan üzerinde bilinen bir kanserojen ve yan etkisinin olmaması, hem ekonomik ve uygulamada kullanılan en yaygın ve fotokatalitik tepkimlerdeki en verimli katalizör olarak bilinmesi, bu katalizörle çalışma yapmaya uygunluğunu göstermektedir.

Filtrasyon teknolojilerinde özellikle membranların üretiminde olduğu gibi fotokatalitik oksidasyon yönteminin kullanıldığı sistemlerde de ışık altında kalan alanı tanımlayan aktif yüzey alanı büyüklüğü verimliliği etkileyen çok önemli bir parametredir. Verimli bir filtre yapmanın, en kolay ve en efektif yolu ise kullanılan TiO_2 tozlarını yüksek yüzey alanlı bir substrata fikslemekten geçmektedir. Yüksek yüzey alanı ise kullanılan substratın lifli olması ve liflerin çaplarının düşük olmasıyla elde edilebilmektedir. Lif çaplarının ince olması nano ebattaki çaplara sahip nanolif yapısını akla getirmektedir. Bu tip fiberlerin üretiminde çeşitli metodlar olup en genel olarak kullanılan yöntem kolaylığı, ekonomikliği ve sistem parametrelerini kontrol edebilmekten dolayı elektro-üretim (electrospinning) yöntemidir. Elektro-üretim yöntemiyle nano boyutta lifler üretmek mümkün olmakta ve istenilen yüksek yüzey alanlı substrat bu yöntem ile sağlanılabilmektedir.

Yüksek yüzey alanına sahip bu substrat yapısına TiO_2 'yi değişik yöntemler kullanarak yapıştırmak mümkündür. Fakat seçilen substratın özelliklerine bağlı olarak kaplama yöntemleri sınırlanmaktadır. Bu tez kapsamında, farklı substratlara üniform ve hızlı bir kaplama yapabilen, elektroforetik depozisyon yöntemiyle kaplama yapılmaktadır. Üretilen filtrelerin morfolojik ve fiziksel yapısı hakkında bilgi sahibi olmak için testler yapılmıştır.

Fotokatalitik sistemin kalbinde uygun bir fotokatalizör vardır. Bunun dışında bu fotokatalizörü taşıyacak bir substrat ve kaplama sistemi, fotokatalitik tepkimenin gerçekleşeceği bir reaktör ve yine önemli bir parametre olmak üzere ışık kaynağına ihtiyaç vardır. Bu tez kapsamında bu dört gereksinime yönelik uçaklar için uygulanabilir olacak şekilde yaklaşımlar geliştirilmiştir.

Fotokatalizörler malzeme olarak, özellikle fotokatalikte verimi arttırmak için kullanılan özelliklerden biri olan yüksek yüzey alanını elde edebilmek amacıyla, nanopartikül olarak seçilmiştir. Ayrıca literatürde de nanopartikül boyutundaki aktivitesinin çok yüksek olduğu bilinen TiO_2 anataz tozları içeren ticari degussa P25 TiO_2 tozları kullanılmıştır. Bunun yanı sıra görünür ışıktada aktifleşebilen hemde TiO_2 nin bant aralığını düşürerek, fotokatalitik aktivite verimini arttırmak için çalışılmış olan; gümüş doplu TiO_2 , gümüşle dekore edilmiş TiO_2 ve gümüş nanopartikülle beraber yüzeye depolanmış TiO_2 olarak ayrı çalışmalar yapılmıştır.

Substrat ve kaplama sistemi birbiriyle doğrudan ilgilidir. Uçucu organik bileşiklerin fotokatalitik sistemiyle degradasyonu için nanolif yapıları filtrelerin elektroforetik depozisyonla üretimi, yeni katalizör üretimi ve bunun elektroforetik depozisyonla kaplanması, filtrelerin karakterizasyonları, filtrelerin fotokatalitik testleri, bu tezin ana yapısını oluşturmaktadır. Elektroforetik yöntemiyle depolanmasını kolaylaştırmak için metal kumaşlarda kullanılmıştır. Bu metal kumaşlarında hem ekonomik olması hemde hava geçirgenliğinin yüksek olması çalışma yapma açısından önceliğe sahip olmasına yol açmıştır. Bu çalışmaların hepsinde nano boyuttaki tozları elektroforetik depozisyon yöntemi yardımıyla nanolif veya metal kumaş yüzey üzerine depolama yaparak filtrelerin fotokatalitik verimliliği ölçülmüştür.

Işık kaynağı olarak literatürde floresan ultraviyole (UV) lambalarla çalışma daha çok çalışma olmasına rağmen, yenilikçi, zararlı cıva tarzı kimyasallar içermeyen ve

yüksek verimli ışık kaynağı olmalarından ötürü UV ışık yayan diyotlar (LED) kullanılmıştır. Yüzey alanı reaktörle arttırmanın mümkün olup olmadığını göstermek için yeni bir reaktör tasarlanarak, birden fazla filtre ve UV-LED modülünden geçmesi sağlanarak test yapılmıştır.

Reaktör tasarımında ise iki farklı reaktör kullanılmıştır. Testi kısaca özetlersek, üretilen filtreler, reaktörler içerisine yerleştirilerek, konsantrasyonu kontrol edilebilir düzeyde uçucu organik bileşik içeren gazlar gönderilerek test edilmiştir. İlk yapılan büyük reaktör içerisinde tek bir UV-LED sistemi olan 178 cm² alana sahip bir reaktördür. Bu reaktörden geçirilen hava sıvı fazdaki uçucu organik bileşiklerin gaz fazına geçirilerek kirletilmiş ve proses boyunca kütle spektrofotometresi tarafından izlenerek meydana getirilmiştir. Giriş ve çıkış arasında hiçbir basınçlandırma yapılmaksızın devamlı gaz geçişi sağlanarak filtrelerin verimlilikleri ölçülmüştür. İkinci olarak yapılan küçük reaktörde ise birden fazla UV-LED sistemi olan ve tanesi 48 cm² alana sahip 4 adet filtre yerleştirebileceğimiz ve daha yüksek verimliliklerin elde edileceğini düşünerek tasarlanmış bir sistemdir. Ayrıca UV-LED sisteminin ışık yoğunluğu arttırılarak daha yüksek performans elde edebilen bir sistem yapılması amaçlanmıştır.

Sonuç olarak uçucu organik bileşiklerin insanlar üzerindeki etkileri göz önüne alındığında iç ortamdaki miktarını azaltmak, özellikle kalabalık mekanlara sahip, otel işletmeleri, uçak, otobüs, metro tarzı taşıma araçları üreticilerinin önemli ve güncel bir sorunu haline gelmiştir. Yüksek verimli partikül hava filtreleri (HEPA) günümüzde birçok kalabalık yerde kullanılsa da, özellikle gaz filtrasyonunda yani uçucu organik bileşiklerin gideriminde herhangi bir yeterlilikleri söz konusu değildir. Bu durumlardan ötürü, ticarileştirilebilir ve geliştirilmeye açık bir fotokatalitik oksidasyon yöntemiyle donatılmış filtrasyon sisteminin tasarlanması ve kullanılması bir gereklilik haline gelmiştir. Tezin temel amacı, iç hava mekanlarında kullanılmak üzere, değişik özelliklere sahip tozların hızlı, ekonomik ve ticari bir yöntem olan elektroforetik depozisyonla değişik substratlar üzerine depolanarak yenilikçi filtrelerin yapılması ve geliştirilmesi, filtrelerin kullanılacağı yerlerde LED teknolojisi kullanılarak insan sağlığına zararlı civa içermeyen ışık kaynağıyla aydınlatılarak geliştirilmesi, uçucu organik bileşiklerin üretilen filtrelerle fotokatalitik reaksiyonlar gerçekleştirilerek uzaklaştırılmasıdır.

1. INTRODUCTION

Air pollution issue is one of the most serious problems for humanity, which threatens human life. Outdoor and indoor air quality is directly related with the quality of human's life and its comfort. The indoor environment (home, office, factories and transportation vehicles) had some limitations and restrictions, which are specified by international regulations. Therefore, thousands of studies might be found in academic and patent literature to eliminate contaminant and improve the indoor air quality.

1.1 Motivation of Thesis

The scope of this thesis is to develop feasible photocatalytic filter media for the removal of volatile organic compounds (VOCs). Apart from the particulate filtering, to enhance indoor air quality, volatile organic compounds (VOCs) removal is critically important. For this objective, nanofibrous filter and metal mesh substrates are used for the coating with photocatalytic particles. The most common and effective photocatalyst, TiO_2 is chosen catalyst as the semiconductor. TiO_2 was further modified with Ag using three approaches; silver (Ag) doped TiO_2 , Ag decorated TiO_2 and Ag nanoparticles (NPs) with TiO_2 . Modified TiO_2 were deposited over metal substrates via electrophoretic deposition. Especially air quality of airplane cabin is a big challenge, for example UV lamp is forbidden in airplane cause of the regulations, so UV-LEDs are used as a light source for the VOCs removal system. For this purpose, laboratory scale reactors are designed and manufactured. After the preparation of filters and photocatalytic reactors, photocatalytic oxidation tests was made, and was searched degradation performance of these samples. It is expected to be first step a commercial filters which had high degradation performance.

1.2 Literature Review

In this thesis, literature review has been presented in three subsections; namely, indoor air quality and VOCs, current gas filtration technologies, photocatalytic oxidation (PCO).

1.2.1 Indoor air quality and volatile organic compounds

People's lifestyles have changed strikingly over the last 40 years, especially in industrialized countries. Technological developments and vocational activities are responsible for spending about 90% time of people in indoors (i.e., offices, public transportation facilities, schools and shopping centers, etc.) [1,2]. Indoor air quality (IAQ) refers not only to comfort, which is affected by temperature, humidity and odours, but, also to harmful biological contaminants and chemicals presented in the conditioned space [3]. Therefore, it has become severe health risks for people, such as building related illness (BRI), and multiple chemical sensitivity (MCS) [1–3]. According to World Health Organization (WHO) reports, 4.3 million people died off illnesses caused by indoor air pollution in 2012 [4]. Approximately 235 million people are suffering from asthma in worldwide [5]; which is a severe illness closely linked to IAQ. In addition, IAQ also affects; productivity at work. Benefit of recent improvements in IAQ was calculated to be approximately US\$ 20 billion [1]. Indoor air contaminants involve carbon oxides (CO and CO₂), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and other particulates. These contaminants are released from different sources such as combustion by-products, cooking, construction materials, office equipment and consumer products [6].

The main topic of this thesis is about the degradation of VOCs in air. VOCs are organic compounds, which evaporate easily at room temperature and most of them are known to be toxic and considered to be carcinogenic, mutagenic or teratogenic. VOCs are classified according to their molecular structure or functional group. These are; aliphatic and cyclic hydrocarbons, aromatic hydrocarbons, alcohols, ethers, esters, aldehydes, terpenes, halocarbons, glycols, ketones, siloxanes, alkenes, organic acids, other VOCs. [6, 7].

The VOCs get into environment through evaporation. Evaporation might take place during production, processing, storage and transportation activities. People are exposed to VOCs by inhalation, ingestion and skin contact. Existence of VOCs in

drinking water has become real threat for public health over the last three decades. The predominant VOCs present in water are chloroform (CHCl_3), trichloroethylene (TCE) and tetrachloroethylene (PERC). Benzene, ethanol, toluene, TCE, PERC, xylenes and ethyl-benzene are the most frequently found VOCs in air. Personal activities (smoking, visiting dry cleaner's or service station, etc.) and occupational activities cause exposure to other VOCs [7]. Their possible emission sources were given in Table 1.1. Concentrations of many VOCs are persistently higher indoors than outdoors.

Table 1.1. Classes of VOCs and their possible emission sources [6].

VOC class	Environment and sources
Aliphatic and cyclic hydrocarbons	1-2, 4, 5, 7, 9-11
Aromatic hydrocarbons	1-7, 9, 11, 12
Aldehydes	1-12
Terpenes	1-4, 7-10
Alcohols	1-9, 11
Esters	1-2, 4, 7-9
Halocarbons	1, 2, 7, 11
Glycols/glycolethers/glycolesters	1-4, 7, 9
Ketones	1-4, 6-12
Siloxanes	11
Alkene	2, 7
Organic acids	2, 3, 7-9, 11
Ethers	9
Other VOCs	1, 2, 4, 7, 11
1: Established buildings, 2: New and renovated buildings, 3: School, 4: New car interiors, 5: Carpets, 6: Floor coverings, 7: Wood-based panel and furniture, 8: Solid woods, 9: Paints, 10: Cleaning products, 11: Unflued gas heaters and electric ovens, 12: Office equipment.	

All VOCs are reported to be organic compounds whose boiling point vary between 50 to 260 °C [6]. Organic compounds are grouped into two main categories; polar and non-polar compounds. This polarity or non-polarity is related about the covalent bond of these compounds. Polar compounds have a bond between 2 non-metal atoms that have different electronegativities and therefore have unequal sharing of the bonding electron pair. Non-polar compounds have a bond between 2 non-metal atoms that have the same electronegativity and therefore have equal sharing of the bonding electron pair, besides that, non-polar compounds are measured as

volumetric. In addition, polar compounds easily interact with metal and other surfaces. A classification of indoor organic contaminants can be seen in Table 1.2.

Table 1. 2. Types of VOCs properties.

Description	Boiling Point Range (°C)	Example Compounds
Very Volatile (gaseous) Organic Compounds (VVOCs)	<0 to 50-100	Propane, butane, methyl chloride
Volatile Organic Compounds (VOCs)	50-100 to 240-260	Formaldehyde, Limonene, toluene, acetone, ethanol (ethyl alcohol), 2-propanol (isopropyl alcohol), hexanal
Semi Volatile Organic Compounds (SVOCs)	240-260 to 380-400	Pesticides (DDT, chlordane, plasticizers, fire retardants)

1.2.2 Current indoor air filtration technologies

Three basic strategies could be applied to reduce indoor pollution and improve indoor air quality. The first strategy is focused on the control of the pollution source, which can be accomplished by its removal, confinement or replacement [1]. The second strategy is related to ventilation system, by increasing the amount of outdoor air to dilute indoor pollutant concentration, however this strategy does not always work well due to safety limits of pollutants and also because outside air may bring in more pollutants [8]. The third strategy involves the use of purification/treatment technologies.

Air purification/treatment technologies are; mechanical filtration, electronic filtration, adsorption, ozonation, UV photolysis, photocatalytic oxidation, cold plasma or non-thermal plasma (NTP), biofiltration, botanical purification, membrane separation. These techniques are briefly described below, and their comparison showed in Table 1.3.

Mechanical filtration; is a simple and extensively used technique for removing suspended particles from indoor air. This technique does not retain gases but in some studies have reported removal of ozone by up to 36% in indoor air [1, 9].

Electrostatic filtration; involves particle removal. Particles are ionized and then deflected by an electric field to be trapped on opposite polarity plates. Some researchers have observed that these filters can generate hazardous particles and may also create new pollutants such as ozone and other compounds derived from the ionization of VOCs [1, 10].

Adsorption; is a successful application to retain contaminants on the surface of an adsorbent material such as activated carbon, zeolites, silica gel, activated alumina, mineral clay and some polymers [1]. Activated carbon (AC) and hydrophobic zeolites are the most commonly used among of these, because of their large surface area and high adsorption capacity [11, 12]. Adsorption process is shown in Figure 1.1. A mixture of VOCs with concentrations in the 20-30 ppbv range was treated, and AC filter removal efficiency was about 70-80 % for most of VOCs studied (toluene, benzene, o-xylene, 1-butanol, limonene, undecane and formaldehyde) [13]. However, this method had some disadvantages too. High relative humidity which caused water condensation on the surface pores and pollutant load variations affects adsorption efficiency [14]. Moreover, regeneration process had additional costs, desorption process required to be at about 300 °C and during desorption process, it could make re-emission of the already adsorbed components. Another negative issue is that airborne bacteria can deposit on the adsorbent surface and grow because of the high biocompatibility of the carbon materials [1,15].

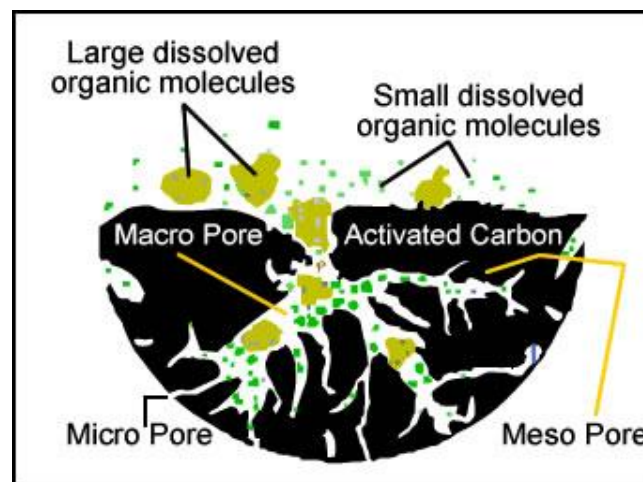


Figure 1. 1. Adsorption process with activated carbon [16].

In **Ozonation**; ozone (O_3) an oxidizing agent, is produced in generators using oxygen from the air. Ozone generators eliminate odours and microbial agents but ozone concentration should be in the range 50-100 ppbv because of exposure limit, and these range does not guarantee the efficient removal of many indoor VOC pollutants. It has been reported that indoor ozone generators causes secondary organic aerosols to be formed, especially in the presence of terpenes [1,17].

UV Photolysis, ultraviolet (UV) radiation is known to have a removal effect on bioaerosols. It promotes decomposition of contaminants, such as viruses, bacteria, chemicals, dust mites, through a process called photolysis oxidation or UV photolysis. The wavelength range is between 180 and 365 nm for air or surface disinfection. UV photolysis has limited use because of its tendency to produce ozone and radicals with harmful effects [18]. On the other hand, UV radiation only removes some gaseous pollutants and contrary, it may release toxic photoproducts. It also consumes substantial amount of energy [10].

Plasma is a highly ionized gas produced by high voltage electrical discharges, and generally consist of electrons. Actually plasma precipitates particles via electrostatic phenomena and produces UV radiation, which promotes oxidation of molecules and the removal of viruses and bacteria. Also this method produces free radicals causing the break of chemical bonds and the mineralization of VOCs [19]. Cold plasma can be generated with corona discharge, dielectric barrier discharge and glow discharge. However, it has several disadvantages, such as poor energy efficiency, especially for the treatment of low VOC concentrations [20].

Biofilters are cost effective and eco-friendly alternative to physical-chemical air pollution control methods. This technology was used against a large variety of VOCs and inorganic gases and its by-products are harmless [21]. Bioreactor design is very important in biofiltration, it could be change for the treatment of gaseous pollutants. It has various types such as; packed bed bioreactor, bioscrubber, biotrickling filter and membrane bioreactor. It has some limitations in the case of poorly soluble or recalcitrant substances, and the potential release of dust and microorganisms [1].

Botanical purification, is a complementary system to biofiltration, constituted of a vegetable plant and a packing material-substrate. The polluted air pass through the plant's root system, and uses either the leaves or root to adsorb pollutants from

indoor air. The purification cannot be done effectively for high concentration pollutants [22,23].

Lastly, **Membrane separation** is a technique that relies on the use of semipermeable membrane. The membrane allows diffusion of certain VOCs from a gas stream to another fluid. Especially zeolite-based membranes have been used for separating mixtures of gaseous compounds with similar boiling points or molecular weights, etc. However, the main drawbacks are cleaning requirement and the increase in pressure drop. In the literature [24] research on low levels of VOC is limited.

Table 1. 3. Comparison of filtration methods and their properties [1].

