ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INDIUM ZINC OXIDE (IZO) NANOCOMPOSITE SYNTHESIS BY SOL-GEL AND ULTRASONIC SPRAY PYROLYSIS METHODS

M.Sc. THESIS

Zeynep Tutku ÖZEN

Department of Metallurgical and Materials Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ULTRASONİK SPREY PİROLİZ(USP) VE SOL-GEL YÖNTELERİ İLE İNDİYUM ÇİNKO OKSİT (IZO) NANOKOMPOZİT TOZ ÜRETİMİ

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HAZİRAN 2019

Zeynep Tutku ÖZEN, a M.Sc. student of ITU Graduate School of Science Engineering and Technology 506161441, successfully defended the thesis/dissertation entitled "INDIUM ZINC OXIDE (IZO) NANOCOMPOSITE SYNTHESIS BY SOL-GEL AND ULTRASONIC SPRAY PYROLYSIS METHODS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 03.05.2019
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To my family,

FOREWORD

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ABBREVIATIONS

ITO	**:** Indium Tin Oxide
IZO	**:** Indium Zinc Oxide
LCD	**:** Liquid Crystal Display
LED	**:** Light Emitting Diode
MB	**:** Methylene Blue
MOCVD	: Metal Organic Chemical Vapor Deposition
OLED	: Organic Light Emitting Diode
RAPET	: Reaction under Autogenic Pressure at Elevated Temperature
SEM-EDS	: Scanning Electron Microscopy – Energy Dispersive Spectroscopy
TCO	**:** Transparent Conducting Oxide
TFT	**:** Thin Film Transistor
USP	**:** Ultrasonic Spray Pyrolysis
UV	**:** Ultra Violet
XRD	: X-Ray Diffraction

SYMBOLS

M	: Molarity
°C	: Degree Celcius
µm	: Micrometer
nm	: Nanometer
ml	: Mililiters
K	: Kelvin
MPa	: Mega Pascal
Hz	: Hertz
α	: Alpha
2θ	: 2 Theta
eV	: Electron Volt
rpm	: Rounds per Minute
ρ	**:** Density

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INDIUM ZINC OXIDE (IZO) NANOCOMPOSITE SYNTHESIS BY SOL-GEL AND ULTRASONIC SPRAY PYROLYSIS METHODS

SUMMARY

Research on the production of particles with a size smaller than 100 nanometers has become very important, recently. The nanoparticles generally have very different properties due to their very high surface to volume ratio. Today's technology deals with the production of these unique materials. Production methods of nanoparticles have been classified as TOP-DOWN methods and BOTTOM-UP methods. In this context, nanomaterials are being used industrially. This rapid increase in the development of nanomaterials has enabled the development of new nanomaterials, testing their properties, researching new applications and working on different synthesis mathods. A great number of nanoparticles / nanomaterials are produced and tested under laboratory conditions. Due to process control challenges and high production costs, industrial scale production and commercial applications still have difficulties.

Another rising scientific topic is composite materials. Composite materials can be defined as composition of at least two different materials in order to use them where single one of them is not sufficient for related application. For example, carbon fiber composite material is made of acrylic fiber, tar and nylon. This composite is 4-5 times lighter and almost 3 times stronger than steel. Thanks to these features, carbon fiber is used in automotive, aerospace, construction and energy applications.

Nanocomposites combines the benefits of both nanoparticles and composite materials. Nanocomposites improve the properties of materials such as mechanical properties, electrical conductivity, flame retardancy, thermal stability, chemical stability, optical clarity, surface appearance etc. Nanocomposite materials are currently used as thin film capacitors for computer chips, solid polymer electrolytes for batteries, automotive engine parts and fuel tanks, impellers and blades, oxygen and gas barriers. The usage area of nanocomposites is very famous and developing research area.

Indium zinc oxide (IZO) is a nanocomposite having the properties of indium oxide (In_2O_3) and zinc oxide (ZnO). Transparency, gas permeability and conductivity of zinc oxide make it one of the best candidate for optoelectronic and photocatalytic applications. IZO is one of the comparable nanocomposite with indium tin oxide (ITO) which is also used for these applications due to its similar transparency in solar spectrum and sheet resistance. However, IZO is more stable chemically than ITO.

IZO is studied mostly to be synthesized as a thin film in literature. Scientist have produced these nanoparticles by chemical vapor deposition, electron beam deposition and pulsed laser ablation tachniques. Synthesis of indium zinc oxide nanocomposite powders is studied very less in literature.

This thesis investigates the production of IZO nanocomposite particles by relatively economical techniques (Ultrasonic Spray Pyrolysis and Sol-Gel) and XRD, SEM-EDS and Raman Spectrometer analyzes of produced particles. In addition,1 to 1 Zinc oxide (ZnO) and indium oxide (In_2O_3) nano-composite particles production is done instead of, indium doped Zinc oxide (ZnO). Finally, the results of the characterization studies of IZO nano-composite particles analyzed were compared with the literature.

For the synthesis of Indium Zinc Oxide (IZO) nanocomposite particles, Indium nitrate and Zinc nitrate hexahydrate salts and pure water were prepared. The prepared solution was used in the production of IZO by both USP and Sol-Gel method. USP method working conditions; 1.3 MHz ultrasonic frequency, 600°C operating temperature and 3 hours operating time. Experiments were performed in air (1L / min). The Sol-Gel method is also included by the bottom-up approach, such as the USP. The method is primarily based on the formation of the Sol, followed by Gel formation and drying of the formed gels. The gels formed were filtered and dried with filter paper. In this study, it was determined that calcination can be carried out at 600°C and 700°C regarding to DSC-TGA analysis carried out before.

X-Ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Energy Distribution Spectroscopy (EDS) and Raman Spectroscopy analysis techniques were used for characterization studies of IZO nanocomposite powders produced after experimental studies. The XRD analysis results of the IZO nanoparticles produced by USP and Sol-Gel techniques, including both In_2O_3 and ZnO peaks, are evidence that the composite structure is formed. According to SEM-EDS analysis, the morphology and chemical composition of IZO nanoparticles produced by both methods were analyzed. According to the analysis results, no impurity was found in IZO nano-composite particles.

SEM analysis gives information about the morphology of the particles synthesized. According to this analysis, it was observed that IZO nanocomposite particles produced by Sol-Gel method were synthesized more intensively than particles synthesized by USP method (more particles) and the particle sizes were smaller. Particle sizes of USP synthesized IZO nanoparticles are ranging between 100-600 nm, while Sol-Gel synthesized IZO nanoparticles have 50-200 nm particle sizes. Effects of acidic catalisor usage on Sol-Gel technique is aldo investigated. As a result acidic catalisor addition causes 200-400 nm particles while acidic catalisor free samples have 30-100 nm particle sizes. Effects of proces temperature can be summarized as, lower process temperatures leads homogenous particle distribution, while higher temperatures leads wider particle size tolerances. On the other hand, when looking at particle morphologies, it was observed that IZO nano-composite powders synthesized by USP method have more spherical morphology than those synthesized by Sol-Gel method. IZO nanocomposite particles produced by Sol-Gel method and calcined at 700°C were investigated by Raman Spectrometry. The results were compared with the literature and found to be consistent with the literature.

ULTRASONİK SPREY PİROLİZ(USP) VE SOL-GEL YÖNTELERİ İLE İNDİYUM ÇİNKO OKSİT (IZO) NANOKOMPOZİT TOZ ÜRETİMİ

ÖZET

Son zamanlarda nanoteknoloji ile ilgili yapılan çalışmalar bir çok farklı alana temas etmeye başlamıştır. Nano boyutlu malzemelerin gelişimindeki bu ivme, kendilerinin hacimsel boyutlu hallerinden çok farklı özellikler sergilemesine bağlanmaktadır. Günümüz teknolojisi nanopartikülleri aşağıdan yukarı ve yukarıdan aşağı şeklinde gruplandırılan üretimlerinin maliyetlerinin azaltılması ile de uğraşmaktadır. Bu kapsamda oldukça popüler bir çalışma alanı olan nanomalzemeler, endüstriyel olarak da kullanılmaya başlanmıştır. Nanomalzemelerdeki gelişimin bu hızla artması, yeni nanomalzemelerin geliştirilmesi, özelliklerinin test edilmesi, yeni uygulamaların araştırılması ve farklı sentez yöntemleri üzerine çalışmalar yapılması gibi farklı alanlarda istihdam sağlamıştır. Günümüzde çok sayıda nanopartikül/malzeme laboratuvar koşullarında üretilip, test edilmektedir. Proses kontrol zorlukları ve yüksek üretim maliyetleri nedeni ile endüstriyel ölçekli üretim ve ticari uygulamalarında hala zorluklar vardır.

Nanomalzemelerin endüstride yer edinmesiyle gelişen teknoloji zaman zaman farklı uygulamalarda saf nanomalzemelerle de yetinememeye başlamıştır. Nanomalzemelerin yapısal ve fonksiyonel özellikleri çok bileşenli nanomalzeme sentezi ile mümkündür. Süreç mükemmelliği, maliyet azaltma ve ileri teknolojiler kapsamında geliştirilmek istenen malzeme çalışmaları nano-kompozit malzemelere yönelmeye başlamıştır. Nano-kompozit malzemeler iki veya daha çok bileşenden oluşan, nano malzemelerin bir araya gelerek kendilerinden daha iyi özelliklere sahip yeni bir malzeme oluşturduğu malzeme grubudur.

Günümüzde üretilen nanopartiküller tıp, kimya, haberleşme, optik, elektronik gibi çok önemli sektörlerde kullanılmaktadır. İletkenler, yalıtkanlar, katalizörler, kendi kendini temizleyen kumaş ve boyalar, ilaçlar, antimikrobiyal malzemeler, arıtma sistemleri ve bilgi saklama ortamları nanomalzemeler kullanılarak üretilmektedir. Örneğin, silikat parikülleri gaz bariyeri sağlamaları için kullanılabilir. Böylelikle polimer bazlı plastik filmlerin nemlenmesi sağlanır ve bu filmlerden üretilen gıda paketlerinin içinde bulunan gıdaların kuruması önlenmiş olur. Silisyumkarbür (SiC) nanopartikülleri Magnezyum içerisinde kullanılarak hafif ve dayanıklı bir kompozit malzeme oluşturur. Silisyumdioksit (SiO_2) kristal nanopartikülleri, karbon fiberler arasındaki boşlukları doldurarak spor ekipmanlarındaki mukavemeti arttırır. Gümüş (Ag) nanopartikülleri, kumaşlarda kullanıldığında bakterileri öldürerek, kumaşın koku tutmamasını sağlar. Çinko oksit (ZnO) nanopartikülleri, kaplama malzemesi olarak kullanılır ve odun, plastik ve tekstil ürünlerini mor ötesi (UV) ışınlardan korumaktadır.

İndiyum çinko oksit (IZO) nano-kompozit partiküllerinin araştırma konusu olması, günümüzde transparan ve iletken bir kaplama olarak özellikle LCD ve OLED teknolojilerinde kullanılan indiyum kalay oksit (ITO) nano partiküllerine bir

alternatif aranmasıyla ortaya çıkmıştır. ITO, iletken olması ve görünür ışık dalga boylarında transparan olması sebebiyle transparan iletken oksitlerin (TCO) kullanıldığı uygulamalarda önemli bir malzemedir. Transparanlık, gaz geçirgenliği ve iletkenliği düşünüldüğünde IZO, ITO'ya alternatif olabilecek bir malzemedir. IZO'nun bu özellikleri yanı sıra kimyasal olarak daha stabil bir malzeme olması da bu malzeme üzerine yapılan çalışmaların sayısını arttırmıştır.

Literatürde IZO genelde ince film kaplama olarak çalışılmıştır. Bilim insanları bu malzemeyi kimyasal buhar biriktirme (CVD), elektron demeti biriktirme ve darbeli lazer uzaklaştırma gibi yöntemlerle sentezlemiştir. Ayrıca literatürde genelde IZO nano-kompozit olarak değil, indiyum doplanmış çinko oksit şeklinde üretilmiştir.

Bu çalışmada İndiyum Çinkooksit (IZO) nano-kompozit partiküllerinin, diğer yöntemlere kıyasla daha kolay ve ekonomik olan, Ultasonik Sprey Piroliz (USP) ve Sol-Gel yöntemleri ile üretimi yapılarak, XRD, SEM-EDS ve Raman spektrometresi ile yapısal karakterizasyon çalışmaları yapılmıştır. Ayrıca, Çinko oksite (ZnO), İndiyum dopantı yerine 1'e 1 ölçülerinde İndiyum oksit (In_2O_3) ve Çinko oksit (ZnO) içeren İndiyum Çinko oksit (IZO) nano-kompozit tozu sentezi üzerine çalışılmıştır. Son olarak analizi yapılan IZO nano-kompozit partiküllerininkarakterizasyon çalışmalarının sonuçları literatür ile karşılaştırılmıştır.

Indiyum Çinko oksit (IZO) nano-kompozit parçacıklarının sentezi için İndiyumnitrat ve Çinkonitrat hegzahidrat tuzları ve saf su kullanılarak 0,1 M başlangıç çözeltileri hazırlanmıştır. Hazırlanan bu çözelti hem USP hem de Sol-Gel yöntemi ile IZO üretiminde kullanılmıştır. USP yöntemi çalışma koşulları; 1,3 MHz ultrasonik frekans, 600°C çalışma sıcaklığı ve 3 saat çalışma süresidir. Deneyler hava ortamında (1L/dak.) gerçekleştirilmiştir. Sol-Gel yöntemi de USP gibi aşağıdan yukarı yaklaşımına dahil olan bir yöntemdir. Yöntem öncelikle Sol oluşumunu, ardından Gel oluşumunu ve oluşan jellerin kurutulması esaslarına dayanmaktadır. Oluşan jeller filtre kağıdı ile süzülmüş ve kurutulmuştur. Kurutulan jellerin kalsinasyonuna yönelik tapılan DSC-TGA analizinden bu çalışmada, 600°C ve 700°C sıcaklıklarında kalsinasyon işlemlerinin yapılabileceği belirlenmiştir.

Deneysel çalışmalar sonrasında üretilen IZO nano-kompozit tozların karakterizasyon çalışmaları için X-Işınları Difraktometresi (XRD), Taramalı Elektron Mikroskobu (SEM) ve Enerji Dağılım Spektroskopisi (EDS) ve Raman Spektroskopisi analiz tekniklerinden faydalanılmıştır. USP ve Sol-Jel teknikleri ile üretilen IZO nanopartiküllerinin XRD analiz sonuçları, hem In_2O_3 hem de ZnO piklerini içermesi kompozit yapının oluştuğunun bir kanıtı olarak karşımıza çıkmaktadır. Bu doğrulama literatürdeki değerlere göre ve Xpert yazılımı kütüphanesinde ICDD 01-075-1533 kart numarası ile yer alan çinkooksit ve ICDD 03-065-3170 kart numarası ile yer alan indiyumoksit pikleriyle uyumuna bakılarak yorumlanmıştır.

SEM-EDS analizi sonuçlarına göre, her iki yöntemle de üretilen IZO nanopartiküllerinin morfolojileri ve kimyasal bileşimleri analiz edilmiştir. Kimyasal analiz sonuçlarına göre IZO nano-kompozit partiküllerinde empüriteye rastlanmamıştır. Sentezlenen indiyumoksit nanopartikülleri elemental olarak yalnızca indiyum ve oksijen, çinkooksit nanopartikülleri yalnızca çinko ve oksijen, IZO nanopartikülleri ise yalnızca indiyum, çinko ve oksijene sahiptir.

SEM analizi ile sentezlenen parçacıklarının morfolojisi hakkında bilgi sahibi olunmuştur. Bu analize göre Sol-Gel yöntemi ile üretilen IZO nano-kompozit parçacıklarının, USP yöntemiyle sentezlenen parçacıklara göre daha yoğun sentezlendiği (daha fazla parçacık) ve parça boyutlarının daha küçük olduğu gözlenmiştir. USP yöntemi ile üretilen nanopartiküller parka boyutları 100-600 nm arasında değişirken, Sol-Gel yöntemi ile üretilen nanopartiküller 50-200 nm arasında değişen parka boyutlarına sahiptir. Öte yandan, parça morfolojilerine bakıldığında, USP yöntemi ile sentezlenen IZO nano-kompozit tozlarının, Sol-Gel yöntemi ile sentezlenenlere göre daha küresel morfolojiye sahip oldukları görülmüştür. Farklı sıcaklıkta gerçekleştirilen proseslerin etkisi parka boyut dağılımını etkilemiştir. 600°C'de prosese tabi tutulan nanopartiküllerin parça boyutları ±100 nm toleransında değişirken, 700°C'de prosese tabi tutulan nanopartiküllerin parça boyutları ±250 nm toleransında dağılım göstermiştir. Sol-Gel prosesinde asidik katalizör olarak kullanılan sitrik asit kullanımı parça boyutunda artışa sebep olmuştur. Sitrik asit kullanılmadan hazırlanan çözeltide parça boyutu 30-100 nm arasında değişirken, sitrik asit eklenen çözelti ile sentezlenen indiyumoksit nanopartiküllerinde parça boyutu 200-400 nm bandında gözlemlenmiştir.

Sol-Gel yöntemi ile üretilmiş ve 700°C'de kalsine edilmiş IZO nanokompozit partikülleri Raman Spektrometrisi ile incelenmiştir. Elde edilen sonuçlar literatür ile karşılaştırılmış ve literatürdeki verilerle uyumlu olduğu tespit edilmiştir.

1. INTRODUCTION

The word “Nano” means dwarf in latin language. Today, nano word is used for the one in a billion of any physical magnitude. The length unit nanometer stands for the one in a billion of a meter or in other words one in a million of a milimeter. Figure 1.1 indicates some particles which can not be seen by eye in the nanometer scale.

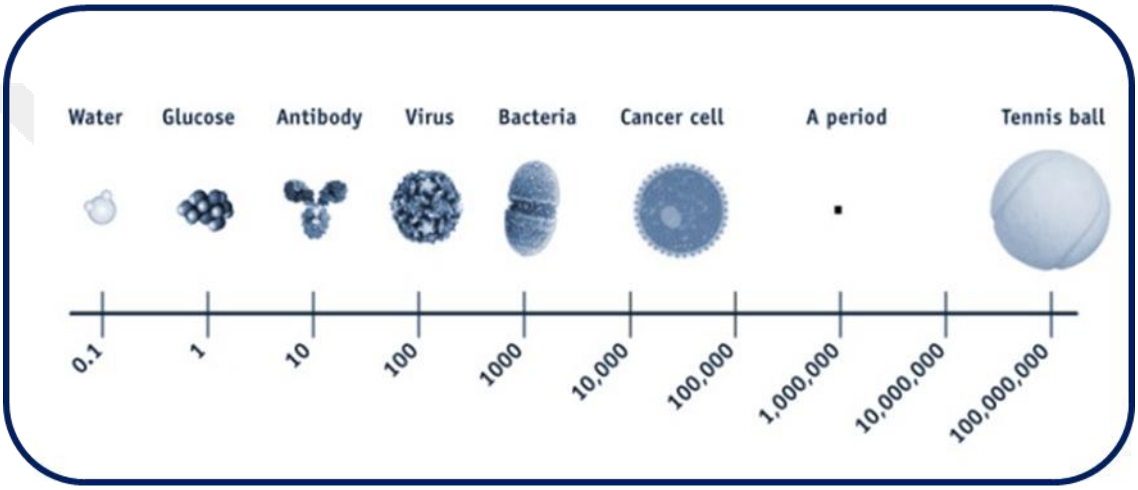

Figure 1.1 : Nanometer scale [1].

Material powders having at least one dimension under 100 nm are called nanoparticles. The unforeseen properties of the nanoparticles caused by their size, have studied by scientists of various areas [2]. The production of materials with selected physico-chemical properties is very important for the development of new technologies. For this purpose, chemical and material engineers have produced many materials which are among the indispensable of our lives in different classes such as plastics, explosives, drugs, surfactants, metals, metal alloys and ceramics by mixing new molecules or mixing known materials. In recent years, however, the strategy is based on the reduction of well-known substances into nanoparticles, changing their chemical composition and properties as desired. The main reason for the concentration of interest on this subject is the fact that the substances exhibit unusual characteristics and functionality in a certain size range, unlike the volumetric structures. The well-known reasons of the attractiveness of nano-particulate properties are the quantum dimension effects, the size dependency of the electronic structure, the unique characters of the surface atoms and the high surface-to-volume ratio. The presence of said effects makes the particle size critical for the physico-chemical properties of the material. In addition, the control of materials at the nano-size level allows the realization of miniaturized devices having unique functionality, such as nanostructures, sensors, nanomachines, and high density data storage cells. In addition, by combining an enormous number of nanoparticles, complex, human-sized machines can be constructed. Obviously, the first step in nano-technological new developments is the production of nanoparticles [3, 4].

1.1 Synthesis of Nanoparticles

There are lots of synthesis techniques of nanoparticles which can be selected according to desired morphology, particle size and purity. These methods can be classified up to their powder propagators physical properties. TOP-DOWN methods begin with coarser structures and make them finer untill nanoscale by giving energy to the initial bulk material via mechanical and/or chemical processes. On the other, BOTTOM-UP techniques begin with atomic or molecular sizes and enlarge the particles up untill the nanoscale. The difference between these methods is illustrated in Figure 1.2. Some of the bottom-up techniques can be stated as aerosol pyrolysis, chemical vapor deposition (CVD), ultrasonic spray pyrolysis (USP) and sol-gel. Moreover, mechanical alloying, high energy milling and laser ablation can be stated as top-down methods [4].