Treatment	Waste generation	Energy consumption	Market sales
Mechanical Filtration	Spent Filters	Moderate	High
Electronic Filtration	Spent cleaning plates	Moderate	High
Adsorption	Spent absorbent	Moderate	High
Ozonation	-	High	High
Photolysis	Depleted lamps	High	Low
Photocatalysis	Catalyst/lamps	Moderate	Moderate
Non-thermal plasma	-	High	NC*
Membrane separation	Clogged membranes/ contaminated solution	High	NC*
Botanical Purification	Organic waste	Low	Low
Biofiltration	Biomass and packing material	Low	NC*

*Not commercialized

1.2.3 Photocatalytic oxidation

Photocatalytic oxidation or photocatalysis promotes degradation and mineralization of pollutants in the air by using a semiconductor materials and an irradiation source in the presence of oxygen. The semiconductor, which is known as a catalyst and light source plays a key role on the oxidation process. Oxidation occurs at positively charged holes as electron acceptors, generated by exciting an electron, only when the energy provided is higher than the band-gap energy. In addition, the positively charged hole reacts with water molecules or OH^- to generate strong oxidant $\text{OH}^\bullet$ radicals.

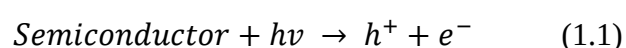
Photocatalysis is an alternative to catalytic thermal oxidation, because it can occur at room temperature. If we compare to other methods, it is affordable because of the low power consumption and little maintenance needed [25]. In addition to the degradation and mineralization, photocatalysis has also bactericidal effect [26]. Photocatalytic oxidations had some disadvantages too, these are short lifetime of the catalyst and generation of harmful by-products [1].

TiO₂ is currently the most widely used catalyst. It is an inexpensive, non-toxic and biocompatible material, which has high photo-efficiency and activity. Other semiconductors such as ZnO, ZnS, CdS, Fe₂O₃, SnO₂ are also commonly used [27].

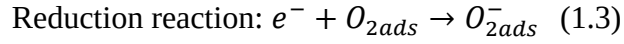
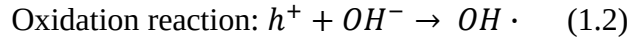
Quici et al. [28], worked on decomposition of 10-500 ppbv toluene gas phase with TiO₂, which was irradiated with 185-254 nm wavelength UV-lamp. Their removal efficiency was found to vary between 30% and 90%. Another research group [29] studied PCO with using TiO₂ for removal of 2-propanol and toluene mixture (80-400 ppbv) and tested at different humidity values. These group reached the 100% removal rate, whereas the conversion of toluene was reduced to 50% in the presence of 60% relative humidity. Ourrad et al. [30] identified 20 VOC reaction intermediates when 750 ppbv limonene PCO was investigated under dry air. The intermediates is a typical problem that should be considered separately for the PCO procedures.

1.2.3.1 Photocatalytic oxidation mechanism

Photocatalytic system key parameters are residence time, relative humidity and film thickness and photocatalysts load, and concentration and types of VOC. These are related to degradation performance in the PCO systems. As it showed in Figure 1.2, photocatalysis is often explained with electronic structures of semiconductor materials, a band model. An electron in an electron-filled valence band (VB) is excited by photo irradiation to a vacant conduction band (CB) which is separated by band gap from the VB, leaving a positive hole in the VB. These electrons and positive holes drive reduction and oxidation of compounds adsorbed on the surface of a photocatalyst in their order [31]. The activation equation (1.1) can be written as follows;



In this reaction, h^+ and e^- are powerful oxidizing (1.2) and reducing (1.3) agents and reactions that take place can be expressed as follows;



Hydroxyl radical ($OH \cdot$), which is the dominant strong oxidant, was obtained from the oxidation of adsorbed water or adsorbed OH^- molecules [27]. Their net reaction with a VOC (1.4) can be expressed as;

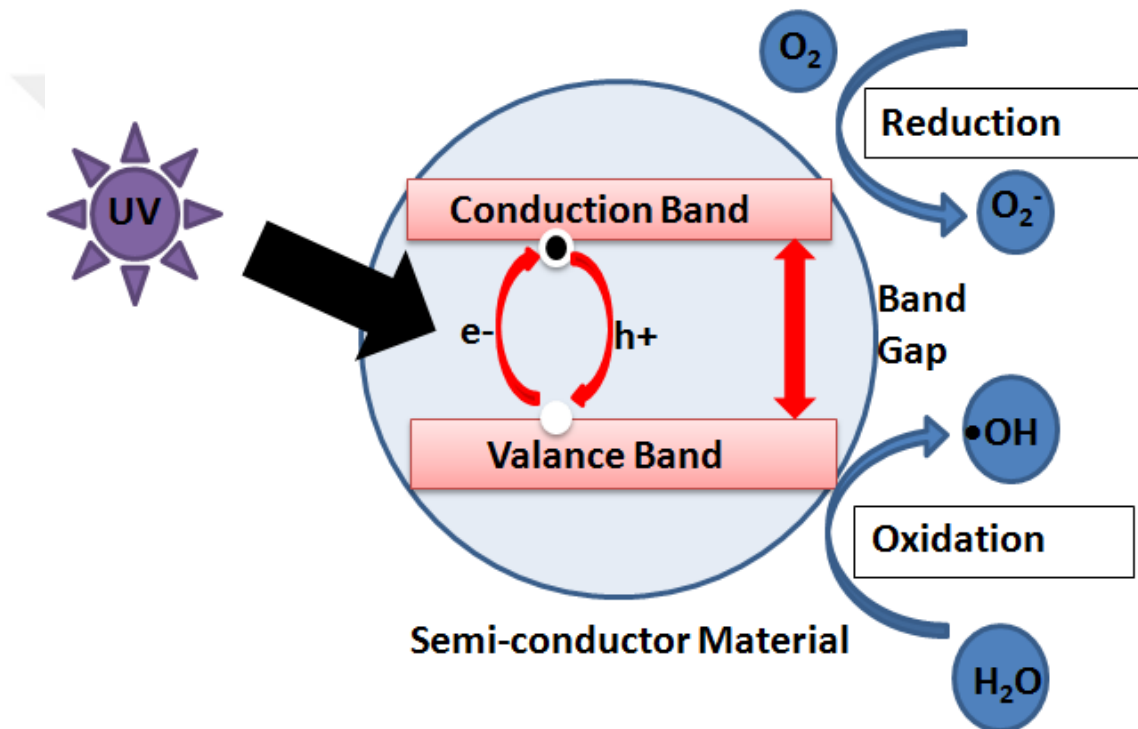
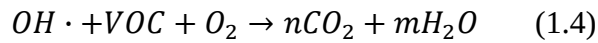


Figure 1. 2. Mechanism of PCO at semiconductor material.

The Langmuir-Hinshelwood (L-H) model has been widely preferred to formulate the rate equations for the PCO reaction. Decomposition or conversion efficiency (η) was calculated from the equation as shown below;

$$\eta = \frac{C_0 - C}{C_0} \quad (1.5)$$

where C_0 is the initial concentration of contaminant and C is the concentration of contaminant at time t .

1.2.3.2 Photoactive materials

Photoactive materials or another name photocatalysts are used for photocatalytic oxidation (PCO) applications. These photocatalysts are commonly metal oxides or sulphides. TiO_2 , ZnO , ZrO_2 , SnO_2 , WO_3 , CeO_2 , Fe_2O_3 , Al_2O_3 , ZnS and CdS are some examples which are characterized by a filled valance band and an empty conduction band [32]. Titanium dioxide, zinc oxide and tungsten trioxide are ranked in the activity sequence; $\text{TiO}_2(\text{anatase}) > \text{ZnO} > \text{WO}_3$ [27]. Based on the stability requirements, the metal sulfide semiconductors are not suitable, because they undergo photoanodic corrosion. The iron oxide polymorphs ($\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\delta\text{-FeOOH}$, etc.) are unsuitable semiconductors, even though they are inexpensive and have normal band gap energies, because they undergo photocathodic corrosion. ZnO appears to be a suitable alternative to TiO_2 ; and the two of them are popular in scientific community. However, ZnO is unstable with respect to unjustifiable dissolution to the yield of $\text{Zn}(\text{OH})_2$ on the ZnO particle surfaces and thus leading to catalyst inactivation over time [32]. Figure 1.3 shows the different semiconductor band positions.

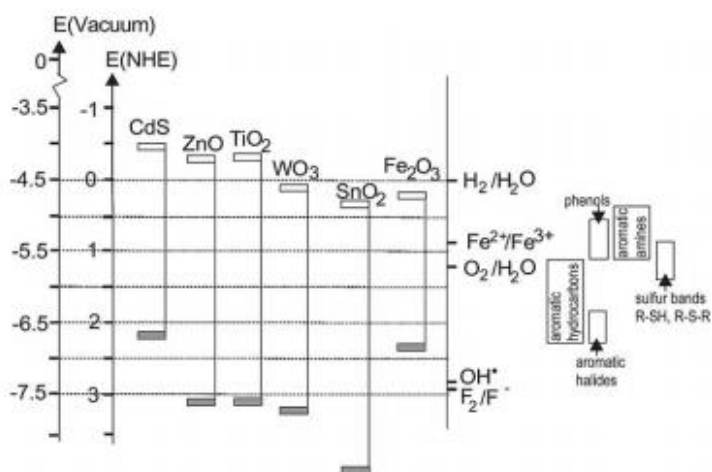


Figure 1. 3. Band positions (top of valance band and bottom of conduction band) of different semiconductors [33].

TiO_2 is biologically and chemically inert. It is, stable against photocorrosion and chemical corrosion, and quite inexpensive. TiO_2 has two active crystal forms; anatase and rutile and their crystal structure types are shown in Figure 1.4. The energy band-gaps of anatase and rutile are 3.23 and 3.02 eV, respectively. Titanium dioxide in the anatase form appears to be the most photoactive and practical of the semiconductors

for widespread environmental applications such as waste water treatment, hazardous waste control, air purification, and water disinfection [32, 33]. Commercially available Degussa or Aeroxide P25 TiO₂ has 70:30% anatase:rutile mixture. Its Brunauer-Emmett-Teller (BET) surface area is about 55 m²/g and crystallite sizes are 30 nm in 100-900 nm diameter aggregates [32, 34]. The nanoscale photocatalyst produced by the acid-assisted sol-gel technique, is composed of mesopores with pore size in the range of 35-44 nm with addition of hydrochloric acid. These nanoscale photocatalysts showed better photocatalytic activity than P25 TiO₂ [36]. A light source at a wavelength(λ) of <387 nm is required to overcome the gap for TiO₂ [22].

In addition, TiO₂ mainly absorbs UVA light, but in order to enhance catalytic activity of photocatalyst, many researchers have attempted to extend the photoresponse into the visible range by doping metal ions into TiO₂ [33, 37]. Visible light responsive TiO₂ was modified via three approaches; doping TiO₂ with transition metal ions, doping nitrogen and utilizing sensitizing dyes [38]. Coupling of TiO₂ with small band gap semiconductor or doping with transition metal ions such as V, Cr, Mn, Fe, Co, Ni or Cu extends light absorption into the visible region. Zang et al. [39] studied the doping of TiO₂ with noble metal ions Pt^{IV}, Ir^{IV}, Rh^{III}, Au^{III}, Pd^{II}, Co^{II}, and Ni^{II} by sol-gel method and the best sample (Rh^{III} doped) had almost %50 degradation performance. A different group [40] reported that inclusion of transition metal ions decreased photocatalytic activity of TiO₂ under UV-irradiation. Doping nitrogen into substitutional sites of TiO₂ narrows the band gap and induces photocatalytic activity in the visible light [41]. Films and powders of TiO_{2-x}N_x have shown an improved activity over TiO₂ under the visible light [42]. A common approach to initiate charge transfer processes in a large band gap semiconductor using visible light utilizes a sensitizing dye. Charge injected from excited Ru(II) polypyridyl complex into TiO₂ can be efficiently utilized for the reduction of carbon tetra chloride [43]. But these semiconductors cannot be used for detoxification of waste waters and air because the dye molecules would also be degraded [39].

1.2.3.3 Substrates

Supported photocatalysts have been developed in an attempt to solve some problems. The most important properties of a suitable substrate for PCO applications are its being chemically inert, presenting a high specific surface area and transparency to

UV radiation. In addition to these, for our purpose a substrate could be conductive for electrophoretic deposition or it could immobilize the photocatalyst on the surface.

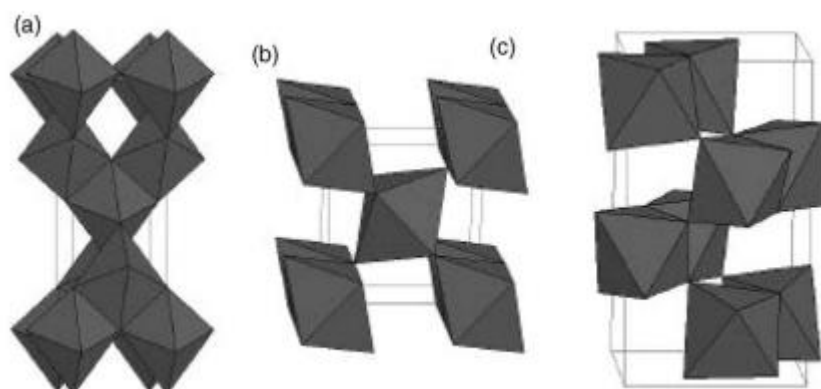


Figure 1. 4. Crystal structures of TiO₂ anatase (a), rutile (b), and brookite (c) [33].

In the literature many different substrates were used for the coating of TiO₂, such as glass, glass beads, cement, quartz, silica, activated carbon, fiberglass, stainless steel, ceramics, monolith, polymers [44, 45]. One of the critical parameters is the surface area for the photocatalytic activity. So, it was decided to use nanofiber substrate due to its high surface area. Polymeric nanofibers have been used in air filtration applications, especially their high surface area is the key property of these materials. Electrospinning is a method where nanofibers are stretched from solution to a fiber by applying an electric voltage. Its usage as a holder of titanium dioxide was previously investigated [44]. Metallic meshes are other substrates for commercially available and inexpensive filter material. Other than that, some kind of metallic foams can be used for substrates, which have better surface area compared to metal meshes.

1.2.4 Coating techniques

Different coating methods are available for the fixing TiO₂ on substrates. Table 1.4. and Figure 1.5. depicts the methods for the coating of functional materials.

Electrospray is one of the approaches to deposit TiO₂ on nanofibers. But this process takes long time and it is difficult to obtain high amount of TiO₂ in the structure of the real dimension filter [46]. Another approach might be dipcoating. TiO₂ and SiO₂ particles were coated onto polyethylene terephthalate (PET) monoliths. After that, coated monoliths were used as filter and tested against trichloroethylene (TCE) removal by photocatalytic oxidation process. After 10 min, all TCE was decomposed

but conversion of CO₂ was balanced at 45 min [47]. P-25 TiO₂ was coated on polydimethylsiloxane (PDMS) and orthophthalic polyester (OP) by spin coating method, followed by degradation test about 2 hours long for the removal of gas phase ethanol, PDMS films had high activity (near 100%) and OP films had 51% degradation rate [48]. Thermal bonding is another method for coating of TiO₂. Foamed polyethylene sheet was chosen as substrate, and dipped into TiO₂ solution and pressed at 70 °C. After the preparation, samples were tested for methylene blue decomposition, and their efficiency was about 100% during 4 hour exposure [49]. PET plate was used as a substrate, and TiO₂ was coated with plasma spraying method. Acetaldehyde was a target pollutant in that article, and after 2 hours 95% degradation rate was obtained [50].

There have been no work on coating polymeric nanofiber structure with electrophoretic deposition (EPD), it is a cost effective and fast method compared to other methods [51]. Photocatalytic degradation of gas phase ethanol occurred with electrophoretically deposited TiO₂ at nanofibrous structure. In this work, we compared the amount of titanium dioxide on dipcoated and electrosprayed samples and their photocatalytic oxidation efficiency. After that, immobilization is a promised, facile method to coat TiO₂ at polymeric structures. On the other hand, for the rapid and same filter production was actualized for all substrate structures. And this coating method at structures has advantage for the mass production with full control in the photocatalytic filter area [51, 52].

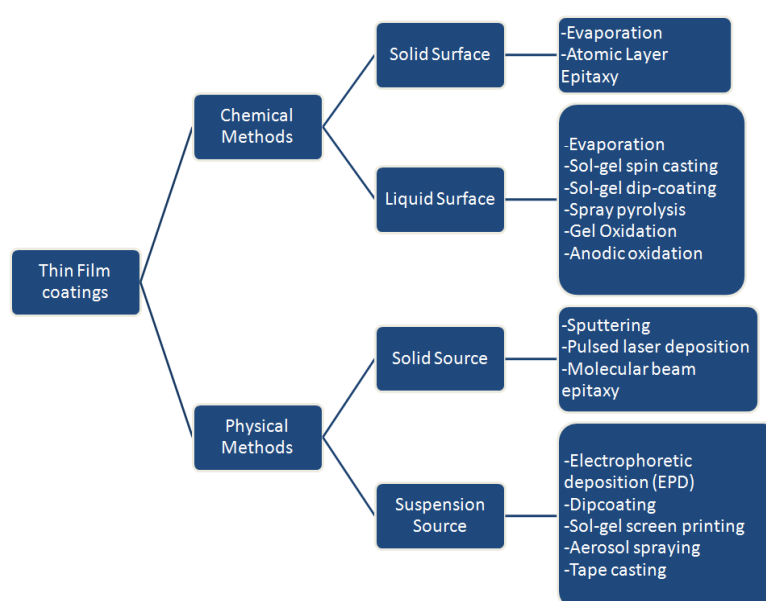


Figure 1. 5. Thin film coating methods.

Table 1. 4. Comparison of some coating methods.

<i>Coating technique</i>	<i>Comments</i>	<i>Reference</i>
Electrospray	Slow process, hard to get high amount of TiO ₂ on structure.	[46]
Dip coating	Economic, hard to obtain uniform coating thickness.	[47]
Spin coating	Cannot use on fiber materials.	[48]
Thermal Bonding	Heat requirement, costly and hard to get uniform coating.	[49]
Plasma Spraying	Low temperature, economic, hard to obtain uniform coating	[50]
Electrophoretic Deposition	Fast and facile process, uniform and controllable coating thickness, hard to obtain crack free surface	[51]

2. PREPARATION OF CATALYST& PCO FILTERS

In this section PCO filter preparation routes were summarized. Sol gel method was utilized to modify PC structure, electrospinning was used for nanofiber production and, electrophoretic deposition was used to coat nanoparticles over nanofiber structure and metal surfaces.

2.1 Electrospinning

Electrospinning is one of the widely studied mechanism to produce nanofibers. It is based on the electrohydrodynamic behaviors of polymer solutions and melts. Though it was invented in the early 1900s by Cooley and Morton (Patent number; 692,631), with the improvement in nanoscience and nanotechnology the interest in that field increased in 1990s [53]. Nanofibers (NFs) are uniaxially stretched from a viscoelastic solution via the electrostatic forces, which differs from conventional fibre spinning methods [54]. Electrospinning is a miscellaneous and cost-effective method when compared to others for producing NFs from various materials which include polymers, suspensions, polymer blends, emulsions, sol-gels, non-polymeric systems such as metal oxides and composite structures [55]. Due to the high surface area, arbitrarily rigid and flexible structure and high porosity, electrospun NFs are widely used for different purposes such as filtration media, nanosensors, micro/nano electronic devices, drug delivery systems and scaffolds for tissue engineering [44]. These applications include filtration, chemical and biological sensors and protective clothing applications [44, 54]. In this study, nanofibrous webs were used as a substrate for inorganic materials such as metal oxides with nanocatalysts. High surface area is very important for the substrate in photocatalytic applications, which also should be an inert material [56]. The diameter of NFs could vary from tens to thousands of nanometers depending on polymer solution and electrospinning parameters.