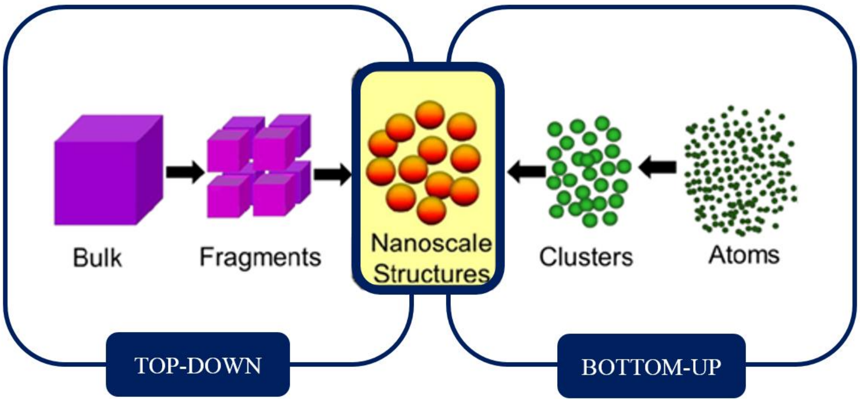

Figure 1.2 : TOP-DOWN and BOTTOM-UP nanoparticle production scheme [4].

Nanoparticle production techniques can also be classified according to initial phase for synthesis. Synthesis methods can begin from gas, liquid or solid phases. Another classification can be made up to used energy type. As mechanical energy is used, the methods where the physical properties are initial are named as physical production methods, and the chemical reactions are considered to be chemical based methods. The production done by bacterias and other organical systems is named biological production technique [4].

1.2 Ultrasonic Spray Pyrolysis (USP) Nanoparticle Synthesis Method

Spray pyrolysis is a process in order to obtain fine particles generally under 0,5 μm. This method is well known especially in medical field and thin film production. However, nanopartile synthesis by this method has been studied for 30 years approximately. Ultrasonic spray pyrolysis method has developed in Grenoble Nuclear Research Center and has patented as “Pyrolysis Technique” name. This method is relatively economical comparing to other fine particle production methods such as chemical vapor deposition (CVD) and Sol-Gel. Spray pyrolysis methods are used especially for production of advanced nanoparticles which are used for fuel cells, gas sensors, photo catalysis, LCD secreens and any other applications. The reason for this selection is spherical and non-agglomerated particules having various chemical compositions, size and morphologies can be synthesized via USP [5-7]. Ultrasonic spray pyrolysis contains propagation of separate droplets from the precursor solution, thermal sepration and the control of phase transformations. consists of 4 steps. Figure 1.3 illustrates the experimental setup of USP.

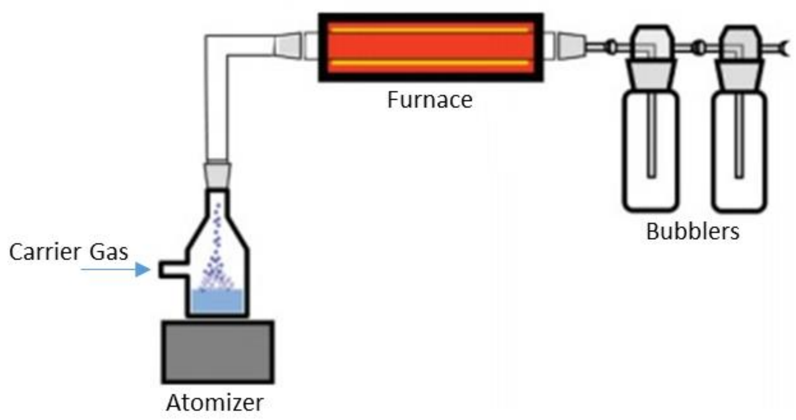

Figure 1.3 : Ultrasonic spray pyrolysis (USP) method setup [8].

First of all, ultrasonic atomiser creates droplets from precursor solution. After that, evaporation in the solution occurs and drop size shrinkage happens. Precursor turns into oxides. Finally, solid particle formation is observed in the system.

The first step of the spray pyrolysis method is aerosol propogation. In order to manage final size of the particles, distribution of the droplets size must be adjusted at the beginning. In order to create droplets, different kinds of atomisers could be used. Pressurized, pneumatic, rotary, electrostatic and ultrasonic types of atomizers are exist [9, 10]. Ultrasonic atomization works by piezoelectrical system in which ultrasonic waves are created by continous oscillations. These ultrasonic waves generates geyser first, after reaching adequate frequency, aerosol generation begins. Ultrasonic atomization relatively preferrable to genarate finer particles. There are two techniques exist for droplet formation. One of these techniques is named as cavitation theory, and the other one is named as capillar theory [11, 12].

Second step of the USP method is formation of particles. This formations occurs as a tranformation of liquid phase to solid phase. Releated steps of particle formation is indicated in Figure 1.4. [8].

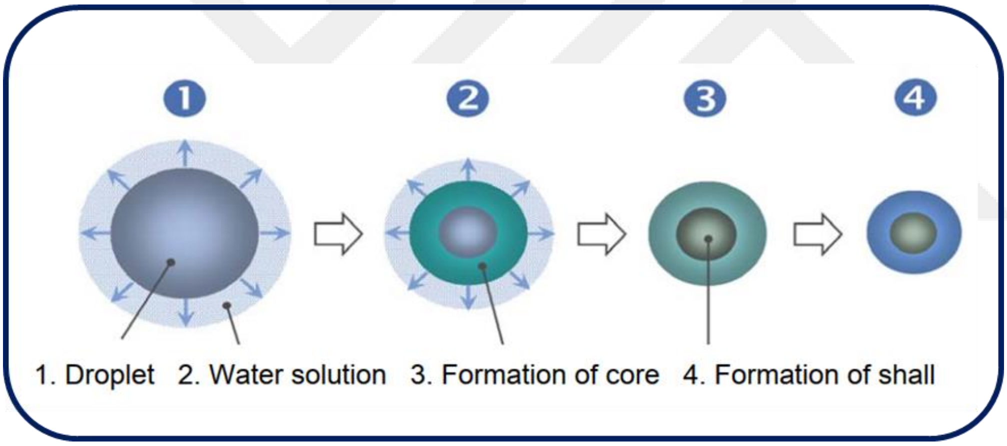

Figure 1.4 : Particle formation steps via ultrasonic spray pyrolysis (USP) [8].

1.3 Sol-Gel Nanoparticle Synthesis Method

Sol-Gel is a nanoparticle production process which is in the category of BOTTOM-UP techniques. The word "Sol" states the a few nanometers sized colloidal particles having stable dispersion in a solvent. "Gel" word means a three dimensional continous network of the sol particles which are built by the agglomeration of colloidal particles and encloses a liquid phase. Sol-Gel method can also named as "Gelation" process which also infers the transformation of sol particles to gels. Sol-Gel method requires less energy comparing the other BOTTOM-UP methods. Also, Sol-Gel is a controllable technique which enables to produce high purity and homogeneous particle synthesis. Inorganic materials, organic-inorganic polymers can be synthesized by this technique. Figure 1.5 indicates the steps of sol-gel technique.

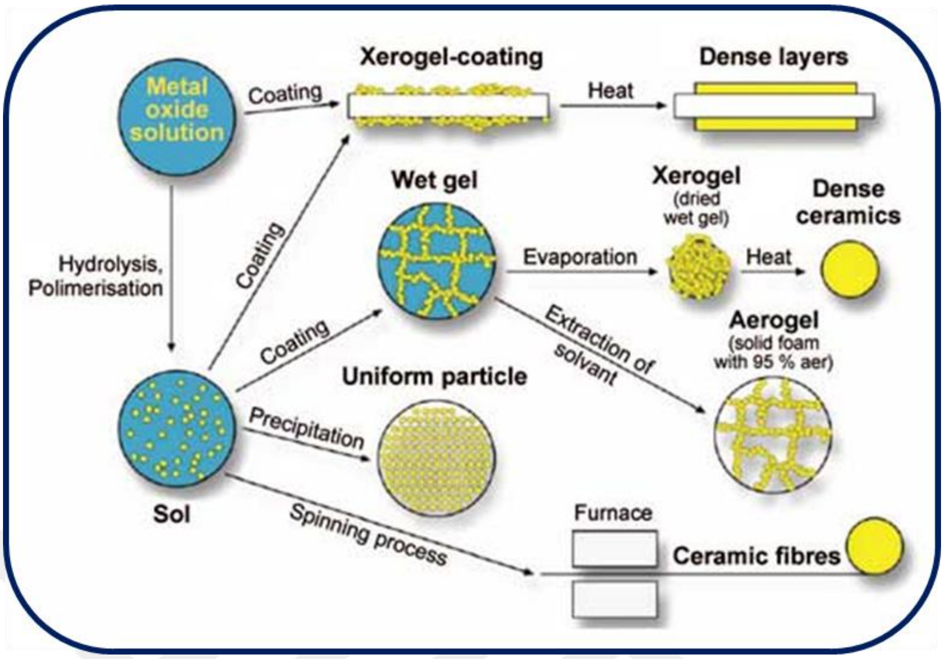

Figure 1.5 : Nanoparticle formation via sol-gel method [13].

Initial step of Sol-Gel process is the selection of beginning solution. This selection affects the final gel structure to become colloidal or polymeric. Some conventional procedures like cold press, hot press or sintering are applied after precipitation of colloidal particles in order to get ceramics. Colloidal particules can distribute into the stable sol. Gel structure could be fiber or coating up to the applied procedure. Also, drying procedure of the gels has an impact on the final products structure and shape. Figure 1.6 shows the hydrolysis and condensation steps of the Sol-Gel process.

If metal bounds to water molecule, aqua ligand (H2O) formation is observed. If one proton separates, hydroxy ligand (OH)- formation is observed. If two protons separate from the precursor, oxo ligand (O-2) formation is observed. Ligand formations with respect to pH and electrical load is indicated in the Figure 1.7 [14].

Hydrolysis of the precursor can be stated as the second step of the Sol-Gel process. This step can be defined as the separation of metallic cation from protons. Metal ion loses its proton by water molecules surrounded over the metal ions.

Metalic salts and alkoxides are used as precursors. The solvent must be selected up to the type of the precursors. During, Sol-Gel process asidic or basic catalysors could be added into the solution. Generally basic catalysors such as, ammonium hydroxide (NH_4OH) are selected [8].

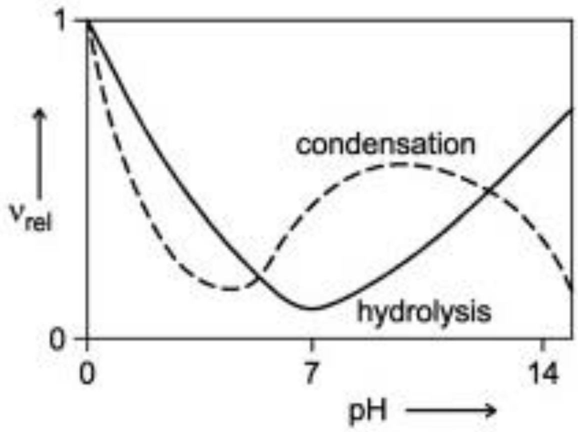

Figure 1.6 : Hydrolysis and condensation pH graph [15].

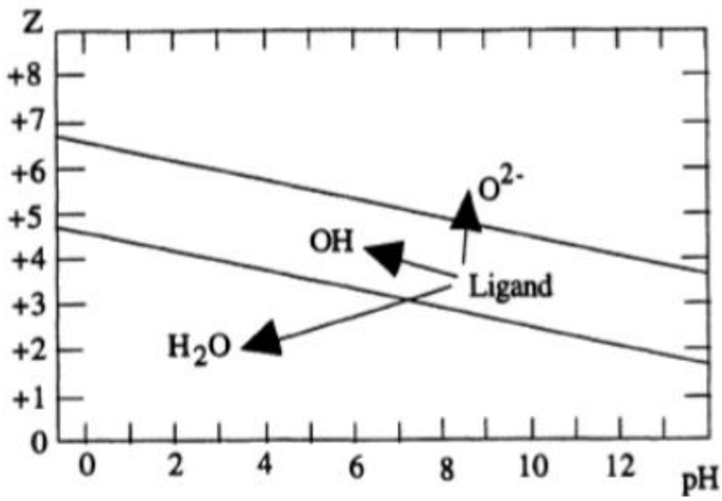

Figure 1.7 : Ligand formation [15].

2. NANOPARTICLES AND NANOTECHNOLOGY

It is unlikely to imagine an industry which would be unaffected by nanotechnology. The usage of nanotechnology which could be stated as the technology of the future and requires interdisciplinar studies, is gradually increasing. Development of nanotechnology has gained a strategic value by innovative Technologies in 21st century. Main goals of nanotechnology can be summarized as:

- To understand the physical properties of nanometer scale structures by analyzing
- Obtaining different and superior material properties / production processes
- More durable, lighter, faster structures, less material and energy use

Unforeseen physical and chemical properties of metallic nanoparticles lead them to be used at various usage areas. Especially, nano composite particles synthesized by the combination of noble (Ag, Au, Pd, Pt) and semi-noble (Cu) metals with semi-conductor materials (TiO_2 or ZnO) has become the focus of scientific interest. Owing to superior features in engineering applications and wide range of using areas, nano composites have key roles in many areas [16].

Nano scale metal particles / powders are indispensable raw materials of advanced technologies, thus, there are plenty of usage areas spread all over the industries. The reason why interest in nano sized materials has increased over the past decades is because of the high technology needs. Dimensions of nanomaterial under 100 nanometers led them to have excellent electrical, optical, catalytic, biologic and mechanical properties [16, 17].

The first nano composite term was introduced in the early 1980s and the nano composite according to the general definition is multi-phase compounds in which at least one phase is nano-sized. Nano composites provide unique properties by creating new materials different from nanomaterials due to the different structures and compositions they contain. These superior properties are manifested as electric-electronic, mechanical, optical, magnetic, biological, photoactive and catalytic properties, and these materials are multifunctional because of the different structures and properties they have. The superiority of the properties of the nano composite particles as well as their controllable shapes and morphologies are influenced by their size [16-19].

The superiority of the properties of the nanocomposite particles as well as their controllable shapes and morphologies are influenced by their size. As nanomaterials have superior properties compared to their volumetric structures, the interest in the development, production and use of new generation nanostructures has increased in the last decade. Support for scientific research, which includes the production and functional use of new generation nanomaterials, is growing exponentially. Thanks to these contributions, many new nanostructured systems and nano devices have been developed, and highly sensitive and customized nano catalysts and sensors are designed especially in electronic and medical fields [17,18].

Recent advances in nanomaterials production and functional use have focused on the design of nanocomposite structures. Nanocomposites with two different functional contents exhibit better properties as a result of the combination of the properties of both nanostructured materials [19].

Ultrasonic Spray Pyrolysis (USP) method is one of the most convenient methods in which metal particles can be placed into ceramic matrix. It is a suitable method for producing homogenous nanocomposite particles with spherical morphology and with different properties. The short working time in obtaining the nanocomposite particles, the feasibility of production in a wide chemical composition and a one-step process provide significant advantages to the USP method against other techniques. The USP technique allows the production of nano-sized particles with a wide range of chemical composition, size and morphology, which are spherical and non-agglomerated. The development of nanocomposite particles by the USP method has been an important issue in recent years and is an important process for the production of new generation nanocomposites and there are limited numbers of studies. Kaneko and the study group produced TiO_2 / Ag nanocomposite particles by spray pyrolysis method. TiO_2 nanoparticles (Step 1), previously synthesized in their process, were added to silver nitrate solution and produced by two-step USP method (Step 2). Transmission electron microscopy (TEM) analysis showed that Ag nanoparticles exhibit a homogeneous distribution in the TiO_2 matrix [5, 20, 21].

The main objective of this thesis is to produce In_2O_3.ZnO nanocomposite particles with Sol-Gel and USP-HR techniques in one step, to control the particle morphology and to investigate its use in different fields of industry.

The long-term objective of the project is to transfer the knowledge and technological applications obtained as a result of scientific and technical research to the fields required in the industry.

2.1 Indium Oxide Powders

Indium is a metal which has discovered in 1863 by a German chemist Ferdinand Reich during his study with a zinc mineral blend. Generally, indium is found mixed with other minerals with very rare amount in nature. It has the atomic number of 49, thus, indium is located in 3A group of periodic table. It has the density of 7,31 g/cm^3. Indium melts over 156,6 C°. Above this temperature indium starts burning with violet-blue colored flame. Indium is named due to this flame as the meaning of latin word "indicum" is violet [22].

The usage of indium could not be clarified too soon after its discovery. Today, indium is a very important element especially for electronic industry. Indium compounds are used in liquid crystal displays (LCD), touch screens, flat screen TVs and solar panels. Especially indium tin oxide (ITO) is preffered for these purposes as it is transparent, electrically conductive, strong adhesive to glass, corrosion resistant and chemically and mechanically stable. In literature, indium is stated as "metal vitamin" as small amount of indium addition or doping creates drastic enhances on base materials' properties. For instance, platinum and gold alloys become harder with small addition of indium. Moreover, there are existing studies about increasing the efficiency of lithium-ion batteries using indium [22, 23].

Indium oxide (In_2O_3) could be amorphous or in crystalline form. Also, there are two different crystalline structures of In_2O_3 exist. One of them is cubic crystalline structure and the other one is rhombohedral. Figure 2.1 demonstrates the bixbyite crystalline structure of In_2O_3 which is a cubic structure having structural vacancies due to a missing anion on a corner. These positions, could be located along the body diagonal (b site) or along the face diagonal (d site). InO_6 octahedra could be linked together inside the In_2O_3 due to these structural vacancies [24].

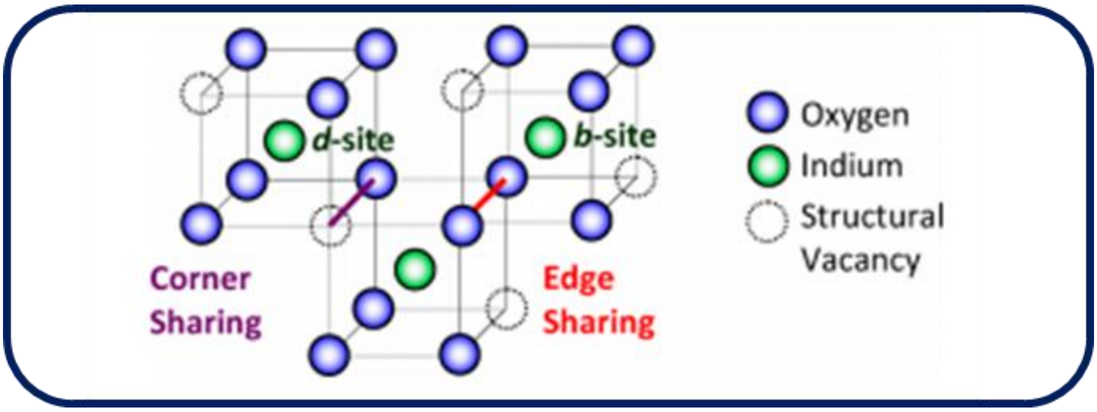

Figure 2.1 : Indium oxide (In_2O_3) crystal structure [24].

Indium oxide (In_2O_3) can be considered as a promising material for the advancement of electrical and optical devices since of its optical and conductive features. It is known as wide band gap, transparent and conducting semi conductor. These properties make it a very important material for technological aspects [25]. In_2O_3 is an n-type semiconductor with a band gap of 3,5 – 3,7 eV. There are numerous usage areas of this material thanks to its unique properties. Final application of the indium oxide powder directly depends on its crystal structure, grain size and history. Generally, these structural properties releated with the production technique of the nanomaterial. Also, particles are named up to their nano geometry. A nanomaterial could be nano-belt, nano-wire, nanopowder or thin film according to its synthesis method [26]. Indium oxide can be synthesized by using indium acetlyacetonate and biological extract, a reaction under the autogenic pressure at elevated temperature (RAPET) etc. However, synthesis of this powder industrially is still developing area as process should continue in ambient temperatures with low energy consumption [27].

Applications of indium oxide in solar cells, field emission display, nanoscale biosensors, gas sensors, lithium ion batteries, optoelectronics and photocatalysis are mentioned in the literature. Moreover, electro-optic modulators, window heater, electro chromic mirrors are made from indium oxide based materials [27].

2.2 Zinc Oxide Powders

Zinx oxide (ZnO) nanopowders have gained a great attention in recent years due to their superior properties releated to electronics, optics and photonics. ZnO is eligable to be used on the applications as sensors, catalysts. Due to these features, ZnO is stated as a “future material”. Multiple usage areas of ZnO are caused by semiconducting, piezoelectric and pyroelectric properties of it [27-29]. ZnO is founded as Wurtzite(B4 Type) structure in ambient pressure and temperature. Space group of ZnO is $P6_{3mc}$ and has a hexagonal structure. Piezoelectricity and pyroelectricity features of zinc oxide are caused by non-central symmetrical structure which is due to the tetrahedral coordination of zinc oxide. Figure 2.2 indicates the wurtzite structre and tetrahedral coordination of zinc oxide.

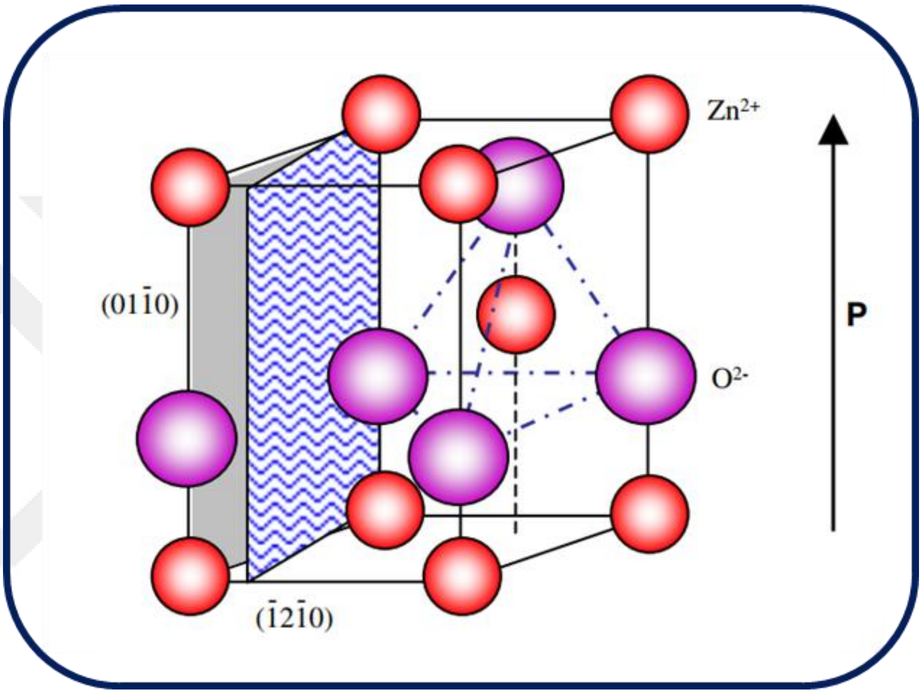

Figure 2.2 : Wurtzite structure of ZnO [27].