Nanofiber formation during electrospinning is due to the electrostatic forces generated between a polymer solution and a collector. When the applied potential is

sufficient to overcome the surface tension of the polymer solution droplet, a jet is formed on the tip of the feeding nozzle. Nanofibers are protruded towards the collector [57]. Schematic view of electrospinning can be seen in Figure 2.1. Electrospinning have some important parameter to control properties of electrospun NFs. Especially, fiber diameter governs properties of NFs, e.g. thinner diameter has more surface area. Parameters such as solution viscosity and conductivity, applied voltage, feeding rate, distance between tip and collector and ambient humidity affect NFs diameter [54]. In many cases, due to increasing concentration of the polymer solution, the increase in the NF diameter was clearly observed. On the contrary, conductivity, applied voltage and distance between tip to collector decrease NF diameter.

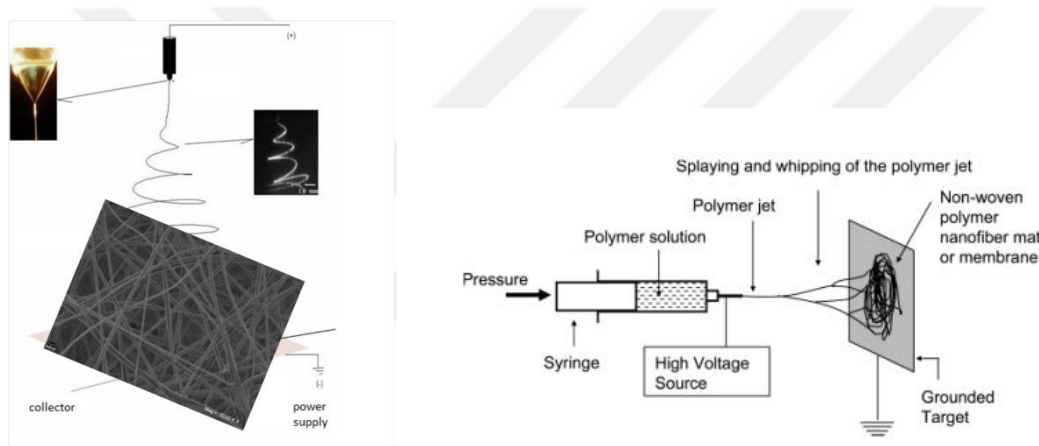


Figure 2. 1. Schematic representation of electrospinning process [58].

2.2 Electrophoretic Deposition

Electrophoretic deposition (EPD) is an electrochemical method, which is used for a wide range of technical applications. EPD is usually performed in a two electrode cell but sometimes in different applications [59] there can be used 3 electrode cell as in the Figure 2.2. Electrophoretic deposition (EPD) was a traditional coating method for the inorganic materials. EPD is an electrochemical method, which is based on the motion of charged particles in a suspension toward an electrode of the opposite charge under an applied DC electric field, as it could be seen in Figure 2.3. The mechanism of EPD involves two steps. In the first step, an electric field is applied between electrodes, charged particles move toward the oppositely charged electrode and this step is named electrophoresis. The second step is that particles collect at the electrode and create a relatively compact and homogenous film and this step is called

deposition [60]. This method has certain requirements in order to be used effectively; the major one is producing a stable suspension that provides charged particles to move freely when electric field is applied. However in a different article [61] which was about mechanism of EPD, about 3 steps were mentioned; namely “charging, transporting and collecting”. EPD could be used as any solid such as a fine powder (<30 μm particle size) or colloidal suspension, including metals, polymers, ceramics and glasses. After the deposition, a heat-treatment step is normally required to consolidate/increase density the deposit and to eliminate porosity. This method facilitates the conversion from the laboratory scale to the industrial at coating works. It has some advantages, such as coating complex shapes, has short deposition time, can get uniform coating thickness. Alternatively, it can coat wide range of inorganic materials from 1 nm to 1 m [51], [62].

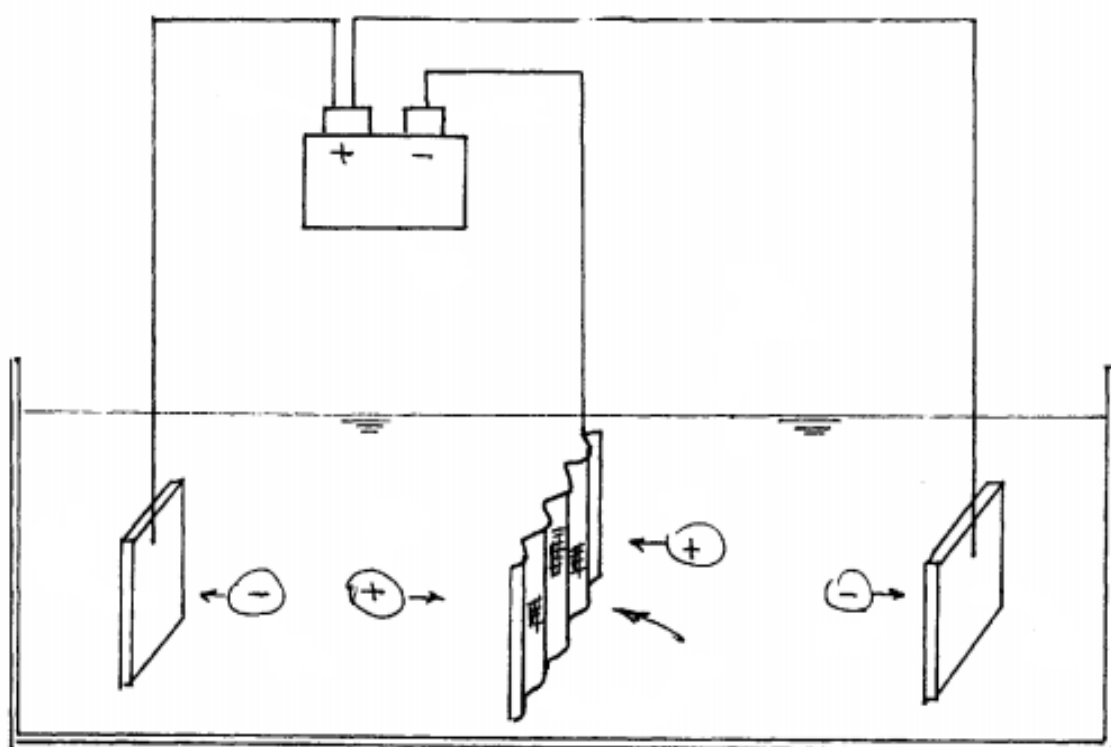


Figure 2. 2. Electrophoretic deposition of TiO_2 at US Patent.

Electrophoresis was discovered in 1740s in a liquid-siphon experiment by Indian scientist G.M. Bose. In 1807 Reuss, a Russian scientist, was the first to observe the electric field induced motion of particles (clay) in water [63]. EPD process was used in 1933 to deposit thorium dioxide on a platinum cathode as an emitter for electron

tube applications. In the last 25 years interest in EPD to produce advanced materials has widely increased both in academia and the industry sector. This process could be used for producing coatings, for shaping monolithic, laminated and graded free-standing objects. Even infiltration of porous materials and woven fiber preforms for composite production were reported [64].

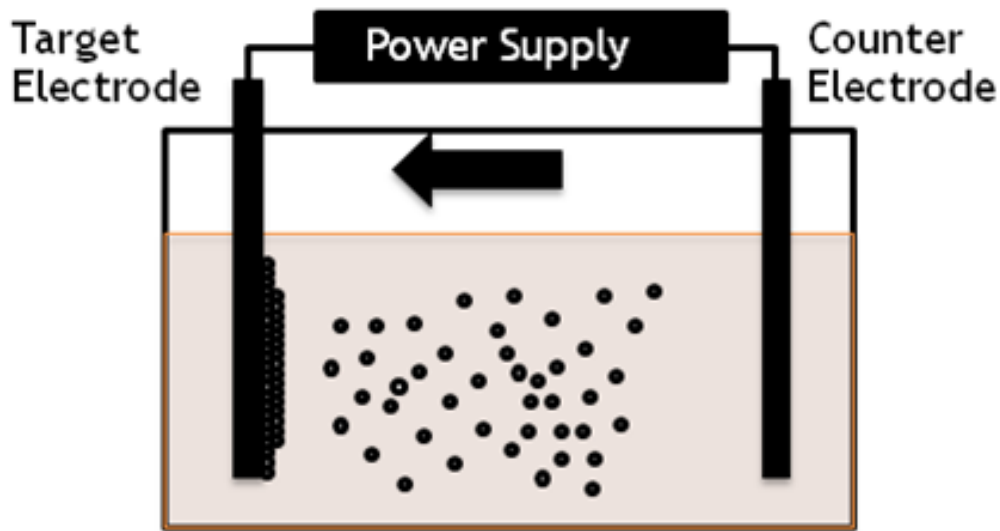


Figure 2. 3. Schematic of electrophoretic deposition.

EPD coatings have already been used in automotive, appliance and general industrial coatings. For example, cathodically coating plant with a capacity of 800 bodies per hour was operated by a German car builder. The process has also advantages, such as high level of automation, low levels of pollution, high throw power and coating homogeneity. Besides it provides high areal covering density compared to dipped or sprayed coatings [64].

For example, Gal-Or et al. [65] infiltrated porous graphite electrodes with silicon carbide (SiC) and silicon oxide particles. For a good infiltration, the particle increment in an external coating should be decreased so that the pores are not blocked. Lower voltages and a higher particle concentration improves the infiltration. Another application is the infiltration of fiber forms, especially with matrix material for composite production [66–68]. For conducting fibers, the preform is used directly as the deposition electrode, however for non-conducting fibers, the preform is positioned in front of an electrode. The main advantage of using EPD for applications is its relative low costs compared to other methods, for example, chemical vapor infiltration [60].

2.2.1 Electrophoretic deposition mechanism

Fundamental mechanism of EPD has been largely described in the literature, was discussed by Sarkar and Nicholson [63]. EPD is mainly based in the framework of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and in relation to the distortion of the particle double layer under the application of a DC electric field. The theory is also applied to mechanisms such as flocculation by particle accumulation, particle charge neutralization, electrochemical particle coagulation, electrical double layer distortion and thinning mechanism [52, 63, 64, 69].

2.2.1.1 Flocculation by particle accumulation

Corni et al. [60] reported similarities between formation of deposits by electrophoresis and gravitation. The pressure is applied by the deposited particles in both processes. The pressure enables to prevail against the interparticle repulsion for the deposition of particles. Thus, the first function of the applied electric field in EPD is to move particles towards the electrode to accumulate. This mechanism can also explain the deposition of coatings onto polymeric substrates such as nanofibers, membranes that are not serving as electrodes.

2.2.1.2 Particle charge neutralization mechanism

Grillon et al. [70] suggested, that the charged particles are neutralized when they reach to the electrode. This mechanism was proven experimentally by Brown and Salt [71]. Single particles, monolayers and powders are deposited via charges created by the addition of salts to the suspension. However, this mechanism cannot be used for longer time depositions or for processes where the particle and electrode contact is not allowed as in the example of depositions on a semi-permeable membrane placed between the electrodes in infiltration process.

2.2.1.3 Electrochemical particle coagulation mechanism

The electrochemical particle coagulation mechanism explains the reduction of the repulsive forces between the particles in suspension. Corni et al. [60] mentioned about the increment of the ionic strength close to the electrode when an electrical potential was applied. This behavior causes the rise of the electrolyte concentration around the particles. The ionic strength was similar to that required to flocculate a suspension. Due to that reason, rise of the electrolyte concentration produces a

decrease of the repulsion force between the particles close to the electrode which means low zeta potential, and, as a result, the particles coagulate. Time is needed for the increase of the electrolyte concentration next to the electrode, thus a certain time has to pass for the deposition. Required time is inversely proportional the square of the applied voltage ($t \propto 1/E^2$), in another words, higher applied voltage requires shorter time for deposition. This mechanism is reasonable when the electrode reaction generate OH^- ions, for example, suspensions containing water. However the mechanism is not applicable if there is any increment of electrolyte concentration near the electrode [60].

2.2.1.4 Electrical double layer (EDL) distortion and thinning mechanism

Sarkar and Nicholson [63] proposed a model, which depends on irregularity of the particle double layer, to explain the invalidation of the electrochemical coagulation mechanism with the same electrolyte concentration near the electrode. It was mentioned that when a positive particle and its shell are moving to the cathode, the double layer is disrupted (thinner ahead and wider behind) as shown in Figure 2.4. and Figure 2.5 due to fluid dynamics and to the effect of the applied electric field. In consequence, the counter ions (negative) have smaller coulombic attraction to the positively charged particles and thus they can more easily react with other cations moving towards the cathode [60, 63]. This process reduces the thickness of the double layer and for this reason, when another particle with a thin double layer is approaching, two particles come close enough to interact through London Van der Waal attractive forces and coagulate. This mechanism is reasonable to consider a high concentration of particles close to electrode (or high collision frequency). This mechanism works also for incoming particles towards thin double layer heads, coagulating with already deposited particles.

In the sequel Fukuda et al. [69] showed Sarkar and Nicholson[63] previous model was not complete and proposed a new theory based on a concentration of H^+ at the cathode. Concentration of H^+ was decreased due to particle discharge or other chemical reactions in cathode. Thus, pH level increases towards the isoelectric point, zeta-potential decreases and the particles coagulate. This mechanism is general for all suspensions containing hydrogen ions.

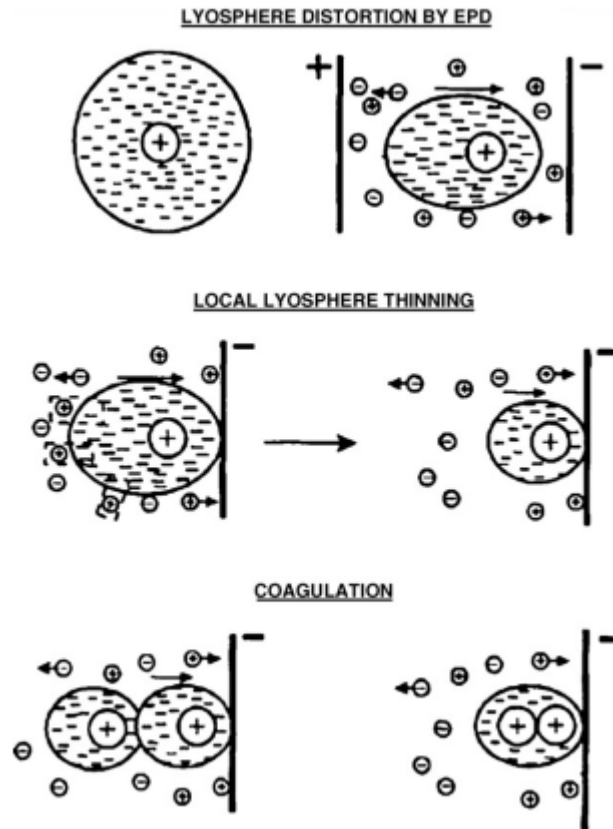


Figure 2. 4. Schematic representation of the deposition mechanism due to electrical double layer distortion and thinning [60].

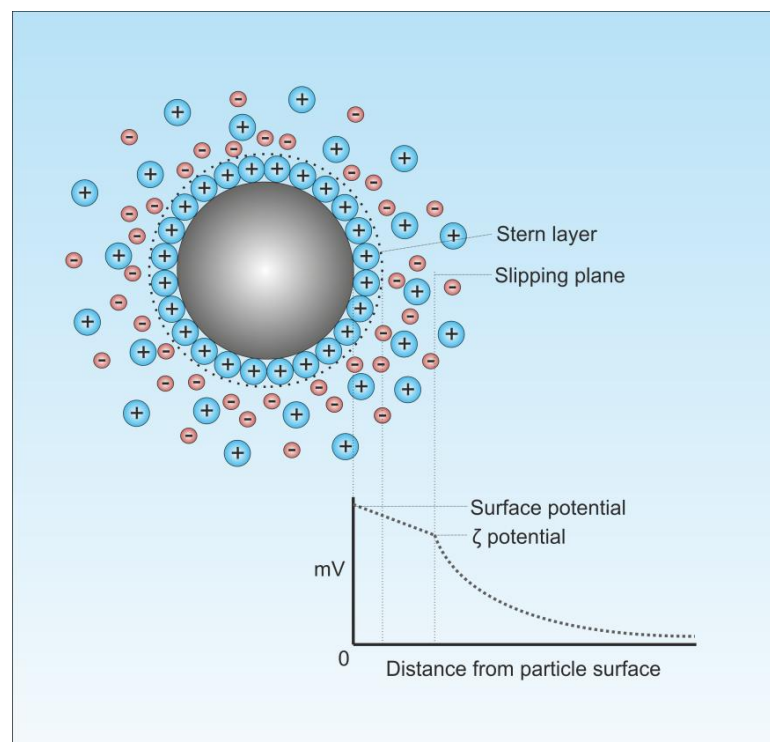


Figure 2. 5. Schematic of zeta-potential. Received from “en.wikipedia.org/wiki/zetapotential”

2.2.1.5 Novel theories and models

Electrodynamic particle aggregation during EPD process was watched under steady and alternating electric fields [60, 72, 73]. The models produced equations for the time evolution of the probability of separation between deposited particles in different conditions. These equations are able to explain and model the experimental works, aggregation of colloidal particles deposited near an electrode in a DC electric field by taking into account convection of electro-osmotic flow about the particles [74]. During the EPD process, accumulation of charged particles on an electrode were analyzed with numerical simulations [74]. But these studies describe the local points of particle interactions, and in light of this information these equations can be used to optimize the EPD process [60].

Van der Biest et al. [75–77] carried out theoretical works by producing a model to predict the yield of the EPD process, calculating the changes of the electric field onto the suspension, caused a potential drop over the growing deposit. This model was verified for Al_2O_3 suspensions in ethanol with different concentrations.

Van Tassel and Randall [78] deposited electrophoretically the alumina powder from an acidic suspension. They obtained a very uniform, dense alumina film and observed an inconvenient voltage rise across the deposited film layer. The two effects can be explained by the formation of an ion depleted conduction layer in the solvent at the deposited electrode. Thus, the electrophoretic force on the particles in layer is higher than the force on particles in the rest of the system, otherwise high voltage system produces a large self-leveling effect for deposition thickness [60, 78].

2.2.2 Electrophoretic deposition of nanoparticles

The electrophoretic deposition of inorganic nanoparticles (size < 100 nm) is a special method employed to produce variety of materials, which are inorganic materials generally with metallic and ceramic based structures. These are monolithic ceramics, ceramic coatings and films, ceramic laminates, ceramic matrix composites [51, 60] and carbon nanotubes (CNTs) that can be subsumable for nano dimension materials.

In theory, any materials can be coated by EPD starting from water-based or non-aqueous suspensions of nanoparticles. For example, BaTiO_3 and Eu-doped BaTiO_3 thin films have been deposited from acetylacetone suspensions [79], aqueous

suspensions[80] and ethanol suspensions [81] . Zinc oxide and zirconia nanoparticles have been deposited the same way as a BaTiO₃.