Materials used in optoelectronic devices with respect to semiconductors usage, should stand the rules of band gap engineering. High exciton binding energy (60 meV) and wide band gap (3,4 eV) of zinc oxide make it very important for technological applications, especially for mechanical actuators and piezoelectric sensors. Moreover, it is prooved that ZnO can ensure room temperature ultraviolet (UV) luminescence. ZnO is also transparent in the visible light. ZnO can be highly conductive by doping. These features enable zinc oxide and zinc oxide compounds to be used in UV laser diodes, sensors and nanotechnology-based devices such as displays. The efficiency of zinc oxide could be enhancd by alloying, doping and making it composite. Nevertheless, due to the newness of the fields, there are not enough information about composite zinc oxide based powders efficiency.

2.3 General Informations About Nanocomposite Powders and Indium Zinc Oxide (IZO)

A material having at least one dimension below 100 nanometers is called nanomaterial. Properties of a material in nano size distinguishes from its bulk properties. For example, a gold nanoparticle has red colour while bulk version of it has yellow color. This situation caused by the difference of refraction and transmittance properties of gold against visual light according to its particle size. On the other hand, composite materials enable taking the advantages of both materials inside the composite material. Therefore, nanocomposite powders have a great number of unique properties comparing to conventional ones regarding to have both nanomaterials properties and composite materials properties. These peerless properties of nanocomposite powders enable them to be used in very special and important applications. As reported by Beercroft and Ober [30], devices which need nonlinear optical properties, laser, magnetic and high refractive index properties can be made from nanocomposite powders as many as semiconductor materials used for printing, data storage and magneto-optics.

Indium zinc oxide is a nano-composite which is made from indium oxide (In_2O_3) and zinc oxide (ZnO). It contains the properties of both these oxides. IZO is one of the most favorable nano-composite for optoelectronic and photocatalytic applications. Indium tin oxide (ITO) shows similar properties with IZO in these applications. The lack of its performance in some specific applications leds scientist to search IZO instead of it.

IZO has the melting point of 1900-1920°C. Therefore, it can be used for high temperature applications.

Since the study on IZO is a quite new area, there is not too much information about the properties and the final commercial usage of it.

2.4 Usage Areas of IZO

Indium zinc oxide (IZO) is a promising material for the industrial usage of many applications. IZO can be in nanocomposite powder form, thin film coating form and even in indium doped zinc oxide form in literature. Each form has its own unique usage area.

IZO has got its own fame as a coating material with respect to transparent conducting oxides (TCO's). TCO's are used in optoelectronic devices (displays, LCD's, smart windows, solar panels), electromagnetic shielding etc. High transparency, thermal stability and good electrical properties of IZO thin films make it a potential material for TCO deposition. IZO thin film coated polymer substrates for this kind of usages have enhanced protection properties for scratching [31].

Oxide thin-film transistors (TFTs) are generally used in LCD secreens in order to prevent pixels to become mixed and enhance the display stability. Transparent semi-conductors makes TFT's completely transparent. Therefore, these transparent TFT's are used for transparent screen panels. ITO is a well known transparent semi-conductor used in TFT's. In order to incrase the transparency, resolution and the performance of the secreens amorphous silicon is not sufficient by itself. Therefore, studies on that field has increased. IZO is one of the most close material with ITO. IZO used TFT's have higher potentials for its final products [32].

Photocatalytic activity can be defined as acceleration of a photo reaction as a catalyst with the combination of light. For example, TiO_2 nanoparticles create sunlight affected radicals which decompose organic materials; therefore, are used for self-cleaning surfaces [33]. Murali and his colleagues have studied on photocatalytic activity of the indium doped zinc oxide films synthesized by plasma-assisted chemical vapor synthesis route. According to their study, 4% and 8% indium doped zinc oxide nanoparticles are evaluated using the degradation of methylene blue (MB) under ultraviolet irradiation. 4% indium doped zinc oxide nano materials showed better results as a photocatalyst [34].

2.5 Production Techniques of IZO

In literature, indium zinc oxide (IZO) is generally produced as thin film coating. Thin film coating of In_2O_3-ZnO system is studied by metal organic chemical vapor deposition (MOCVD), laser deposition, sputtering, sol-gel and spray pyrolysis methods. With the consideration of reaching higher purity and more controllable composition, IZO thin film deposition is studied by Keshavarzi and his colleagues with electron beam evopartion technique on glass substrates and achieve coating of IZO particles distributed with average 50 nm particle size. This method generates a transparent conducting oxide (TCO) layer on a substrate.

TCO's are extensively used for optoelectronic applications [35]. Therefore, thin film coating of IZO is important for that kind of applications thanks to its optical and electronical properties. Electron beam deposition setup is illustrated in the Figure 2.3. In this technique, electron beams are produced by a tungsten filament and then targeted to material which used as a coating material. E-beams tranforms source materials to gaseous phase. Finally, substrate is coated by the thin film of the source [36].

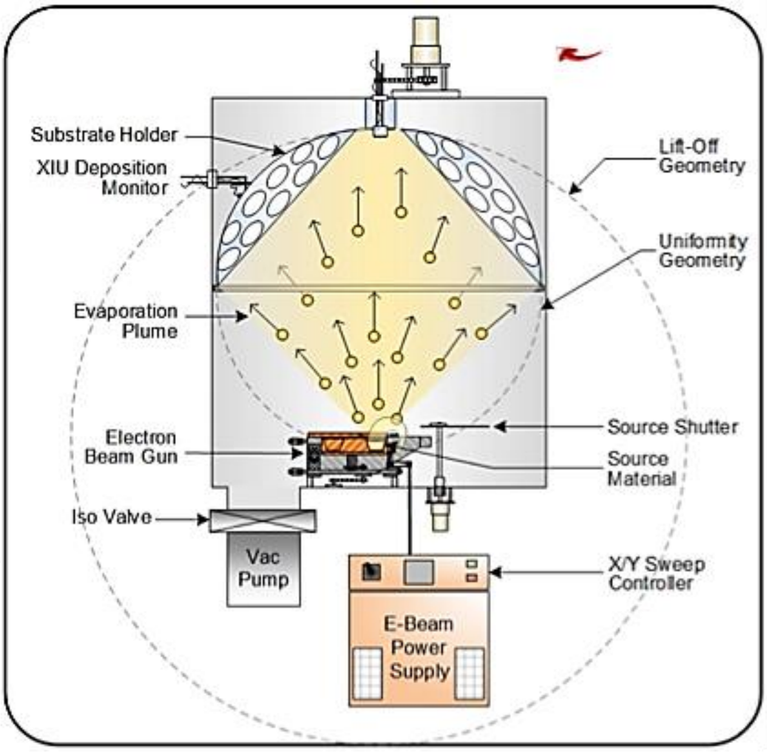

Figure 2.3 : Schematic explanation of metal organic chemical vapor deposition [36].

Indium doped zinc oxide nanoparticles can also produced by top-down methods. Khashan and Mahdi have studied production of IZO nanoparticles by pulsed laser ablation in liquid (PLAL) technique which is one of the top-down methods. Advantages of this technique are simple, clean, economical (does not need extreme temperature or pressure), new nanophase generation. This method attracted scientists after the invention of ruby laser in 1960's. The setup of this method is shown in Figure 2.4. This method only needs a laser pulse and a focal lens to create micro-nano particles. In order to prevent the creation a deep crater on the target, both target and the container are rotational. The involved steps are as following; laser penetration of the liquid, shock wave emission, pulsed laser ablation of the solid, laser induced bubbles generation, nanocluster formation, chemical reactions and nanoparticle generation.

According to the study of Khashan and his friend, they first placed a zinc target to create zinc oxide nanoparticles with the usage of de-ionized water as a liquid. After that they have replaced the target with an indium plate using the surrounding liquid which containd zinc oxide nanoparticles in it. Finally, they have created indium doped ZnO nanoparticles below 100 nm particle size [37, 38].

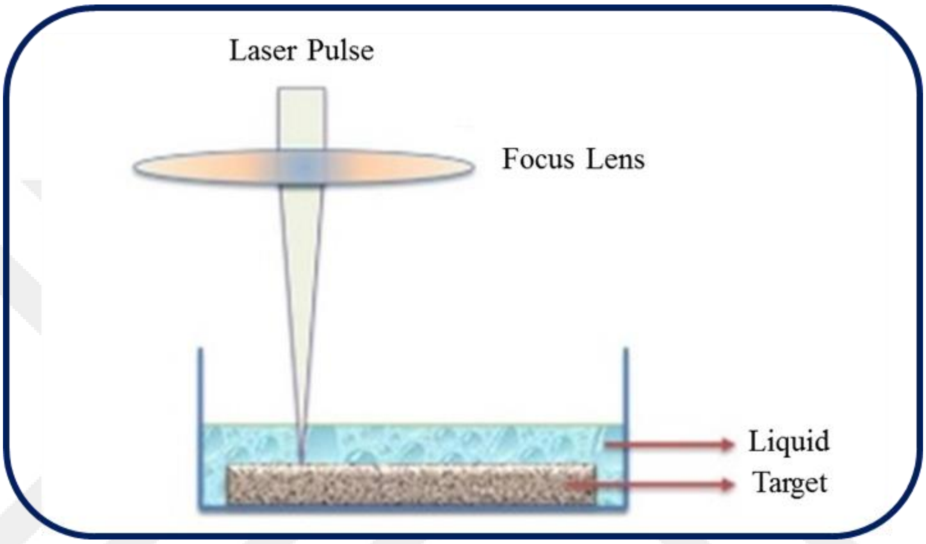

Figure 2.4 : Pulsed laser ablation in liquid method setup [37].

IZO films can be deposited by aerosol assisted chemical vapour deposition (AACVD) technique. Thin films get coloured when the film thickness changes due to atmospheric pressure usage. This situation could has drawbacks with respect to its usage as a TCO material. According to the study of Nolan and his colleagues, indium doped zinc oxide films having the thickness of approximately 215 nm have been synthesized with this technique. Doping of the indium to the zinc oxide leds them to be oriented well and create more preferred morphology [39].

3. RELEATED STUDIES

Production of indium zinc oxide (IZO) nanocomposite particles is relatively new area. The main reason leds scientists to search IZO is to replace ITO with a new and comparable material. However, IZO has its unique properties which will cause them to be used in various usage areas.