Nanoparticles were deposited by EPD such as, nanosized lead hydroxyapatite, zirconate titanate, silicon carbide, europium oxide, ceria, vanadium pentoxide, hydrous ruthenium oxide, gamma ferric oxide, nickel, iron, aluminum, silver, nickel ferrite, silica, polyimide, zirconia, platinum, diamond, yttria, zeolites, palladium, cadmium selenide, cadmium sulphure, gold, iridium, aluminum oxide, titanium dioxide [51, 60].

Photocatalyst coating was performed by EPD of commercial TiO₂ nanoparticles (Degussa P25) on silicon carbide (SiC) and carbon fibers; while alternatively metallic fibres and meshes could be used as a substrate [82, 83]. In more recent work, titanium dioxide particles were coated by EPD for photoelectrodes which was used in flexible dye-sensitized solar cells without the use of a surfactant or any post-thermal treatments [84]. The deposition of TiO₂ nanoparticles via EPD was performed for different applications such as batteries, displays and photocatalysis. For photocatalytic oxidation TiO₂ coatings on stainless steel were prepared using TiO₂ suspension of 20 g/l concentration. These stainless steel plates were immersed directly to suspension of TiO₂ and distance between plates was kept 1.5 cm, where applied voltage was 30 V with using DC power supply. Deposition time was varied from 5 to 30 sec [85].

2.3 Catalyst Production via Sol-gel Method

Photocatalytic materials or catalysts had a key role on the photocatalytic oxidation process. TiO₂ in the anatase form is the most widely used photoactive. The addition of metal dopants to catalyst materials have a dramatic effect on the photocatalytic activity which reduces the band-gap of catalysts [86]. In most cases, the dopant of catalyst increase the efficiency of the photocatalysis via enhanced charged separation [86, 87]. On the other side, increasing the efficiency of catalyst under visible light is important for the practical application of photocatalytic oxidation [88]. Many studies have aimed to improve the photocatalytic activity by reducing the band gap of the catalyst with noble metals [39, 89, 90]. According to the literature, silver has received considerable interest because of its potential applications. It even provides additional properties such as antibacterial activity for medical application, food and

filtration industries. Silver can trap the excited electrons from TiO_2 and leave the holes for photocatalytic reactions [88]. Their wavelength response is in the visible region; moreover, silver particles could enable the electron excitation by creating an electric field and plasmon resonance effect in particles shows that enhancement in this electric field [88, 91]. The effect of Ag doping on titanium dioxide and its photocatalytic activity by UV irradiation was studied by Chao et al. [91] it was observed that Ag doping promotes the anatase to rutile transformation, and results shows that increased specific surface area and enhanced the electron-hole pair separation cause the improvement in photocatalytic activity.

Since the silver (Ag) Ag^+ ions had 126 pm radius and Ti^{4+} ions had 68 pm radius, during sol-gel procedure Ag^+ ions would not enter into the lattice of anatase phase. During calcination, uniformly dispersed Ag^+ ions would gradually migrate from the volume of the TiO_2 to the surface by enhancing their crystallinity, resulting in silver exclusion over the surface. Electron transfer from conduction band of TiO_2 to the metallic silver particles at the interface is possible, because the Fermi Level of TiO_2 is higher than that of silver metal. This results in the formation of Schottky barrier at the Ag- TiO_2 contact region, which improves the photocatalytic activity [88]. But if the photo reduced Ag cannot be highly dispersed in the surface of TiO_2 , efficiency get lower [88];

- It acts as a barrier preventing light absorption by titania
- It prevents the organic substrate from contacting the titania surface
- The silver may become a significant center for electron-hole recombination

By sol-gel method it is very easy to prepare homogenous ion-doped TiO_2 powders and films on various types of supports under mild conditions. The foreign metal ions, affected the TiO_2 phase transformation behavior and structure when they were introduced [91]. Sol-gel included silver and titanium dioxide precursor in a solution for the slow nucleation to nanometer scale powders. Generally, titanium tetraisopropoxide (TTIP) is precursor of titanium dioxide and silver nitrate is the precursor of silver dopant. The solution was stirred and calcinated initially. After that sintering is applied to obtain for titanium dioxide anatase phase. Sol-gel process schematic was given in Figure 2.6.

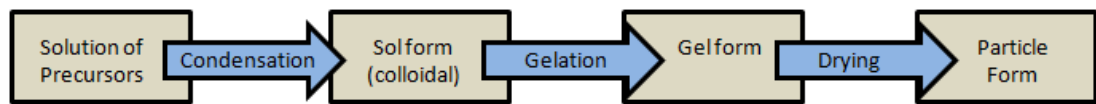


Figure 2. 6. Schematic of particle form preparation from sol-gel process.



3. MATERIALS & METHODS

3.1 Materials

In this section, the materials used in this study were described along with the explanations of why those particular materials were chosen. Thermoplastic polyurethane (TPU) [BASF C95, Germany] was chosen as the polymeric material, which was converted to nanofiber form for holder of TiO₂. Nonwoven polypropylene (PP) was used as substrate of nanofiber mat. Aeroxide P25 [Evonik, Germany] was selected as a catalyst material which is the commercial product of TiO₂. Ethanol [99,8% purity, Merck, Germany] was used as target pollutant for photocatalytic experimental studies. Dimethylformamide (DMF) [99,8% purity, Sigma Aldrich, Germany] was used as the solvent during the preparation of the electrospinning solution. As the solvent for electrophoretic deposition solution ethanol [99,8 % purity, Merck, Germany] was chosen.

3.2 Nanofiber (NF) Production by Electrospinning

In this thesis, nanofiber (NF) mat was produced as a filter material by electrospinning method. NF was chosen due to high surface area and porosity properties, which are very important for photocatalytic oxidation. For electrospinning studies 20 mL Set Inject brand syringes were used with a 21Gx1 ½" needle. Voltage values, feeding rates and distances between tip and collector were optimized before and optimized parameters were used in this thesis. Rotation value of the collector was always the same for orientation of the fibers. Polypropylene (PP) nonwoven was chosen as a holder for produced NF mat spun onto this nonwoven due to its inflammability and convenient procurement from TAC company. Schematic view of electrospinning machine and electrospinning process is given in the Figure 3.1.

Thermoplastic polyurethane (TPU) is a flexible elastomer that has a wide range of applications such as coatings that require high surface area, sealants, transdermal patches, and artificial vessels [58]. TPU was chosen as the proper polymeric material

for electrospinning because of the extreme properties, which include elasticity, abrasion, transparency, resistance to water and oil.

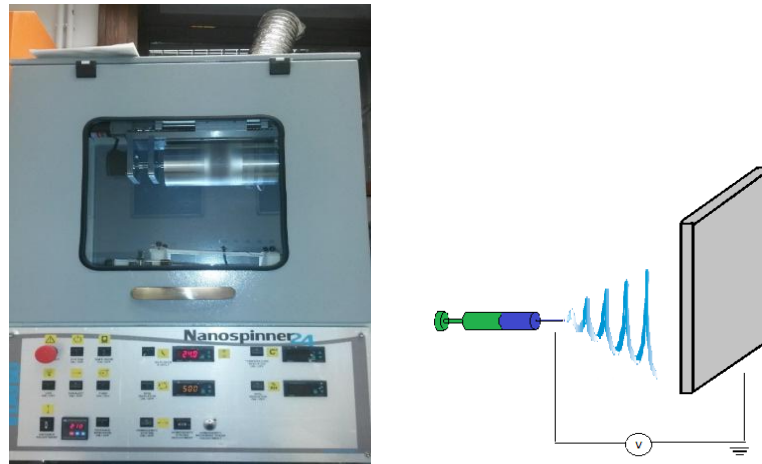


Figure 3. 1. Electrospinning machine and schematic view of the process.

TPU that was used as a polymer, which is called as C95, with high electrospinnability, relatively good rigidity, friction resistance, low thermal expansion and deformation, low creep behavior, gas permeability and good mechanical properties such as tensile strength and torsion modulus was supplied from BASF.

Firstly, electrospinning solution was prepared by TPU, DMF, NaCl and ethyl acetate. DMF was used as solvent of TPU and firstly added at reserved bottle with ratio of 74 wt% of total solution. Subsequently, 0.03 wt% NaCl was added to increase electrical conductivity of solution, and mixed for 15 minutes at ambient condition. Following the solution heated about 90 °C, TPU was supplemented with ratio of 13 wt%. Solution was stirred until being sure that polymer was completely dissolved. During that time, temperature of the solution was decreased to 75 °C. Ultimately, ethyl acetate was added to the solution with ratio of 13 wt% to provide required solution viscosity for fabrication process. The solution was stirred for a while and stirring operation was applied until the temperature was cooled down to room temperature. The solution picture is shown in the Figure 3.2., and it clearly shows its color and consistency.

The prepared TPU solution was electrospun onto PP substrate by these following electrospinning parameters;

- Applied voltage 24 kV

- Tip to collector distance 150 mm
- Feeding rate 0,65 mL/h
- Collector speed 200 rpm



Figure 3. 2. %13wt. TPU solution for electrospinning.

Collector was moved horizontally for homogenous distribution of NFs in a wide area and to obtain homogenous filter media. Dimensions of the prepared NFs were 44 cm height and 18 cm width. According to these dimensions, total filter area was 792 cm², two filter samples could be obtained for each produced electrophoretic deposited media. Electrospun nanofibers were dried at 60 °C for 1 hour to remove solvent.

3.3 Electrophoretic Deposition on Nanofibrous Structure

After the electrospinning, prepared nanofibers were cut into 22 x 18 cm dimension and dried at 60 °C. For the electrophoretic deposition process, AE8155, [ATTO, Japan] was used as power supplier. TiO₂ suspension with varying concentrations were used for electrophoretic deposition process (1, 5, 10 g/L). The mechanism of EPD on nanofiber is given in the Figure 3.3. Aluminum foil is layed out at bottom of the glass container before the suspension is filled. Then a 22 x 18 cm² plate was covered by aluminum foil to provide electrical conduction and after that nanofiber mat was covered onto aluminum foil. Then the voltage applied between aluminum foil (next to the nanofiber web) and other aluminum foil (bottom of the suspension) where the distance between electrodes is 2 cm. According to literature [92], high voltages (>50 V) and long deposition time (>5 min) causes formation of cracks in the coatings. Our experimental study was performed at 10 V and 300 sec samples.

Dipcoating samples were prepared to examine amount of TiO_2 . Prepared sample were shown in the Figure 3.4. Parameters are given in Table 3.1. and 3.2.

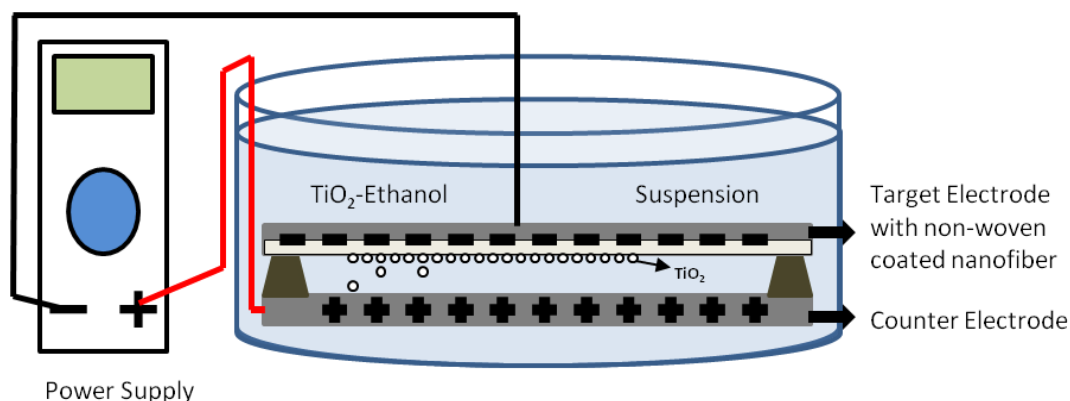


Figure 3. 3. Schematic and picture of EPD on nanofiber mat.

Table 3. 1. Experiments of electrophoretic deposited samples at nanofiber.

Experiment Number	Voltage (V)	Time (s)	Concentration (g/l)	TiO_2 per area (mg/cm^2)
NF-1	10	300	1	0,090
NF-2	10	300	5	0,266
NF-3	10	300	10	0,410

Table 3. 2. Experiments of dipcoated samples at nanofiber.

Experiment Number	Voltage (V)	Time (s)	Concentration (g/l)	TiO_2 per area (mg/cm^2)
Dipcoated Samples	0	300	1	0,046
	0	300	5	0,151
	0	300	10	0,278

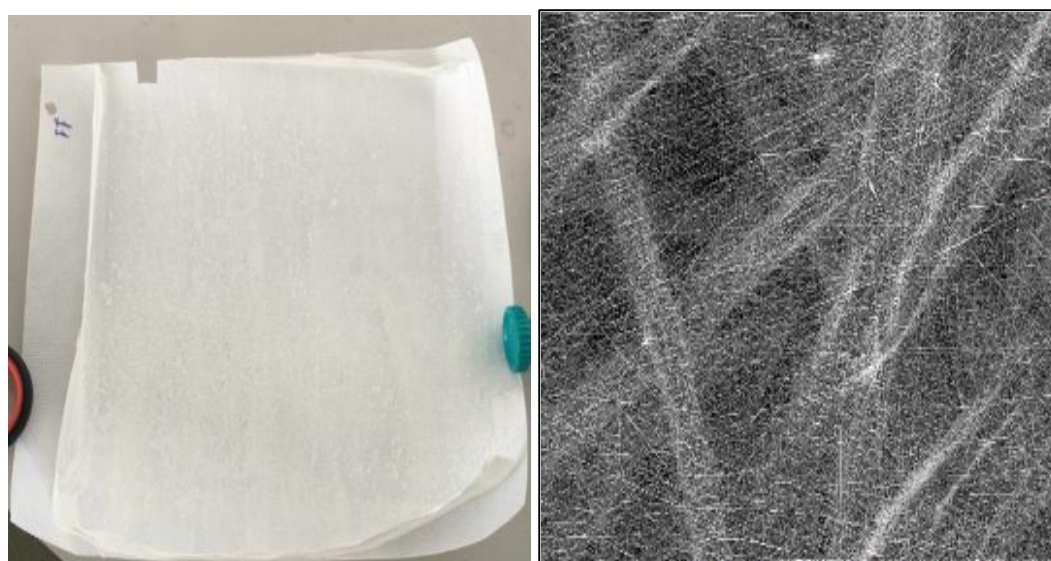


Figure 3. 4. Produced nanofiber filter and nanofiber structure with SEM picture.

3.4 Electrophoretic Deposition on Metal Meshes Structure

In this study, commercial TiO_2 (Degussa or Aeroxide P25) was deposited on stainless steel metal meshes and the samples were analyzed to see the effective physical parameters with Taguchi method. Firstly, stainless steel 316 meshes were cleaned up with detergent and acetone. After that, cleaned meshes were cut into $6 \times 10 \text{ cm}^2$ pieces. Samples were coated inside TiO_2 suspension according to the Taguchi method parameters. The schematic of deposition was shown in the Figure 3.5. Produced metal mesh filter was shown in the Figure 3.6.

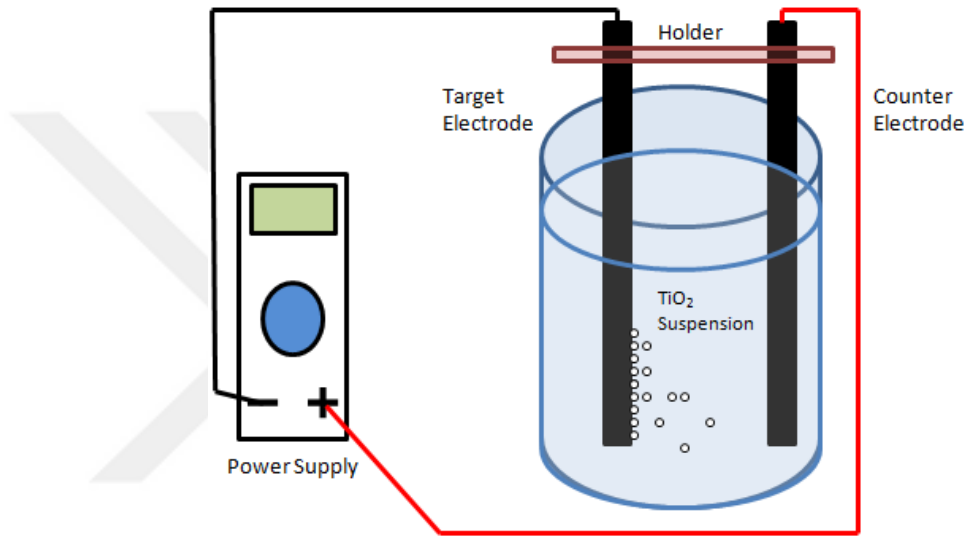


Figure 3. 5. Schematic of EPD on metal mesh structure.

Taguchi method helps to determine optimum parameters for electrophoretic deposition. According to Taguchi method, parameters were chosen as voltage, time and concentration, and output parameters as photocatalytic activity. So, the use of L9 table was decided for optimization. Their details were given in the Table 3.3.

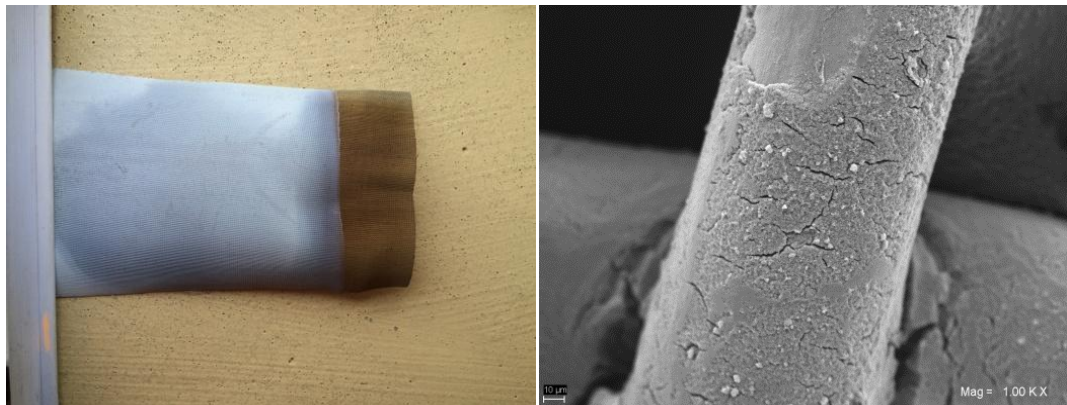


Figure 3. 6. Produced metal mesh filter and structure with SEM picture.

Table 3. 3. Taguchi (L9) optimization study of EPD on metal meshes.

Experiment Number	Voltage (V)	Time (s)	Concentration (g/l)	TiO ₂ per area (mg/cm ²)
SS-1	0	30	1	0,089
SS-2	10	300	1	0,091
SS-3	100	180	1	0,986
SS-4	0	180	5	0,041
SS-5	10	30	5	0,061
SS-6	100	300	5	4,040
SS-7	0	300	10	0,127
SS-8	10	180	10	0,131
SS-9	100	30	10	0,421

3.5 Decorated with Silver and Silver Doping

We had three concepts, to combine silver (Ag) and TiO₂ together;

The first one is the coating of Ag over TiO₂ using AgNO₃ solution. The second one is silver decoration by mechanical means in the solution state, and third one is silver doping inside of TiO₂. Schematic representations of the material designs were given in the Figure 3.7.

As the first approach, Ag decorated TiO₂, was produced which is the easiest way to change the electronic properties of TiO₂. Degussa P25 was mixed into AgNO₃ solution to obtain 2% mole of Ag over TiO₂ surface. Both of particles were put into distilled water and stirred at 24 h. After stirring operation, it was dried at 100 °C for 12 h. After that to improve anatase phase of TiO₂, was calcinated at 400 °C for 6h [93].

As a second approach, Ag nanoparticles were mixed with Degussa P25 and the details were given below at synthesis of silver nanoparticles topic.

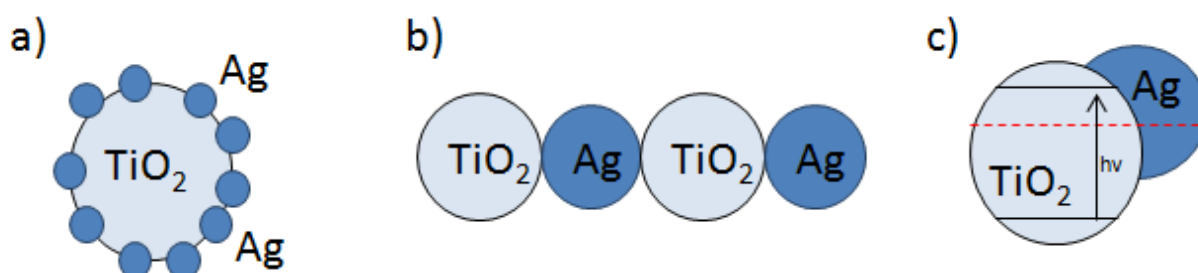


Figure 3. 7. a) Decoration of silver on TiO₂ using AgNO₃ solution, b) Mixture of silver and TiO₂ nanoparticles by mechanical mixing c) Silver doped TiO₂.

As the third approach, we aimed to insert Ag ions into TiO_2 crystal. Doping with Ag changes the crystal structure of TiO_2 , where Ti^{4+} ions on the anatase and Ag^+ ions are added into TiO_2 lattice structure. Ag^+ ions could not enter into the lattice of anatase phase to form a stable solid solution. Because of the radius of Ag^+ ion (ca. 126 pm) is much larger than of Ti^{4+} ion (ca. 68 pm). During the drying and calcination process, Ag^+ ions would gradually migrate from the volume of anatase grains towards the surface [91]. Sol-gel method is the most widely used method, where titanium tetraisopropoxide (TTIP) was used as TiO_2 precursor, and silver nitrate (AgNO_3) as the Ag precursor. 25 ml of TTIP was mixed in 48 ml acetic acid in vessel, while in another vessel 0.2866 g of AgNO_3 was added into 150 ml distilled water to obtain %2 Ag mole. After stirring the vessels at room temperature for 2 h separately, AgNO_3 + water solution was added slowly into TTIP and stirred for 12 h. After that, it was dried at 100 °C, and calcinated at 500 °C to obtain anatase crystalline structure [88].

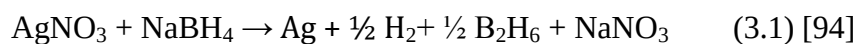
After preparation, particles diameter should be lowered to nano scale to obtain higher surface area. For that ball-milling was used for reducing the macrosize to nano, picture of ball-milling was used for 60 minute with 4 mm diameter of balls (Figure 3.8).



Figure 3. 8. Pictures of ball-milling.

3.5.1 Synthesis of silver nanoparticles

To obtain the Ag nanoparticles, 1mM of AgNO_3 solution in 15 ml water of AgNO_3 was mixed with NaBH_4 (2mM in 35 ml water) inside cold bath, according to (3.1) reaction,



AgNO_3 solution was added to NaBH_4 solution in ice bath. The solution was stirred till the change of color to pale yellow. Synthesized silver nanoparticles were washed with water and nanoparticles were picked up with centrifuge. Obtained particles were added into ethanol and after that, TiO_2 was added to ethanol+Ag suspension. After all these steps, TiO_2 +Ag nanoparticles (NP) suspension was ready to EPD process. Two different synthesized silver nanoparticles can be seen in the Figure 3.9, the left one is followed paper [94], and obtain the successful color (pale yellow), the other one (standing on right) is trial for more particles, but could not obtain yellow color, and is consisted macro particulate structure according to paper.

In table 3.4, TiO_2 per area value was given, otherwise their picture during EPD process was shown in Figure 3.10.

Table 3. 4. EPD of Ag modified TiO_2 at metal mesh.

<i>Experiment Name</i>	<i>Voltage (V)</i>	<i>Time (s)</i>	<i>Concentration (g/l)</i>	<i>Basis weight of the coating (mg/cm²)</i>
Ag Decorated	10	300	1	0,020
Ag Doping				0,012
Ag NP+ TiO_2				0,120

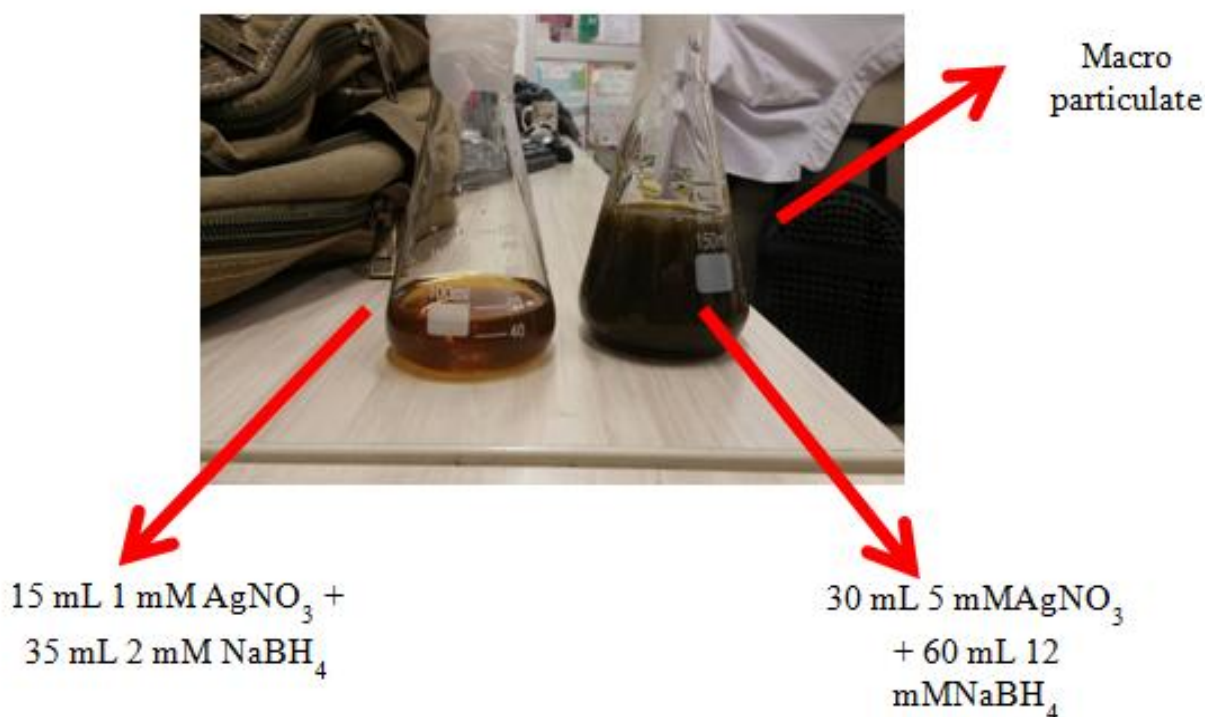


Figure 3. 9. Synthesized silver nanoparticles in colloidal state.

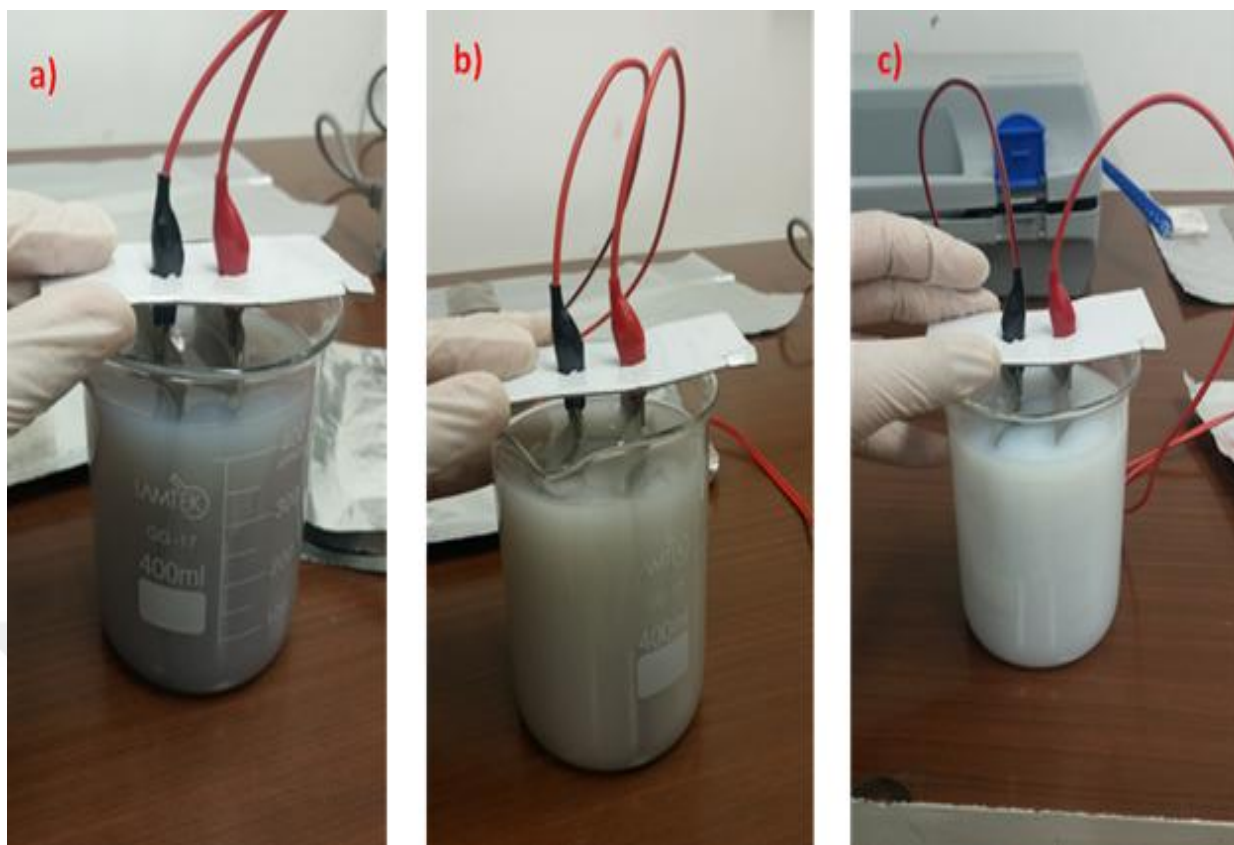


Figure 3. 10. Silver modified TiO_2 suspensions during EPD process a) Silver decorated TiO_2 , b) Silver doped TiO_2 , c) Silver nanoparticle mixed with TiO_2 .

3.6 Characterization of Filters and Particles

To investigate the coating morphology and uniformity samples were analyzed via scanning electron microscopy (SEM) Quanta FEG250 and Zeiss EVOMA10 model was used from MEMTEK, ITU and AKSA. Zeta potential value was measured from all suspensions to determine experimentally electrophoretic mobility, this measurement device model is Malvern Mastersizer in ITUPML. Crystalline phases of the Ag-doped TiO_2 nanoparticles were evaluated using X-ray diffraction (XRD), XRD model is Bruke D8 Advance in ITUPML. Ultraviolet-Visible Spectroscopy (UV-Vis) was done to obtain band-gap value for Ag decorated TiO_2 nanoparticles, as model Shimadzu UV2600+DRS in TEMAG Lab., ITU.

3.7 Photocatalytic Oxidation Performance of Filters Produced via EPD

To enlighten the PCO performance of the produced filters, two different PCO reactors were designed and manufactured. The systems are capable of analyzing filters with different sample sizes at different VOC concentrations.

3.7.1 VOC removal test system

VOC removal test system picture and schematic are shown in Figure 3.11. and 3.12. First of all, there was a compressed air gas tank and it was connected to the system with mass flow controller. After that, VOC generator generated VOC gases from the solution and VOC gases and air combined at cross-part. This prepared dirty air leaked into dampener. Subsequently, dirty gas entered photoreactor after the dampener. We had two different reactors for this removal tests. These reactor details are given below. Fully prepared nanofiber filters were cut about 15 cm diameter to fix in first generation photocatalytic reactor shape. For metal mesh samples cut about 6x8 cm dimension in a second generation. For the VOC removal test to be done at 120 ppm, ethanol with air through the reactor and datas were collected continuously. After that, UV light was opened with 14.6 mW/cm^2 during 60 minutes, after that it was allowed to pass through the mass spectrometry and determine the efficiency of removal ethanol.

Some specific parts of the test system need to be described in this subject. Mass flow controllers (MFC) were used to control the speed of air in all system and they came from Alicat Scientific brand and their maximum capacity is 10 l/min. These MFCs are controlled by digital and their sensibility is very high. Air speed was directly related with the concentration of VOC. In our experimental system air speed was designate at 0.8 l/min. VOC generator used liquid sources of VOC and the liquid VOC source was transferred to gas phase by the effect of diluent gas. Syringe pump was used for pushing liquid phase of VOC. Syringe pump (New Era NE-1000) level can set up for the calculation of desired value of ppm. Dampener is a tank, which is used for any condensation and it can be used with heat operation, but we did not use any temperature in our experimental. Mass spectrometry (MS) was used to behold the degradation mechanism and behavior of VOCs in the photoreactor. This device was ordered from Harrington HIDEN company, HPR 20 model. This instrument takes 12 mL/min gas from the system and analyzes the results under vacuum environment.

3.7.2 Design of PCO reactors

Two different PCO reactors were designed and manufactured, which are capable of analyzing filter with their different sizes at for different VOC concentrations.



Figure 3. 11. Figure of VOC removal test system.

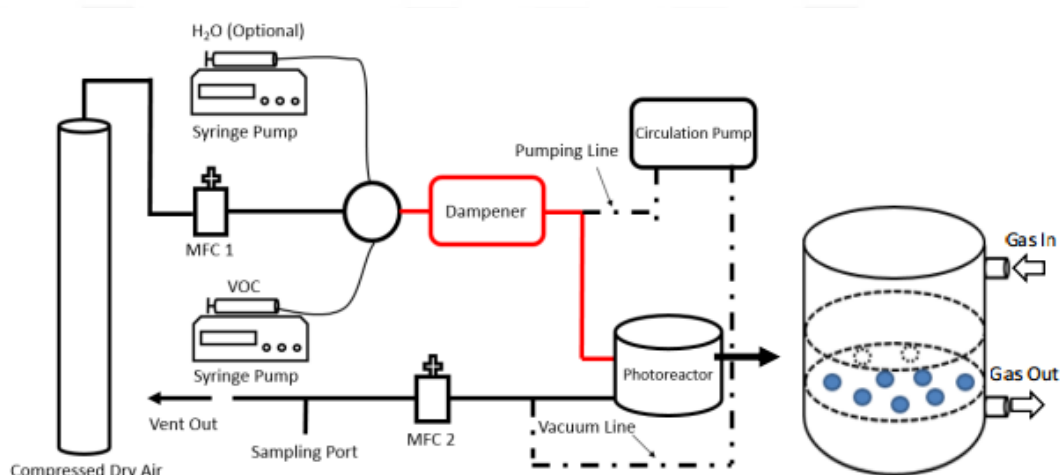


Figure 3. 12. Schematic of VOC removal test system.

3.7.2.1 PCO reactor, 1st Gen

PCO reactor, 1st Gen is a cylinder with 15 cm diameter, where the UV-LED and filter distance was kept 1.5 cm. UV-LEDs are energy efficient and Hg-free alternatives to conventional UV-lamps. UV-LEDs illumination at 365 nm wavelength was found to be appropriate according to previous literature [95]. 25 UV-LEDs (Nichia, NCSU033B model, Japan) were integrated over aluminum printed circuit board (PCB) with heat sink. These PCB materials is consisted of aluminum material coated with chemically and photonically inert material. Filters are illuminated directly with 90° degree by UV LEDs. Active site of the filter must be illuminated homogenously to obtain higher degradation efficiency from the filter. These LEDs have 120° degree viewing angle. The distribution of the illuminated area for different LED configurations were analyzed. Reactor design and photos under

high and low illuminations are shown in Figure 3.13. The system can be tested at different light intensities, and radiance levels, which also causes slight change in the temperature as given in Table 3.5.

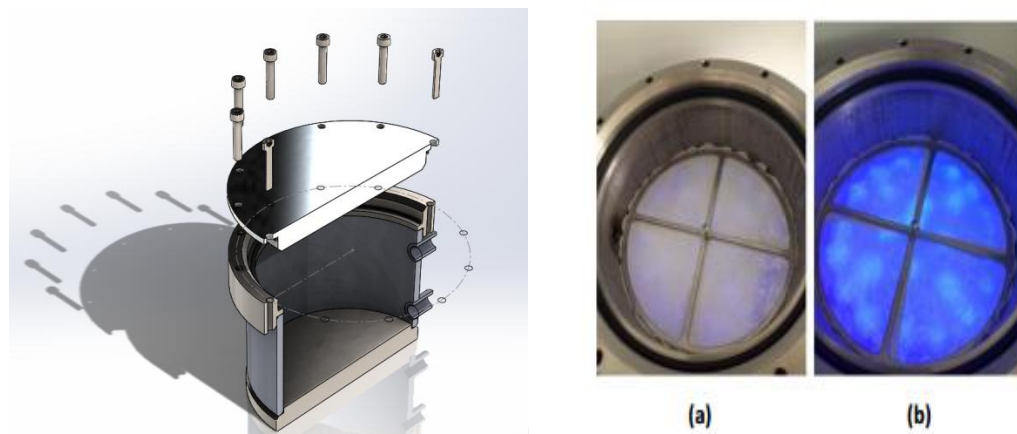


Figure 3. 13. 1st generation reactor with nanofiber a) Minimum light power
b)Maximum light power.

Table 3. 5. Temperature and radiance level of 1st generation reactor.

<i>Potentiometer Level</i>	<i>Radiance level (mW/cm²)</i>	<i>Temperature (C°)</i>
1	3.90	25,9
2	4.50	29,5
3	4.70	30,7
4	7.90	34,6
5	10.80	40,3
6	14.60	44,6
7	20+	54,6

3.7.2.2 PCO reactor, 2nd Gen

PCO reactor, 2nd generation reactor was manufactured from aluminum alloy and had dimensions of 60 x 80 x 310 mm and 1,48 l of inner volume. Totally 60 new UV-LEDs (NCSU276AT-Nichia, Japan) were attached on 5 aluminum PCB (Printed Circuit Board). This system is appropriate for multiple filter measurements. There are 6 pairs of electric connections and by changing the number of filters, UV-LEDs and fans, it is possible to make many variations such as 4 filter, 4 PCB and a fan or 2 filter, 2 PCB and 2 fan etc. Normally it has 4 slots as filter holder, but 5 pieces of filter holder can be mounted in the reactor when higher amounts of surface areas are required. Reactor shape and their pictures under illuminations are shown in the

Figure 3.14. This system tested at different light intensity of UV LEDs, for the temperature and radiance level, these results given in the Table 3.6.

Table 3. 6. Temperature and radiance level of 2nd generation reactor.