Benhaliliba and his colleagues synthesized In-doped ZnO thin films on glass substrates via ultrasonic spray pyrolysis (USP). They have used 0,05 M of Zinc acetate dehydrated ($Zn(C_2H_3O_2)_2.2H_2O$) and indium chloride ($InCl_3$) solution as starting material with the usage of methanol as a solvent. USP is carried out at 250-400°C. They have used In/Zn ratio of 1%. Synthesized thin films were characterized by XRD, SEM, AFM. Also, electrical and photoluminescence analyzes were carried out in this study. IZO thin films deposited at 400°C have exhibited (0 0 2) reflection on XRD analysis. Other IZO films deposited below this temperature also have this peak but with lower magnitudes. However, these films and pure ZnO also have exhibited (1 0 1) and (1 0 3) reflections. All of the deposited films were showed polycrystalline nature which well fit with the hexagonal wurtzite type structure of ZnO. According to the AFM images the morphology of deposited IZO films were homogenous and there were no observed defects or voids on them. The thickness of the films were varying between 260-420 nm. SEM-EDS analysis shows the indium to zinc ratio. The owner of highest ratio was IZO film deposited at 400°C with 2,45%. Surface of the films shows homogenous distribution mostly and there were some clusters. According to all of these metallurgical characterizations, indium doping roughly changes the lattice parameters. Synthesized films have the band gaps around 3eV. The transparency of IZO films were 88%. Intense yellow (2.1 eV) and blue (2.8 eV) emissions were detected. The electrical properties of the indium doped films were also changed [41].

Murali and his colleagues have studied on production of IZO nanopowders with plasma assisted chemical vapor synthesis technique. They have used zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and indium nitrate [$In(NO_3)_3.5H_2O$] as precursors.

These precursors were fed to the system with a carrier gas. Argon plasma gas is used for initiation of plasma arc. Synthesized powders are characterized with XRD, Raman, SEM and EDS analyzes. 4% In-doped zinc oxide particles have showed approximately the same XRD peaks. Both these particles and the pure ZnO particles have peaks (101), (100), (002), (110), (103), (102), (112) and (201). Moreover, these particles have good crystallinity in which agree the wurtzite structure of ZnO. However, 8% In-doped IZO particles showed In_2O_3 phase located along with the main wurtzite peaks. The substitution of In^{+3} ions at Zn^{+2} sites has caused small shift of the peaks to the higher angles. The Raman analyzes in all of three measurements showed a sharp peak centered at 437 cm^{-1} which represents the characteristic peak of hexagonal wurtzite structure of ZnO. Also, there were a peak located at 588 cm^{-1} representing the oxygen vacancies and getting sharper when going to pure ZnO. According to SEM and AFM images, higher amount of indium doping results in the formation of larger particles and some agglomeration. This situation is caused from the defect formation caused by excess indium atoms. Higher indium doping also created segregation of non-crystalline regions. This situation can have disadvantages on the electrical and the optical properties of the material. The scientists also measure the photocatalytic activity of the IZO films. Up to 4% of indium doping, photocatalytic activity of the material has increased. However, increasing the indium content up to 8% has drawbacks on the photocatalytic activity [34].

4. EXPERIMENTAL PROCEDURE

Nano-sized composite particles of IZO are synthesized from indium nitrate and zinc nitrate powders by ultrasonic spray pyrolysis (USP) and Sol-Gel methods. Characterizations of synthesized particles are done in order to determine their particle sizes, morphologies and properties. Also, some characterizations are done to investigate indium zinc oxide nanocomposite powders sectoral potentials.

4.1 Materials and Equipments

Experimental procedures are all carried in the laboratoies of ITU. In order synthesize nanocomposite particles, solution preparation is done first. To mix the indium nitrate [$In(NO_3)$] and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) with pure water, IKA Yellow Line mixer is used.

For the synthesis of IZO nanoparticles with USP, Ramine Baghai Instrumentation ultrasonic atomiser is used. Moreover, Nabertherm brand, R30/250/12-B model furnace is used to elevate the temperature. Polyscience 9006 model cooler is used to cool the system. Particle production has carried in a quartz tube 300 mm length 30 mm diameter.

XRD analysis of the synthesized nanoparticles were investigated via Rigaku Miniflez, Cu-Kα model XRD equipment.

SEM-EDS analysis of the particles were invstigated by using FE-SEM, JEOL JSM 7000F series scannig electron microscope.

4.2 Experimental Design

The experimental procedure consists of 3 main steps. First of all indium zinc oxide (IZO) nanoparticles are synthesized by ultrasonic spray pyrolysis (USP) method. After that, IZO nanoparticles are synthesized by Sol-Gel method. Finally produced particles are metallurgically chracterized using XRD, SEM-EDS and Raman methods.

4.2.1 IZO Production via Ultrasonic Spray Pyrolysis method

In the experiments, zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and indium (III) nitrate ($In(NO_3)$) powders are used. In order to run the experiment, 0,1 M solutions were prepared. 0,04 moles of zinc nitrate hexahydrate (11,892 g) and 0,04 moles of indium (III) nitrate (12,03 g) were solved in 400 ml of distilled water solvent wirh a magnetic mixer having 400 rpm. After stirring the solution for 15 minutes, solution is added to the ultrasonic atomiser (RBI model). Atomiser was cooled with water cooling thermostat system named Polyscience 9006. The furnace that the chemical reactions have occured is Nabertherm brand R 30/250/12-B model having 250 mm of heating zone and reaching maximum 1200°C of temperature in one zone tube furnace. In order to carry the aerosol to the tube furnace, 30 mm diameter, 300 mm length quartz tube and other glass equipments are used. In all experimental procedure of ultrasonic spray pyrolysis method, air with 0,5 l/min. rate is used as an oxidizing gas. Nanoparticles that are synthesized after thermal fragmentation, are collected in 3 tubes filled with distilled water. The experimental setup is shown in Figure 4.1. The set-up of the furnace is shown in Figure 4.1. (b). Briefly, 3 hours of time were give for the reactions in furnace in releated temperatures (600°C and 700°C).

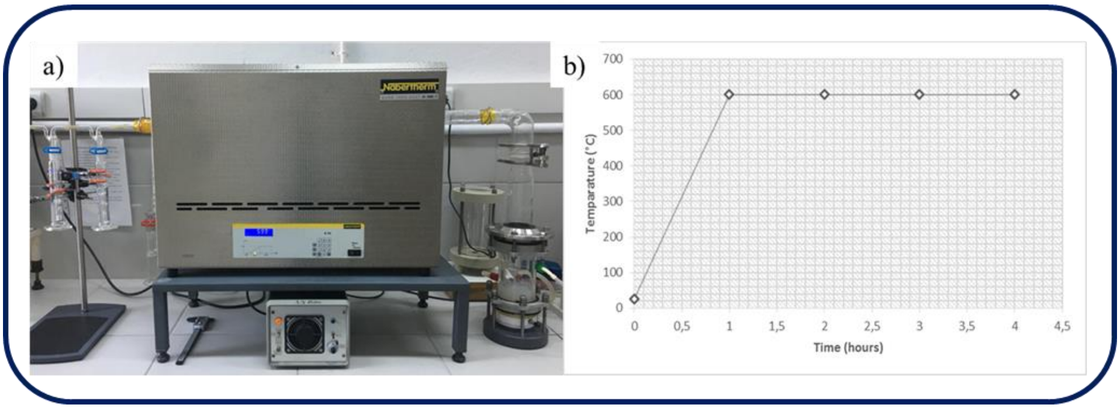

Figure 4.1 : USP experimental setup.

4.2.2 IZO production via Sol-Gel method

In the experiments, zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and indium (III) nitrate $In(NO_3)$ powders are used. In order to obtain 0,1 M solution, 0,04 moles of $Zn(NO_3)_2.6H_2O$ having 11,9 grams of mass and 0,04 moles of $In(NO_3)$ having 12,03 grams of mass are added to the 400 ml of pure water. The powders are solved in the water via magnetic mixer. During mixing of the solution, pH of it is measured. The pH of the first trial was pH=4. IZO nanoparticle production has carried out by acidic catalisor addition. However, In_2O_3 synthesis carried out not only with acidic catalisor but also without acidic catalisor addition. Acidic catalisor added procedure continues with, 5 ml of 0,1 M of citric acid ($C_6H_8O_7$) solution addition to the solution. After certain mixing time, pH was measured as pH=3 and then 5 ml of it added again. This time pH=1. After stirring the solution for 2-5 minutes and then 10 ml of 1 M of NH_3 solution was added to the mixture. pH of the solution was 7 after that addition. 5 ml of NH_3 solution addition route was repeated 2 times again and pH's were 8 and finally 10 respectively. After stirring the mixture for 1 hour, the color of the solution turned to white creating tiny sol particles in it. Finally, solution was filtered and let to dry for 24 hours. After that procedure, dry xerogels were obtained. Figure 4.2. shows the steps of Sol-Gel process.

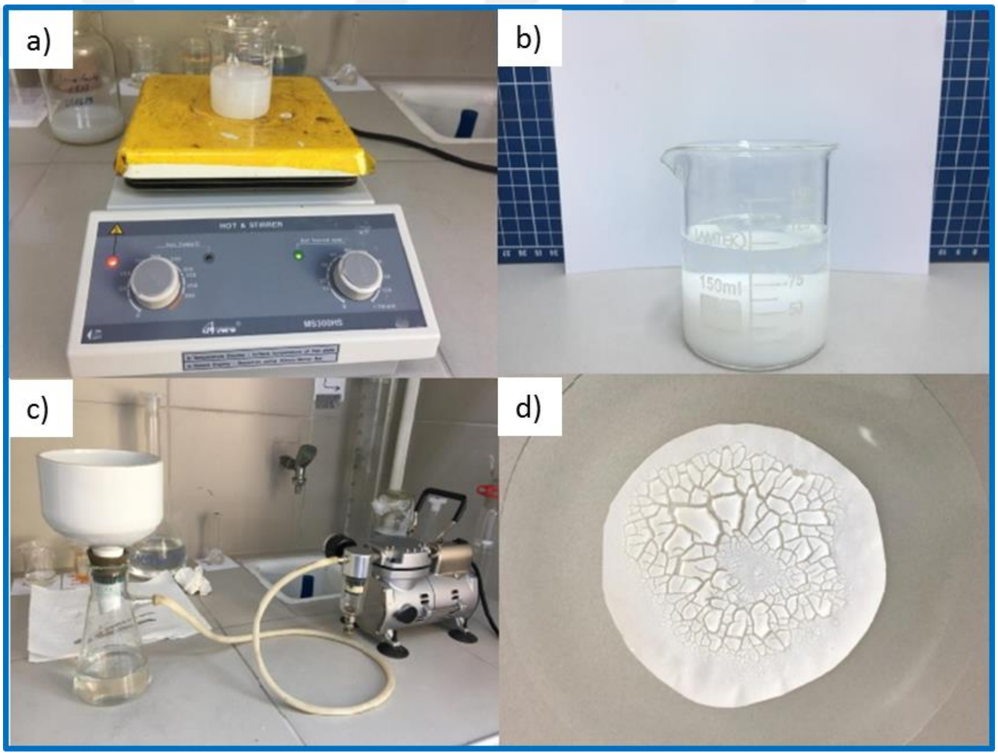

Figure 4.2 : Represantative image for sol-gel process.