<i>Set Value (mAh)</i>	<i>Radiance level (mW/cm²)</i>	<i>Temperature (C°)</i>
75	13.96	48,7
100	14.30	49,3
125	15.77	52,2
150	19.90	58,7
200	20+	61,3

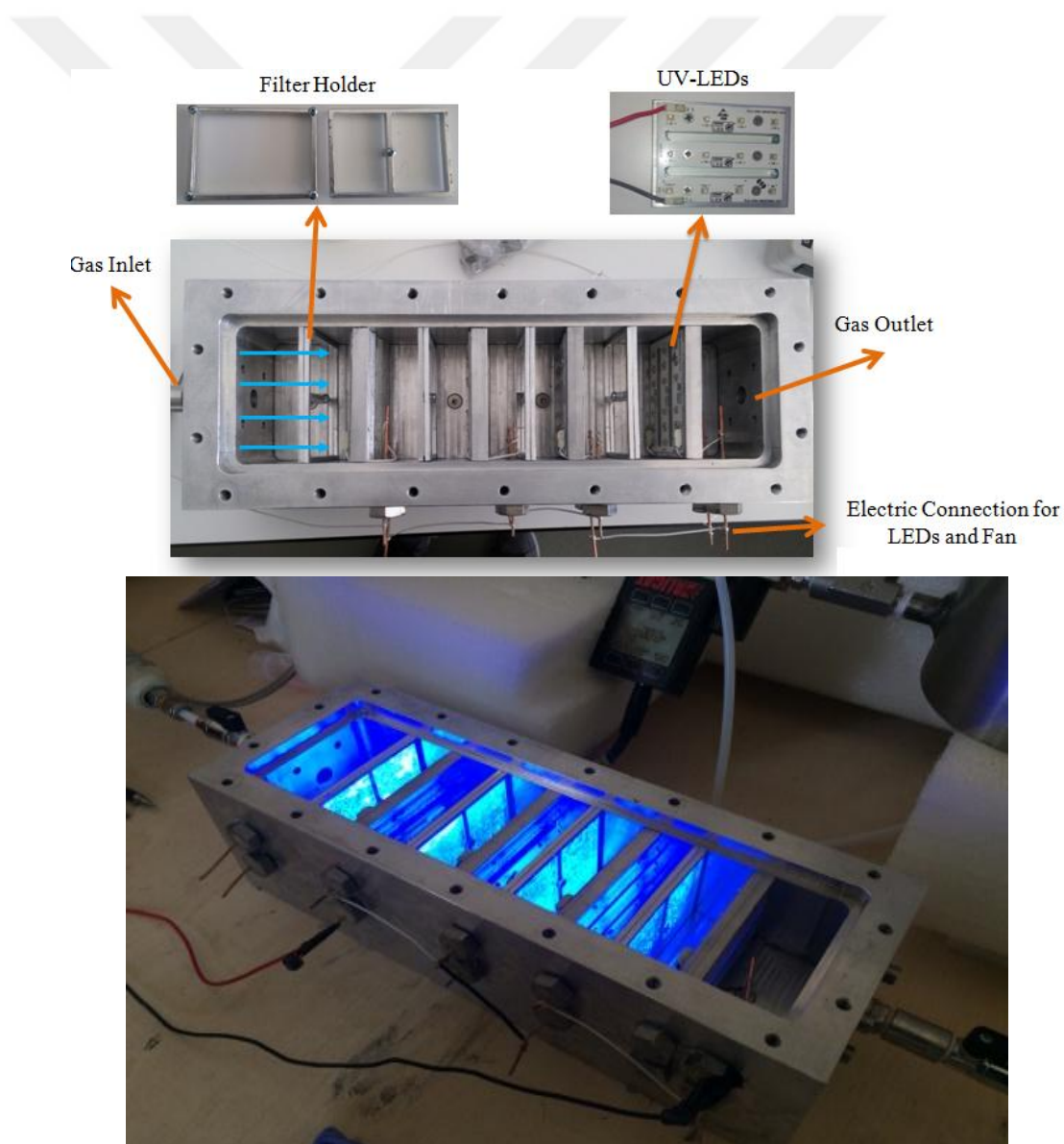


Figure 3. 14. Multiple filter reactor pictures (2nd Gen).

3.7.3 Ethanol removal tests

Prior to the ethanol removal tests, the system was purged and cleaned using air 6 bar pressure, and 0.8 l/min flow rate. Gas form ethanol was obtained using a VOC producer. For that liquid ethanol was pumped from syringe pump to obtain 120 ppm ethanol-air mixture. Air and liquid ethanol mixed at a cross-part, where ethanol phase changed from liquid to gas. After that gas form ethanol passed through the dampener and photoreactor. The produced VOC/air mixture was analyzed by mass spectrometry (MS), which was set to a balance value of 120 ppm. After reaching 120 ppm, UV light was turned on. Samples were illuminated under a power of 14.6 mW/cm² for 60 minutes. The remaining VOC concentration was measured continuously.

4. RESULTS AND DISCUSSION

The obtained results from the morphological and electrochemical characterization of TiO₂ and VOC photocatalytic performance tests were explained in this section.

4.1 Morphological Characterization

Morphological characterization was performed via scanning electron microscopy, XRD and UV-Vis analysis.

4.1.1 Scanning electron microscopy (SEM) results of the filters

SEM is an electron microscope, which constitute images of samples by scanning with a focused beam of electrons. These electrons directly hit the sample, and beams are scattered which is captured by a detector. In a detector, electrons produce signals, which draw surface morphology and structure. SEM is an important instrument for the PCO activity studies to investigate the distribution and dispersion of TiO₂ on the surface.

4.1.1.1 Nanofibrous filters

As seen in Figure 4.1, TiO₂ particles were coated solely on nanofibrous structure via EPD method. So called “infiltration” mechanism was utilized for these samples. As expected higher concentrations (10 g/l) resulted with thicker coating layer. For the 10 g/l sample, it nearly gave a film structure where fibers cannot be seen (Figure 4.1c). It seems 5g/l suspension was already sufficient to coat the fiber surface completely, while 1 g/l suspension was not enough to cover the nanofibers. However, 5 g/l suspension still provides a fibrous upper surface, which increases the total area of the surface. On the other side for a dead-end type filtration procedure, film like coating of 10 g/l suspension would not be possible, since it will reduce the permeability significantly.

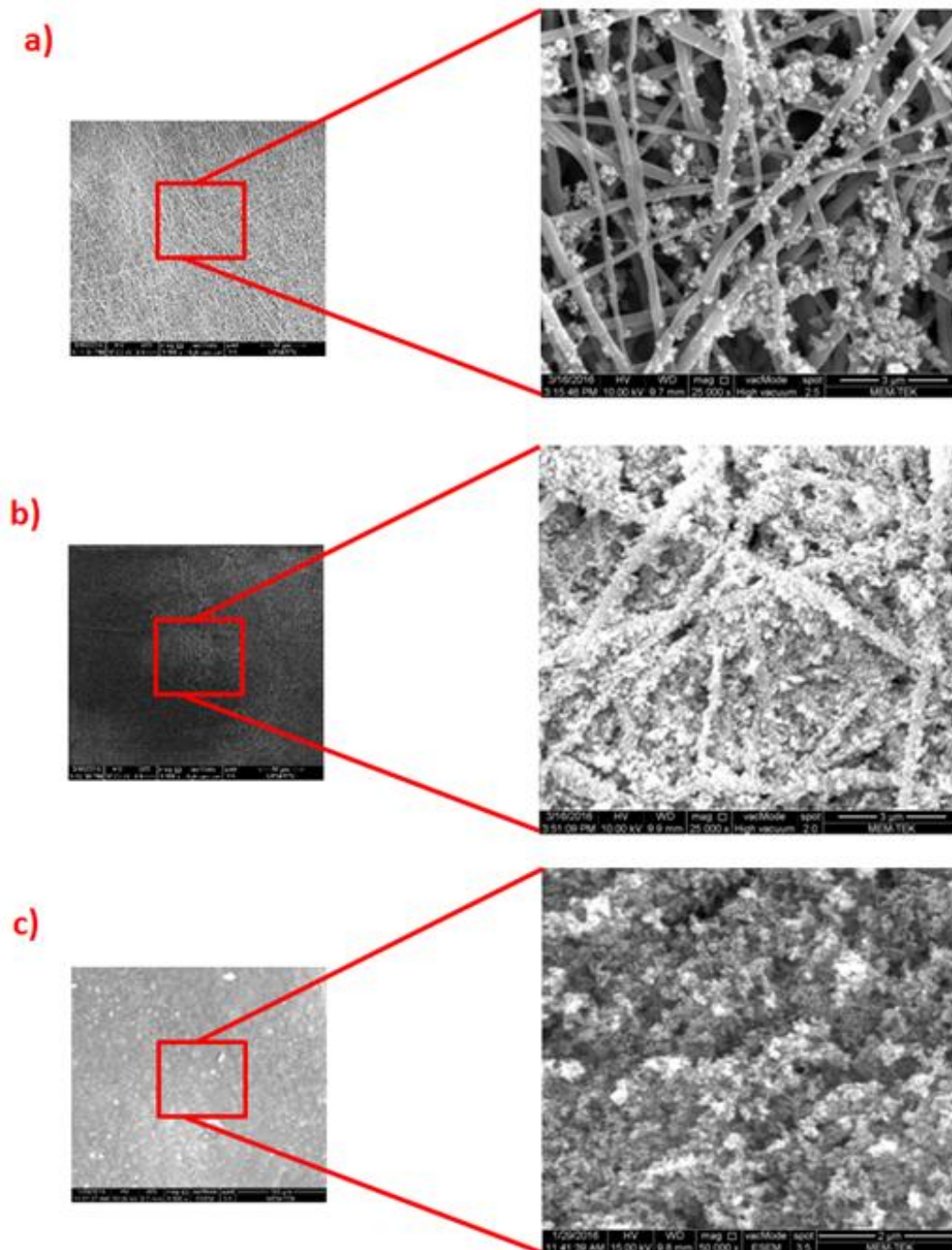


Figure 4. 1. SEM images of nanofibrous filters coated with EPD method for varying suspension concentrations. a) 1 g/l b) 5 g/l c) 10 g/l.

4.1.1.2 Metal mesh filters

For the metal mesh filters, to obtain the optimum EPD parameters, Taguchi method was utilized. For that, we run 9 tests, considering potential, time and concentration as the main parameters. In Figure 4.2, 4.3 and 4.4, optimization study with Taguchi method samples and 4.5, on metal mesh filters and Ag modified TiO_2 coated samples can be seen.

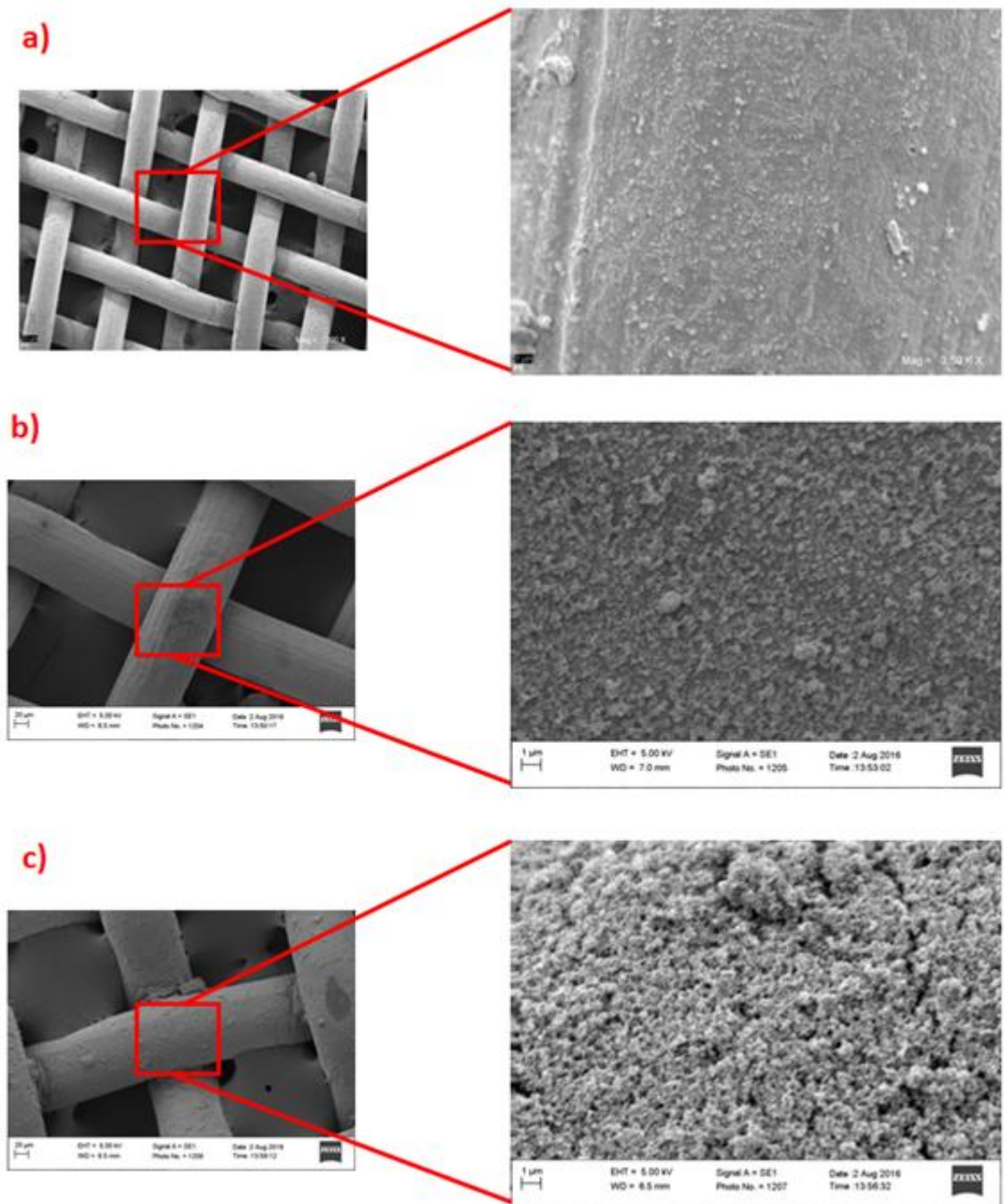


Figure 4. 2. SEM images of metal mesh filters coated with EPD method with using Taguchi optimization method a) 0 V-30 sec, b)10 V-300 sec, c)100 V-180 sec in 1 g/l.

In Figure 4.2, SEM images of the samples coated using TiO_2 suspension of in 1 g/l concentration were given. As seen in Figure 4.2c, a potential with 100 V provided the most homogenous coating in 1 g/l samples. This sample has a nanoparticulate topology, which increases the illuminated surface area. Metal wires had local clusters of TiO_2 when the potential was 0V (Figure 4.2a) EPD is apparently more effective than dipcoating to deposit TiO_2 on metal surface. As seen in Figure 4.2b, the coating thickness was not uniform even for long EPD times, probably due to low potential.

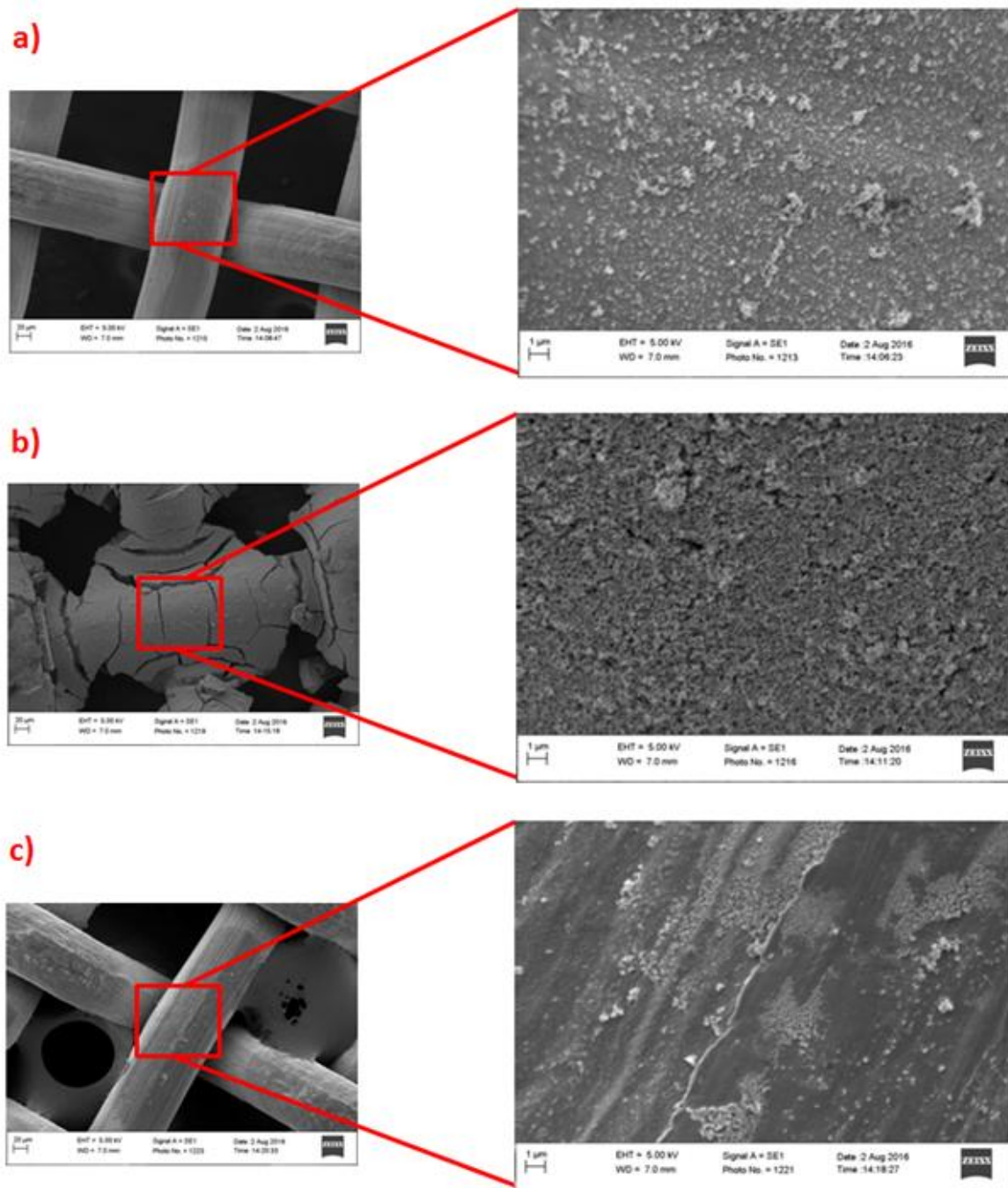


Figure 4. 3. SEM images of metal mesh filters coated with EPD method with using Taguchi optimization method a)0 V-180 sec, b)100 V-300 sec, c)10 V-30 sec in 5 g/l.

In Figure 4.3, SEM images of the samples coated from 5 g/l concentration of TiO_2 suspension were given. Figure 4.3b shows that the highest TiO_2 loading was achieved from the suspension of 5 g/l at a potential of 100 V for 300 sec. Without applying a potential, a nonuniform coating was obtained as seen in Figure 4.3a. For the shorter timings nanoparticles formed totally nonuniform aggregates (about 1 μm). However for the 100 V potential and 300 sec coating, TiO_2 nanoparticles formed a coating of 20 μm thickness which seems pretty brittle with the cracks. Such a

structure was not found to be feasible since under high air flow it might form particulate contamination in the air. As a conclusion it can be deduced that low and no potentials and shorter times were not sufficient to obtain homogenous layer.

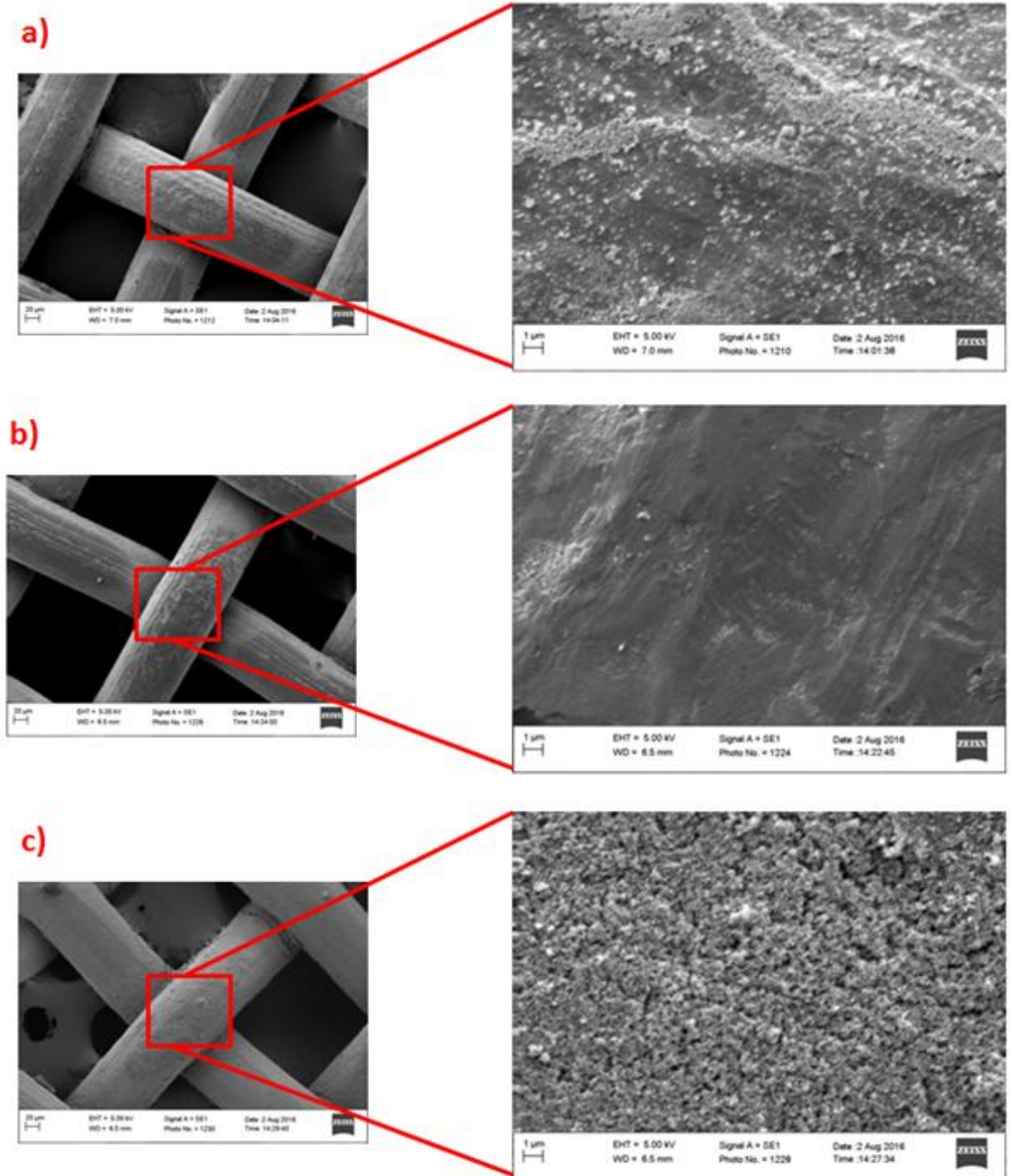


Figure 4. 4. SEM images of metal mesh filters coated with EPD method with using Taguchi optimization method a)10 V-180 sec, b)0 V-300 sec, c)100 V-30 sec in 10 g/l.

In Figure 4.4, SEM images of the samples coated from 10 g/l concentration of TiO_2 suspension were given. Interestingly higher concentration did not lead to thicker

coatings, which might be reduced zeta potential at high TiO_2 concentrations. A high potential and very short coating time was enough for uniform coating as shown in Figure 4.4c. Insufficient coating thickness with non-homogenous structure was observed in Figure 4.4a. In Figure 4.4b, TiO_2 coating was only observed on metal wire crosses.

As given in Figure 4.2c, 1 g/l concentration of TiO_2 suspension and potential of 100 V provided the most homogenous coating in all samples. The most dominant parameter on coating thickness is found to be the suspension concentration [96]. Apart from the suspension concentration, the EPD process is related with time and voltage. In addition to these information, their loading weight and surface morphology gave hints about their PCO removal efficiency results. Figure 4.3b shows that the highest TiO_2 loading was achieved from the suspension of 5 g/l at a potential of 100 V for 300sec. However the thickest coating might not provide the best PCO results, because of the agglomeration. In Figure 4.2c, 4.3b and 4.4c samples coating homogeneity seems better than other samples, hence one can expect higher PCO efficiencies. On the other side dipcoated samples as shown in Figure 4.2a, 4.3a, 4.4b, did not provide uniform TiO_2 coating. However, EPD timing was not very effective on loading of TiO_2 . Besides dipping type and lifting speed might also effect coating performance. In this thesis, EPD process is compared to dipcoating and their common parameter is time and concentration.

Ag doped and decorated particles did not provide homogenous coating, most probably because of the precipitation and dimensions of particles. However it was possible to coat Ag nanoparticle P25 ($\text{AgNP}+\text{TiO}_2$) mixture since the particles still have very small diameters and masses. As seen in Figure 4.5a, Ag decorated TiO_2 got larger and precipitated during washing. In Figure 4.5b, is $\text{AgNP}+\text{TiO}_2$, as are mentioned before, Ag NPs are 12 nm and it could not close over the TiO_2 . So, TiO_2 can see on the metal mesh surface. In Figure 4.5c, is doped TiO_2 as it seems on the surface, some agglomerated particles are stand, it seems not agglomerated, these particles are bigger than P25 TiO_2 . As a result, according to SEM results, Ag doped and decorated TiO_2 is very few on the structure, so does not expect high removal efficiency to compare well coated ones. On the other hand, for this modification it can be tested at visible light and compare to non-modified TiO_2 .

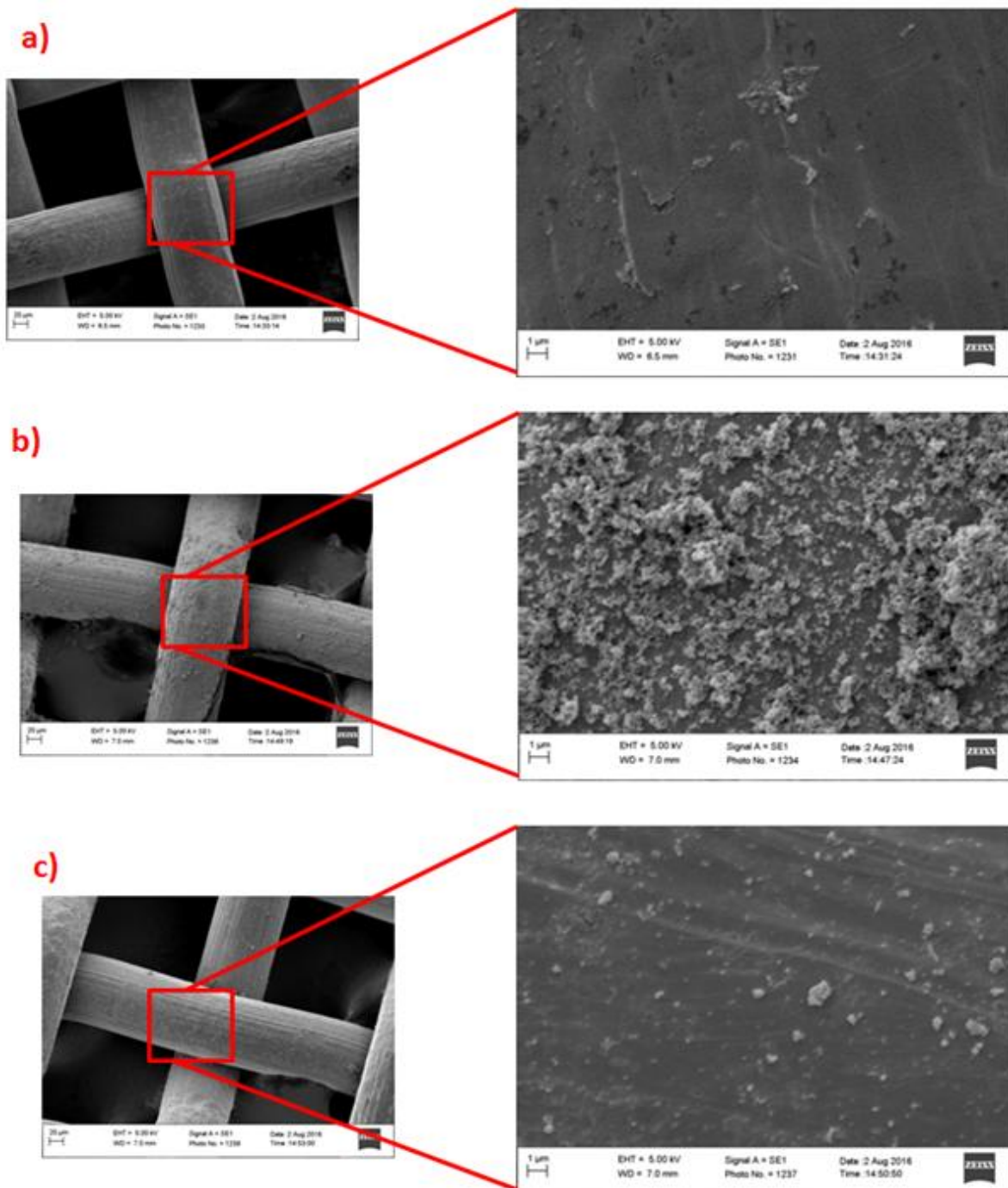


Figure 4. 5. SEM images of metal mesh filters coated with EPD method Ag modified TiO_2 a) Ag decorated TiO_2 , b) Ag nanoparticle with TiO_2 , c) Ag doped TiO_2 .

4.1.2 XRD results of the filters

XRD is an analytical method to determine crystalline structures of TiO_2 , which uses X-ray beams. X-ray beams are reemitted into many specific directions at different angles according to shape and the size of the crystal. These diffracted beams are detected and processed. The diffraction angles and intensities are measured according to Bragg's law and structure of the crystal is explained thereof.

As seen in Figure 4.6. Ag doped TiO_2 has similar anatase phase such as TiO_2 . Peaks marked “A” and “R” correspond to anatase and rutile phases, respectively. As it was seen in figure, the most intensity peak is around 25.3° anatase (101), 37.7° anatase (103), 48.3° anatase (200), 54.2° rutile (211), 62.7° rutile (002), 70.1° rutile (301) and 75.1° anatase (215). Metallic silver crystals had a peak at 38.1° and 44.3° , which were assigned to crystal 111 and 200 plane [97]. The Ag(111) peak at 38.1° in Ag-doped TiO_2 pattern was overlapped of TiO_2 (103,004,112) anatase peak. From the literature [97], gave as the same level about 25° , 37° and 48° in Ag-doped TiO_2 samples.

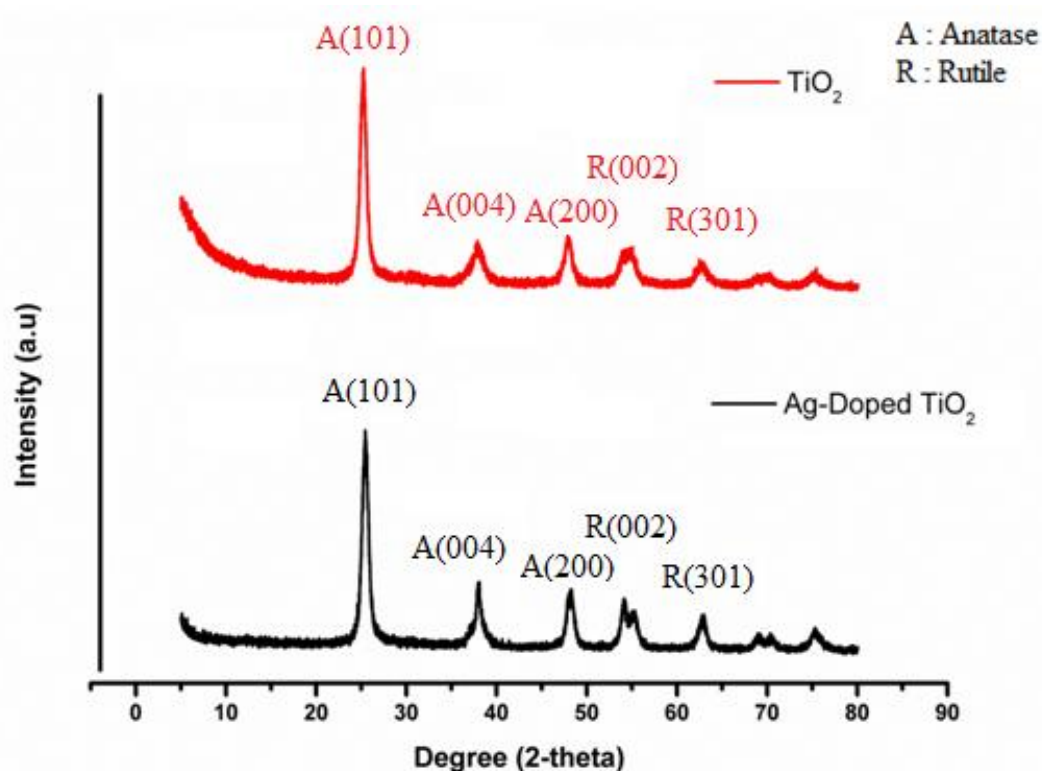


Figure 4. 6. XRD patterns of TiO_2 and Ag doped TiO_2 .

Also from the XRD patterns, crystallite sizes could be determined via Scherrer equation. Crystallite sizes were calculated to be 11.5 nm and 9.55 nm, Ag doped TiO_2 and TiO_2 respectively.

4.1.3 Ultraviolet-visible spectroscopy results

Ultraviolet-visible spectroscopy (UV-Vis) is based on absorption and reflectance spectroscopy of light through materials in the ultraviolet-visible region. It measures intensity of light passing through the sample and compares it to the intensity of before passed through the sample. These two intensities divide in each other, and

results give transmittance, the absorbance is directly related with absorbance. The detector measures these values and gives data about their absorbance or reflectance. After that, it could be calculated with Kubelka-Munk to determine band-gap of materials.

In Figure 4.7, the commercial TiO₂ (Degussa P25) band gap value was shown, and the value is about 3.33 eV, as in the literature. With Ag decoration sample band gap value was reduced to about 2.80 eV (Figure 4.8), which is sufficient for visible light activation. On the other hand the smaller band-gap might lead faster PCO kinetics due to lower recombination rates.

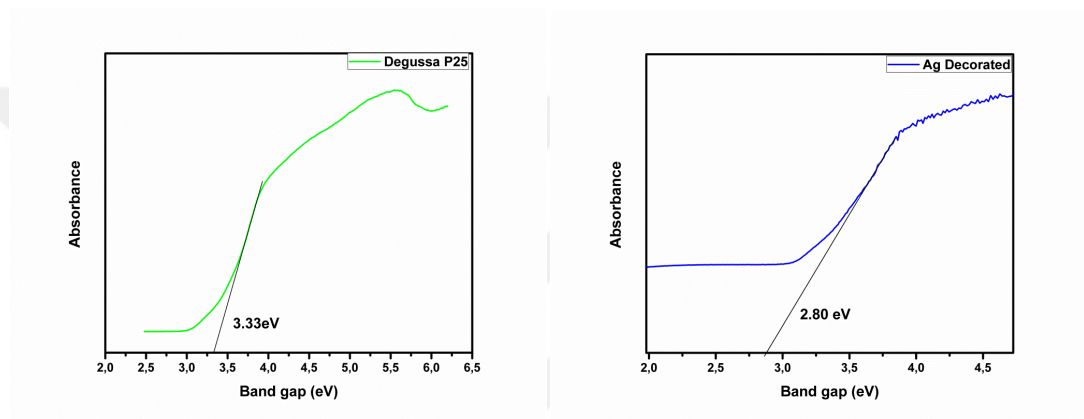


Figure 4. 7. Band gap value of TiO₂ (Degussa P-25) and Ag-decorated TiO₂

4.2 Zeta Potential Results of TiO₂ Suspension

Zeta potential value is critical for the electrophoretic deposition (EPD) process [63]. Deposited mass is related with electrophoretic mobility. Electrophoretic mobility is related directly proportional with zeta potential value. Zeta potential values were measured from the TiO₂ suspensions.

In Table 4.1, 1 g/l suspensions had 2.5 mV zeta potential, its means that, flocculation can occur in suspension. 1 g/l suspension had low electrophoretic mobility value to compare with others. 5 g/l had 5.2 mV zeta potential, so their electrophoretic mobility value much higher than 1 g/l. Deposition process worked better than 1 g/l suspension. Lastly, at Table 4.1, clearly shows that, the highest zeta potential value was obtained using the 10 g/l suspension. This result gave hint about the EPD process working better than the other suspensions. However, high TiO₂ loading does not mean always advantageous for coating. So, Taguchi optimization study results are given in this thesis scope.

Table 4. 1. Zeta potential values of TiO₂ suspensions.

<i>Suspension rate (g/L)</i>	<i>Zeta Potential (mV)</i>	<i>pH value</i>
1	2,5	7,6
5	5,2	7,1
10	8,0	7,0

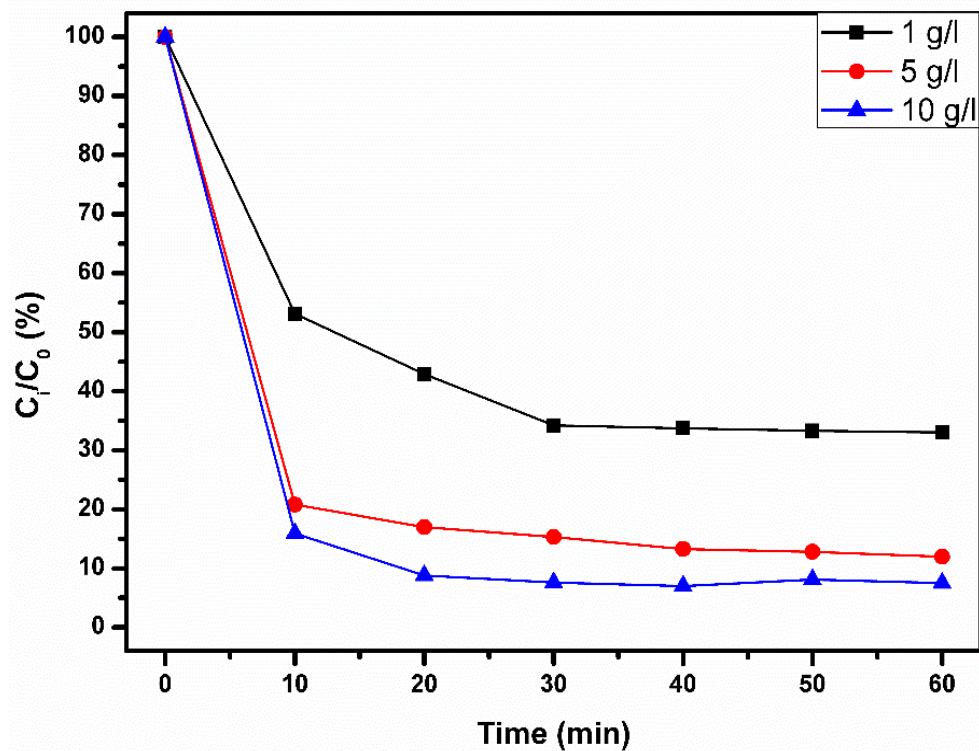
4.3 VOC Removal Performances

VOC removal performance test results given at that parts with using different filters.