Filtered particles are calcinated at 600°C and 700°C. These temperatures are defined according to DSC-TGA analysis of indium-zinc nitrate hydrate mixture. Figure 4.3 demonstrates the DSC-TGA analysis graph of the indium-zinc nitrate hydrate mixture. The first peak of the curve is releated to absorbed water and the second peak is belong to structural water. After the temperature of 600°-700°C, curve is not showing any peaks which represents that there is not mass change at dry gels. Therefore, calcinations at 600°C and 700°C were done.

4.2.3 Characterization of synthesized particles

Metallurgical characterizations of the produced particles were done by XRD, SEM-EDS and Raman analyzes. It was aimed to investigate the particle size, morphology and whether the particles bounded correctly or not, most importantly.

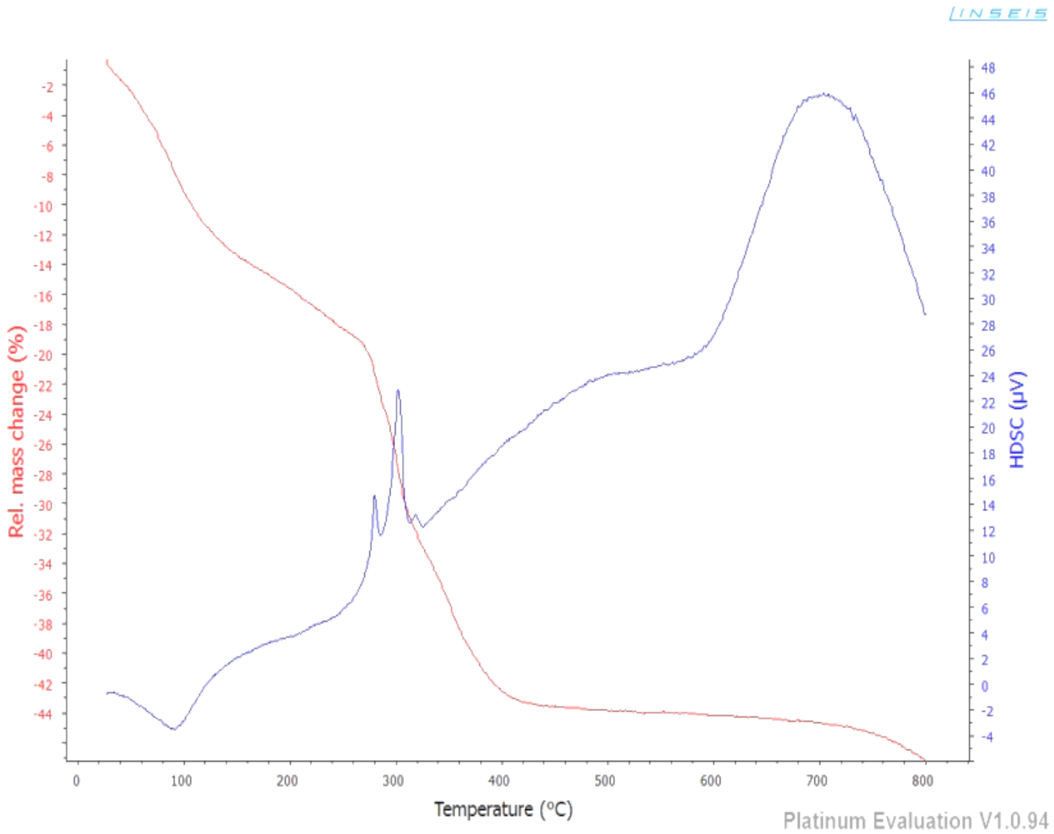

Figure 4.3 : DSC-TGA analysis of In-Zn mixture.

4.2.3.1 X-Ray diffraction (XRD) analysis

In order to investigate the IZO nanoparticles via XRD, sample preparation was done first. Produced particles which were collected in a distilled water, were dropped on an amorphous silicon plate. In order water to evaporate, sample was waited to dry some time. After sample preparation steps, XRD analysis were carried out with Rigaku Miniflex, Cu-Kα model XRD equipment to investigate the crystallite sizes and lattice strains. Finally, graphs were drawn with X'pert High Score + software and compared with literature.

4.2.3.2 Scanning Electron Microscopy (SEM) – Energy Dispersive Spectrometer (EDS) analysis

Sample preparation is the first step of SEM-EDS analysis. In this study, aluminum plates were sanded and polished to be used as base plate. As the particles to be investigated were collected in distilled water, prepared base plates were dried after dropping the solution containing IZO particles. Jeol FE-SEM JSM 700F model SEM equipment was used to anlayze morphology and chemical composition. Finally, result graphs and tables were compared with literature.

4.2.3.3 Raman spectrometer analysis

Raman analysis of Sol-Gel synthesized, and calcinated particles were carried out in a Raman Spectrometer equipment, Horiba HR800UV model, Raman spectrometer equipped with a 632 nm laser for chemical analysis. Finally, results were compared with literature.

5. EXPERIMENTAL RESULTS AND DISCUSSIONS

In this section, experimental results of the synthesized IZO nano composite powders via USP and Sol-Gel, were investigated. Moreover, XRD, SEM-EDS and Raman characterization results of produced particles and their comparison with literature is done.

5.1 Results of XRD Analysis

In order to evaluate the materials and the process synthesized zinc oxide and indium oxide were analyzed first. Figure 5.1 demonstrates XRD analysis results of ZnO, produced by USP at 600ºC. From the pattern 2θ values of synthesized zinc oxide are located at 38°, 49°, 58°, 33°, 34° and 36° respectively.

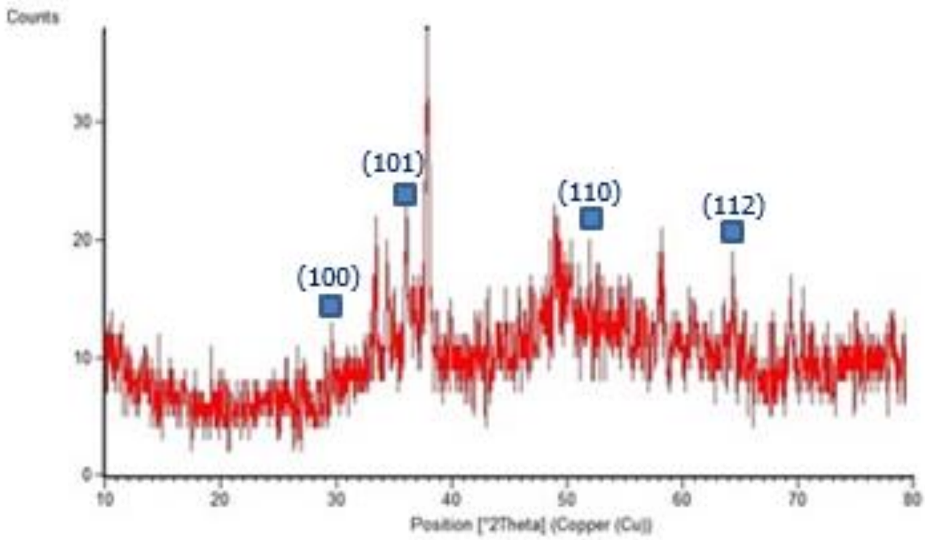

Figure 5.1 : XRD pattern of ZnO nanoparticles produced by USP.

The analysis was compared with the study of Murali and his colleagues. Figure 5.2 demonstrates the XRD analysis results of ZnO from their study [34]. The results of this study and the literature are matching with respect to 2θ values locations and widths. Also, main peaks (100, 101, 110 and 112) are in a match with ZnO with the card number of, ICDD 01-075-1533, from Xpert softwares materials index.

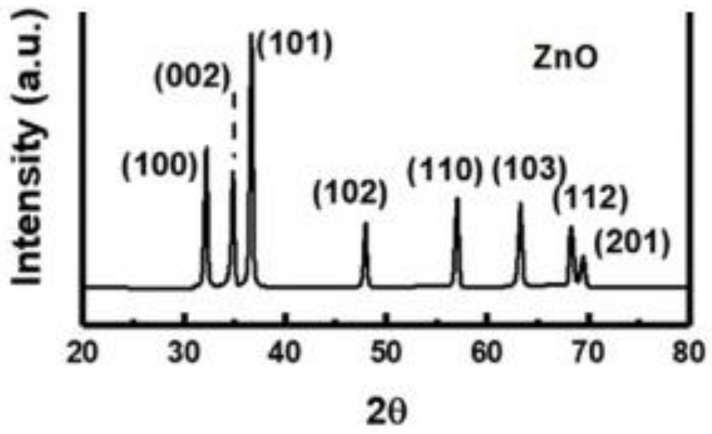

Figure 5.2 : XRD pattern of ZnO nanoparticles from literature [21].

Figure 5.3 demonstrates the XRD pattern of synthesized indium oxide. The main peak located around 30° followed by the peaks at 52°, 36°,61° and 21° respectively. Main peaks (222, 400, 440 and 622) are in a match with In_2O_3 with the card number of, ICDD 03-065-3170, from Xpert softwares materials index.

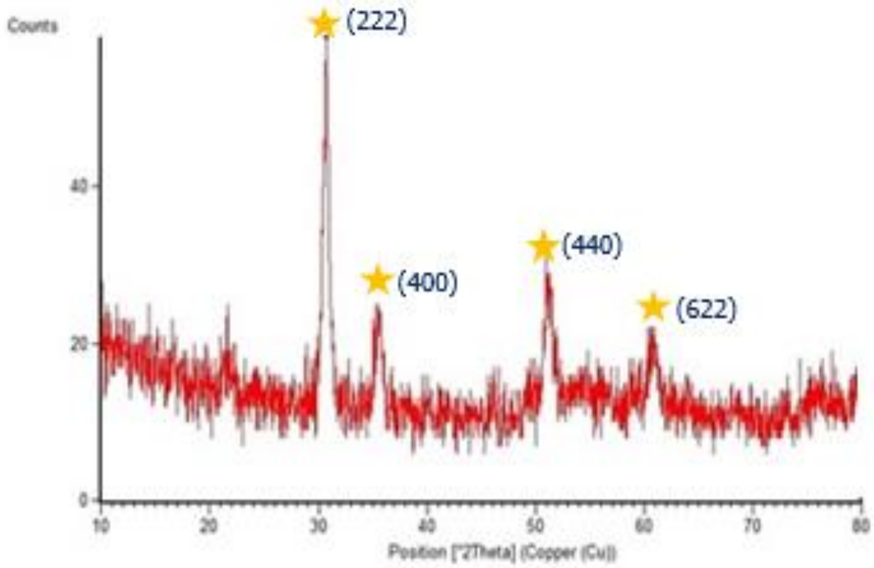

Figure 5.3 : XRD pattern of In_2O_3 nanoparticles synthesizd by USP.