4.3.1 Nanofibrous filters, infiltrated

As a result of PCO tests, 3 different concentrations of TiO₂ solution was decided to choose 10 V have less agglomeration to 100 V for the results of SEM samples. On the other side, time is important parameter loading TiO₂, was chosen about 300 second to compare with 30 second coated one.

The most effective parameters were found to be 10 V potential and 300 sec EPD time. As shown in Figure 4.8, 1 g/l filters had almost %60 ethanol removal efficiency, while 5 g/l and 10 g/l had almost %90 removal efficiency within half an hour.

**Figure 4. 8.** Photocatalytic test results of EPD on nanofiber structure.

4.3.2 Metal mesh filters

Coatings of the metal meshes were applied according to Taguchi optimization, which was tabulated in Table 4.2. According to the results, the optimized coating parameters was found to be 100 V potential, 180 sec EPD timing while concentration of TiO_2 suspension is 1 g/l. This sample was labeled as SS-3 and it exhibited 96.5% PCO removal efficiency. On the other hand, according to SEM images the most heavily coated sample was SS-6, which was produced at a potential of 100 V, for 300 sec with the 5 g/l TiO_2 suspension. However this sample has 86,7% removal efficiency of ethanol. It might be due to topology of filters. In SS-3 sample has a nanometric scale particles are seen, but in SS-6 the surface is more covered with aggregates. According to these results, the third efficient filter is SS-9 filter, which was produced at a potential of 100 V for 30 sec from the TiO_2 suspension of 10 g/l. The filter removal efficiency was measured to be 59.6%. Interestingly 100 V potential lead to better results compared to those produced at lower potentials.

After performing PCO tests, analysis of means (ANOM) and analysis of variance (ANOVA) was done. The best parameters can be given for voltage; 100 V, for time; 300 sec and for concentration; 10 g/l according to the ANOM results. Besides, according to the ANOVA results, the voltage affected the PCO result about 89.3%, while time and concentration affect result 9.5%, 1.2% respectively. It can be concluded that only the voltage is reliable since the p value was smaller than 0.5.

Table 4. 2. Taguchi optimization study of PCO efficiency of TiO_2 via EPD method.

<i>Experiment Number</i>	<i>Basis weight of TiO_2 coating (mg/cm^2)</i>	<i>PCO Removal Efficiency (%)</i>
SS-1	0,089	17,7
SS-2	0,091	18,0
SS-3	0,986	96,5
SS-4	0,041	18,3
SS-5	0,061	29,4
SS-6	4,040	86,7
SS-7	0,127	57,1
SS-8	0,131	35,6
SS-9	0,421	59,6

In Figure 4.9, 4.10 and 4.11 PCO performance of the samples prepared according to Taguchi optimization were given.

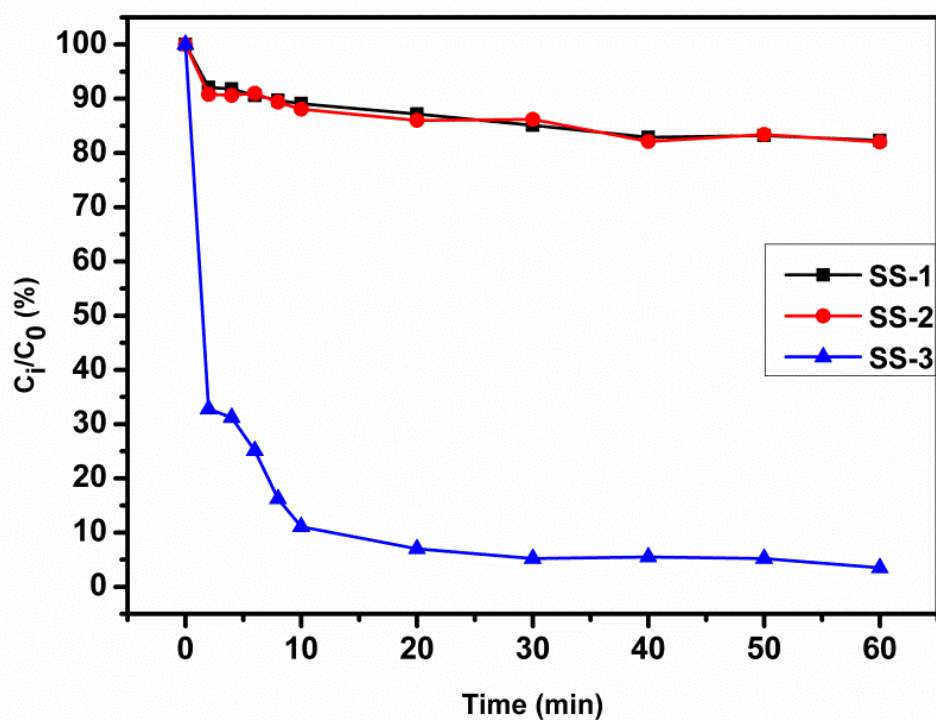


Figure 4. 9. PCO removal efficiency of stainless steel mesh samples coated with 1g/l TiO₂ suspension (SS-1; 0 V-30 sec, SS-2;10 V-300 sec, SS-3; 100 V-180 sec).

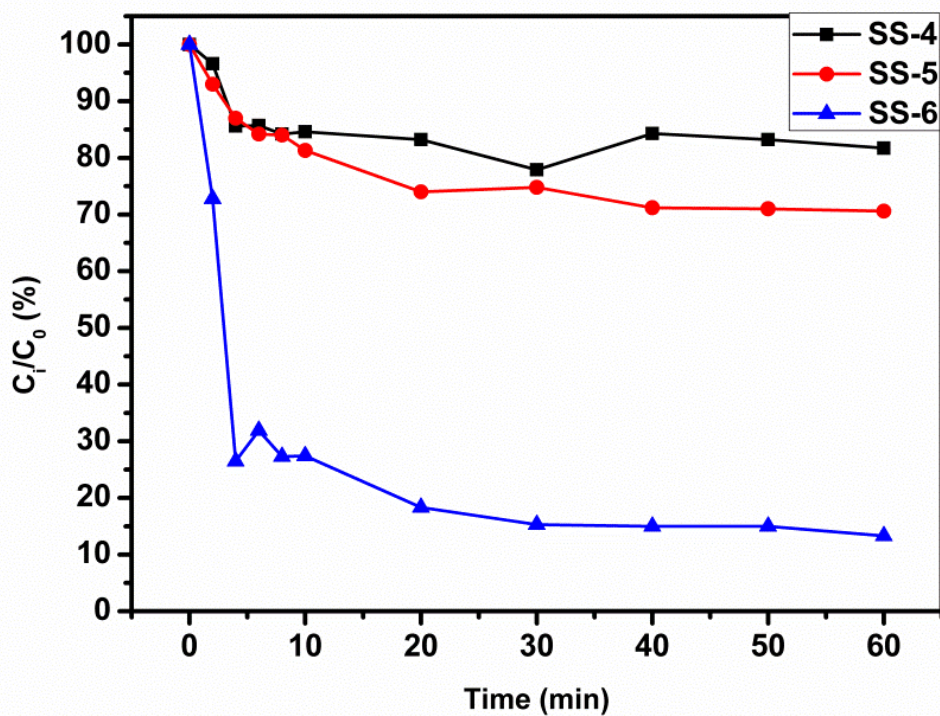


Figure 4. 10. PCO removal efficiency of stainless steel mesh samples coated with 5g/l TiO₂ suspension (SS-4; 0 V-180 sec, SS-5; 10 V-30 sec, SS-6; 100 V-300 sec).

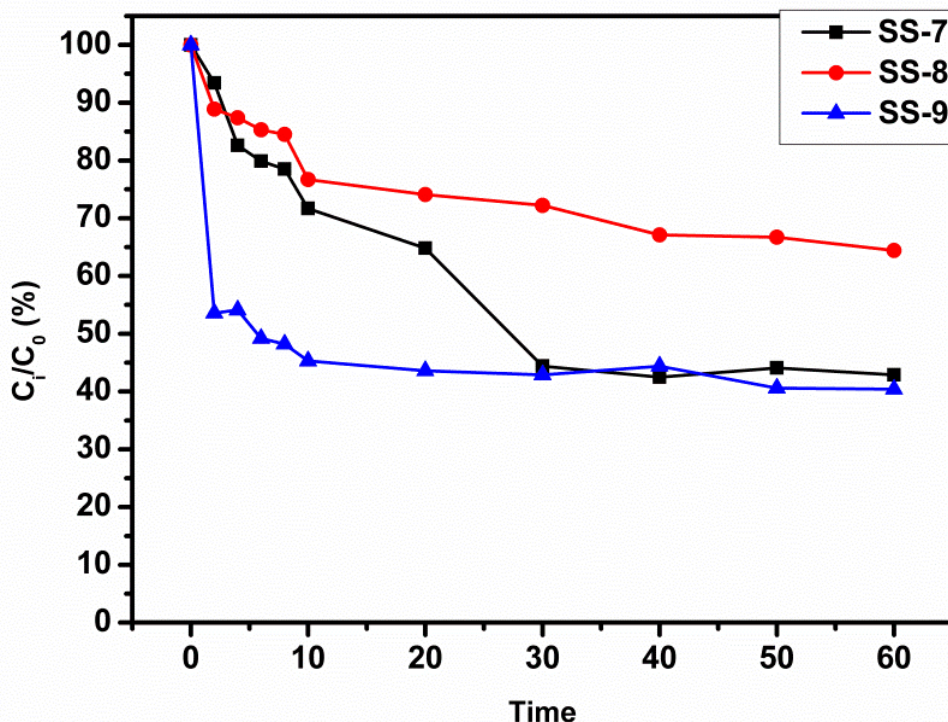


Figure 4. 11. PCO removal efficiency of stainless steel mesh samples coated with 10g/l TiO_2 suspension (SS-7; 0 V-300 sec, SS-8; 10 V-180 sec, SS-9; 100 V-30 sec).

4.3.3 Filters modified with silver

As explained in the previous chapters there were 3 approaches for the filter preparation with silver/ TiO_2 mixtures. Ag decorated and doped TiO_2 had large diameters, which is due to agglomeration and following precipitation. Ag-doped nanoparticles had a diameter up to about 886 nm. In Figure 4.12 the precipitation is clearly seen, which did not allow effective EPD process. But for the filters SS-1, SS-2, SS-4 and SS-5, there were close amounts of TiO_2 on their surface. It was possible to analyze performance of Ag modified (Ag doped TiO_2 , Ag decorated TiO_2 and Ag NP+ TiO_2) samples, which was summarized in Figure 4.13.

The comparison of PCO removal efficiencies of Ag modified TiO_2 samples and $\text{TiO}_2(\text{P25})$ samples were given in Table 4.3. These table shows that Ag-decorated and Ag modified TiO_2 has some potential for photocatalytic activity. Doped one has 24,8% removal efficiency of ethanol (this materials does not contain P25). So, if Ag decorated and doped TiO_2 can be attached on substrate surface, their PCO removal efficiency gets higher. AgNP+ TiO_2 mixture has better results from the others, because it can be deposited on substrate.

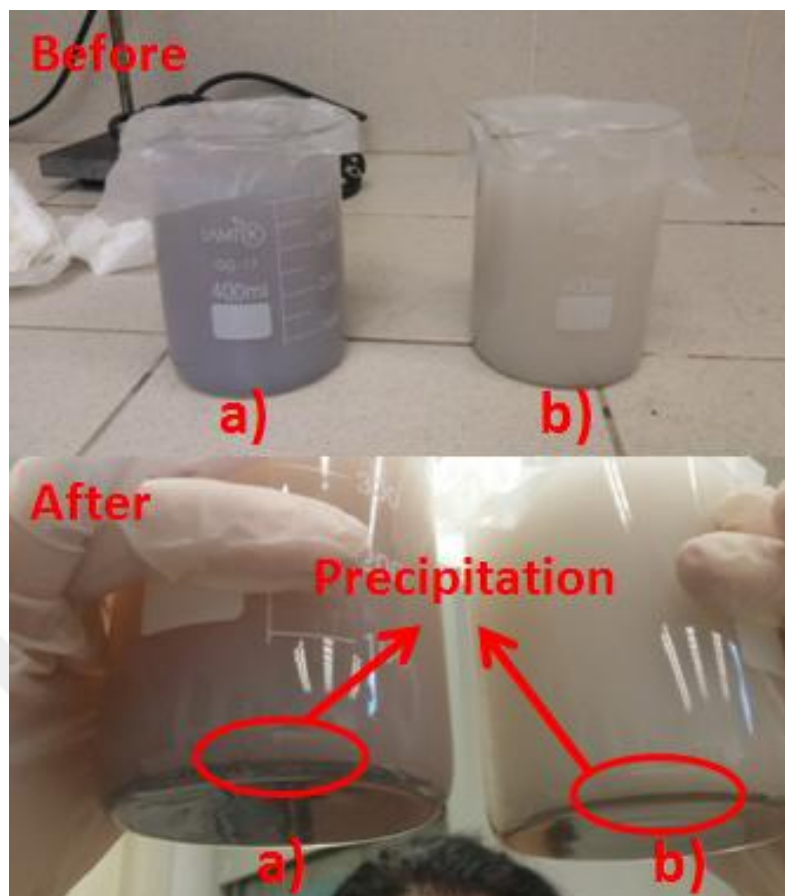


Figure 4. 12. Silver modified TiO_2 suspensions before and after EPD process a) Silver decorated TiO_2 , b) Silver doped TiO_2 .

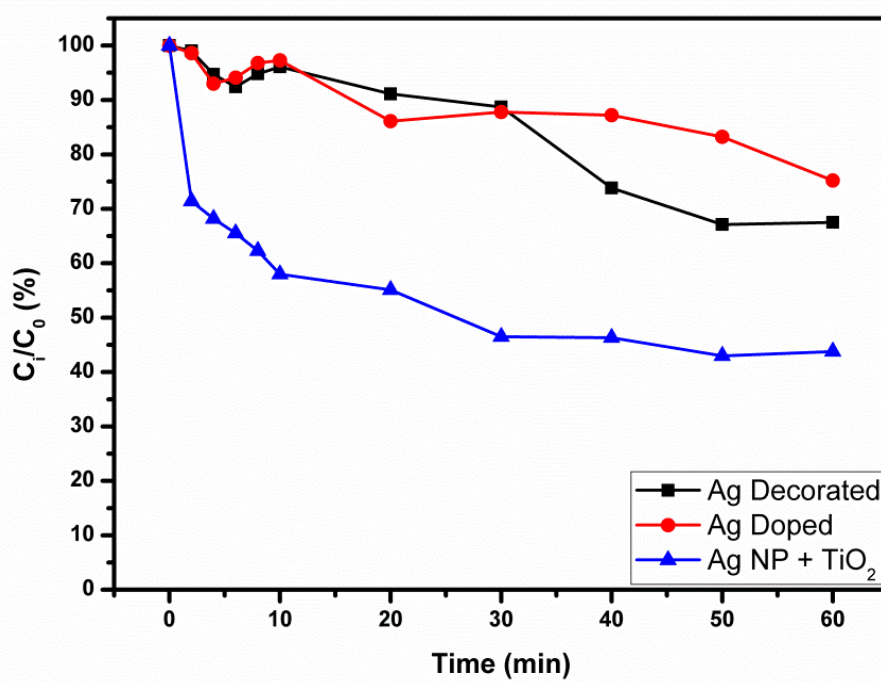


Figure 4. 13. PCO activity results of Ag modified TiO_2 .

Table 4. 3. Performance comparison of Ag modified TiO₂ and TiO₂ samples.

<i>Experiment Number and Name</i>	<i>Basis weight of TiO₂ coating (mg/cm²)</i>	<i>PCO Removal Efficiency (%)</i>
SS-1	0,089	17,7
SS-2	0,091	18,0
SS-4	0,041	18,3
SS-5	0,061	29,4
Ag Decorated	0,020	32,5
Ag Doped	0,012	24,8

Ag NP+P25 sample is comparable with SS-7 and SS-8 samples due to their similar TiO₂ amount. Table 4.4 shows the performance of these samples. Ag NP addition seems to be not very effective on PCO removal efficiency. But, it might be effective under the visible light, as indicated in the literature [88].

Table 4. 4. Comparison of removal efficiency in AgNP+TiO₂ and TiO₂ samples.

<i>Experiment Number and Name</i>	<i>Basis weight of TiO₂ coating (mg/cm²)</i>	<i>PCO Removal Efficiency (%)</i>
SS-7	0,127	57,1
SS-8	0,131	35,6
Ag NP+P25	0,120	56,2



5. CONCLUSION AND RECOMMENDATIONS

In this thesis, electrophoretic deposition method was chosen for the fast and uniform coating ability. Photocatalytic system experiments that were performed at low and high VOC concentrations where ethanol was used specifically.

Photocatalytic oxidation performance was analyzed using two different reactors that are capable of measurements at ppm and ppb scales. Polymeric nanofibers and metal meshes were used as the substrates.

Nanofibrous filters coated via EPD exhibited up to 90% ethanol removal performance. Samples coated with suspensions of 1 g/l and 5 g/l concentrations have 45% and 80% ethanol removal efficiency, respectively. Nanofibrous substrate provided the advantages such as high surface area and usefulness for depth filters. However it cannot operate at higher temperatures because of polymeric structures. For the high temperature operation such as plane, cars, factory chimney; metal mesh come into play and their results have also been taken.

EPD was also performed on metal meshes. Taguchi statistical optimization method was carried out. According to ANOM the optimized parameters were 100 V, 300 seconds and 10g/l concentration of TiO_2 . However, according to ANOVA results voltage is the most critical parameter for photocatalytic activity with a 89.3% effect, on the other hand time effects 9.5% and concentration effects with only 1.2%.

From the conducted studies, metal surface is successfully coated with the electrophoretic deposition by TiO_2 with Ag modification. Though it was a non-uniform coating, Ag decorated samples had 32.5% and Ag doped samples had 24.5% removal efficiencies against ethanol. Beside Ag NP+ TiO_2 coated samples exhibited 56.2% removal efficiency. According to these results, Ag modified samples might be promising if it is fixed to the surface properly. Their estimated PCO results might be in the order of Ag NP+ TiO_2 < Ag decorated < Ag doped, if it fixed within the same amount of modified TiO_2 on metal mesh.

As for the future studies on nanofibrous structures, their heat resistance might be improved with novel materials such as ceramic reinforced nanofiber materials or glass fibers. We have achieved the highest efficiency with the least amount of TiO_2 on nanofibrous structures. In addition faster and more economical methods might be recommended for nanofiber production methods (solution blowing, centrifugal spinning). For metal mesh coating it can be pleated to improve the surface area or another metallic structures can be used such as metal foam which have higher surface area from metal mesh.

Ag modified TiO_2 coating can be a good alternative, though severe agglomeration was observed in this study. Some sort of chemical methods or chemicals might be used to enhance the zeta potential or to decrease modified TiO_2 particles' diameter, these development will lead to high performance filters. And these filters can be tested in visible light and can be compared under UV and visible light. Apart from the Ag, it can be modified with different metals or metal oxide. In addition to that, it will exhibit good performance filters when combined with carbon compounds or carbon adsorbers.

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