These peaks were compared with the results of Chandradass and his colleagues' study which is shown in Figure 5.4. As it shown from the graphs main peaks 2θ values and their widths of analyzed sample and the literature are matching. However, the length of them are different. It may be considered that the higher and the sharper peaks represent bigger particles. Thus, synthesized In_2O_3 particles of this study could have smaller particles.

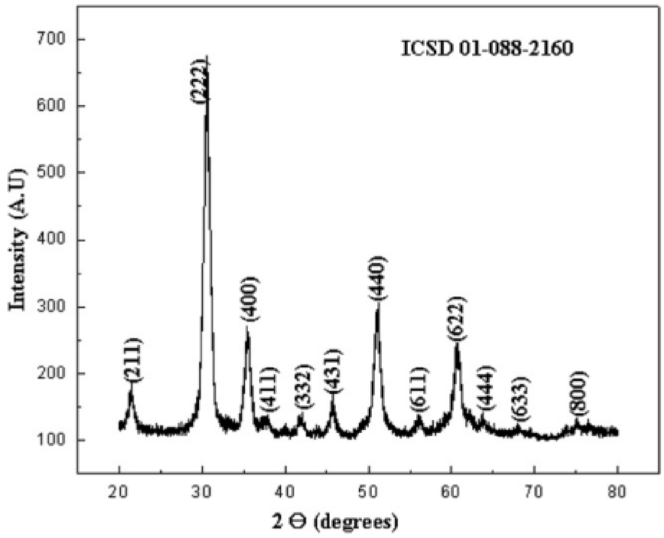

Figure 5.4 : XRD pattern of In2O3 nanoparticles from literature [27].

Figure 5.5 demonstrates the XRD pattern of Sol-Gel synthesized indium oxide with calcination temperature of 600ºC. The main peak located around 30° followed by the peaks at 52°, 36°,61° and 21° respectively. Main peaks (222, 400, 440 and 622) are in a match with In_2O_3 with the card number of, ICDD 03-065-3170, from Xpert softwares materials index.

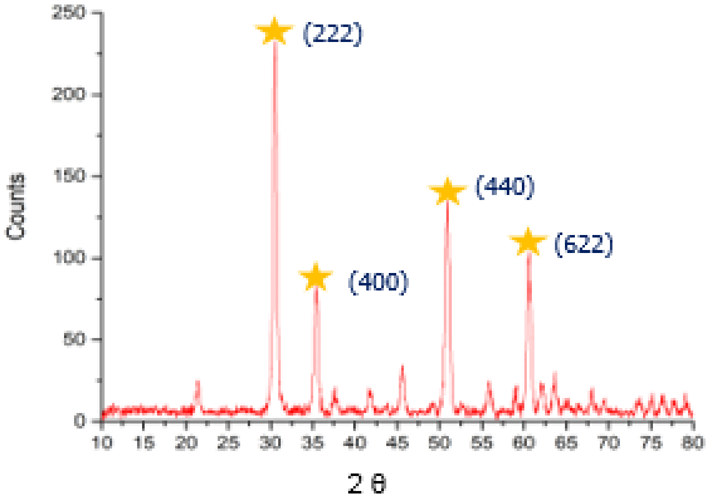

Figure 5.5 : XRD pattern of Sol-Gel synthesized In_2O_3 with calcination temperature of 600 ºC.

Figure 5.6 demonstrates the XRD pattern of Sol-Gel synthesized indium oxide with calcination temperature of 600ºC and citric acid addition. The main peak located around 30° followed by the peaks at 52°, 36°,61° and 21° respectively. Main peaks (222, 400, 440 and 622) are in a match with In_2O_3 with the card number of, ICDD 03-065-3170, from Xpert softwares materials index.

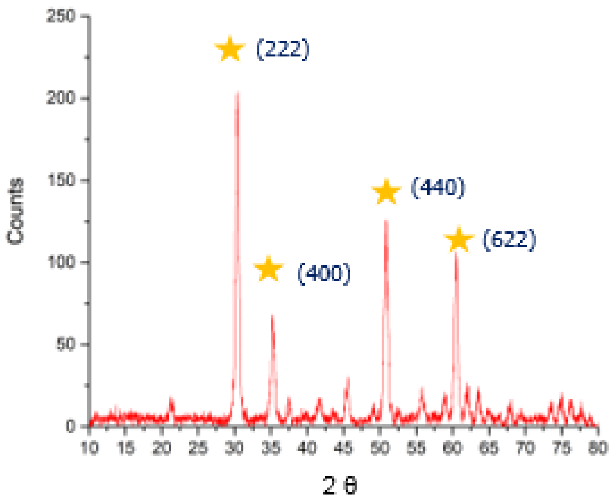

Figure 5.6 : XRD pattern of Sol-Gel synthesized In_2O_3 with calcinatio temperature of 600 ºC and citric acid addition.

After the investigation of zinc oxide (ZnO) and indium oxide (In_2O_3) nanoparticles it is clear that these particles can be synthesized by USP method succesfully. The next step of the XRD analysis was realized for indium zinc oxide (IZO) nanocomposite powders synthesized via Sol-Gel technique. Figure 5.7 investigates the XRD pattern of IZO nanoparticles synthesized via Sol-Gel and then calcinated at 600°C.

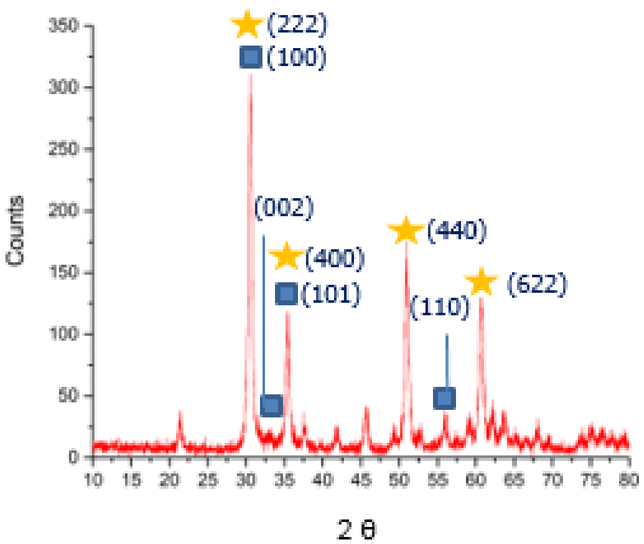

Figure 5.7 : XRD pattern of Sol-Gel synthesized 600°C calcinated IZO nanoparticles.

Figure 5.8 demonstrates the nanoparticles of IZO synthesized via Sol-Gel with the citric acid catalisor addition with the calcination temperature of 600°C. According to comparisons of the peaks from Xpert software both acidic catalisor added and acidic catalisor free samples containing In_2O_3 and ZnO.

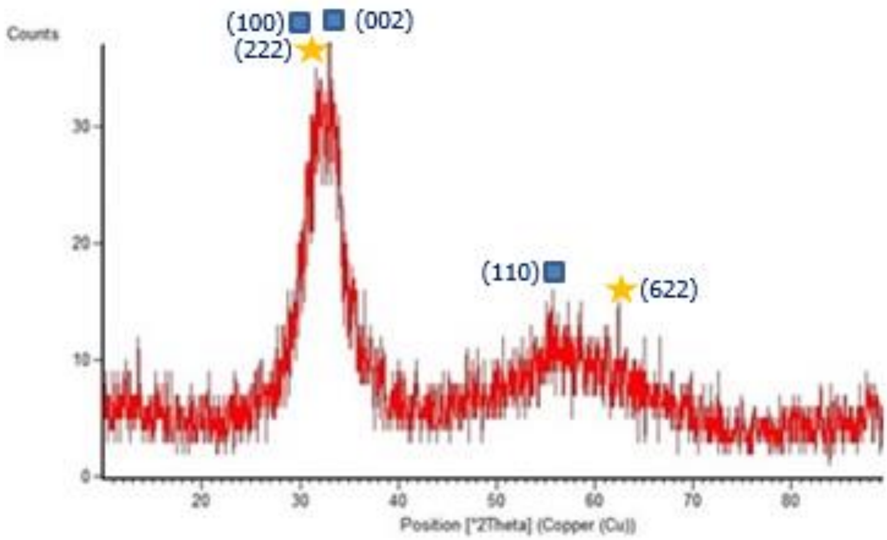

Figure 5.8 : XRD pattern of Sol-Gel synthesized 600°C calcinated IZO nanoparticles with citric acid addition.

Figure 5.9 shows XRD analysis result of Sol-Gel synthesized IZO nanoparticles with calcination temperature of 700°C and acidic catalisor addition. It can be seen that these samples have matching peaks with In_2O_3 XRD results and ZnO XRD results from Xpert softwares index.

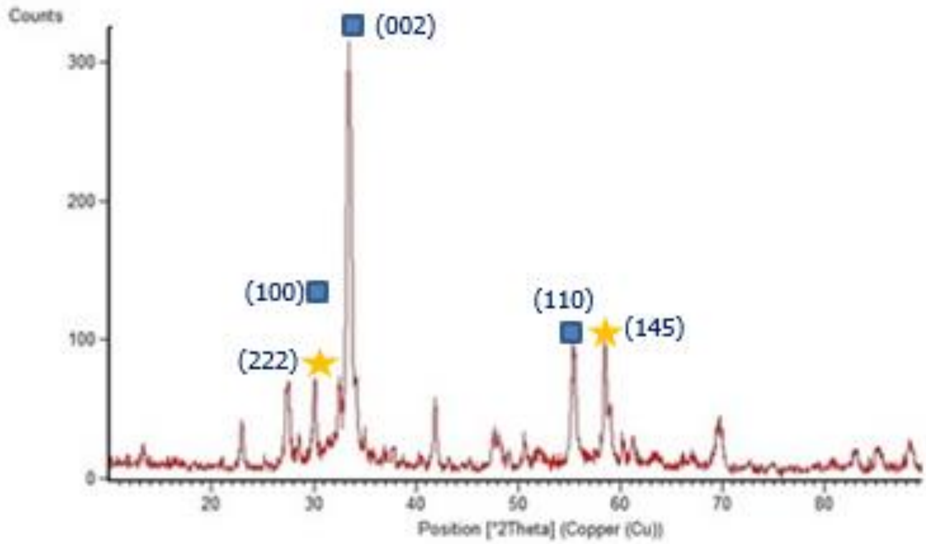

Figure 5.9 : XRD pattern of Sol-Gel synthesized 700°C calcinated IZO nanoparticles with citric acid addition.

2θ values of Sol-Gel synthesized IZO are; 32° and 34° for the sample calcinated at 600°C and 33°, 55°, 58°, 30° and 28° respectively. There are shifts of the peaks to higher angles without matching the pure ZnO nanoparticles. It can be examined by the substitution of In^{+3} ions at Zn^{+2} sites.

Figure 5.10 demonstrates the XRD pattern of IZO nanoparticles synthesized by USP method at 600ºC. It can be seen that these samples have matching peaks with In_2O_3 XRD results and ZnO XRD results from Xpert softwares index.

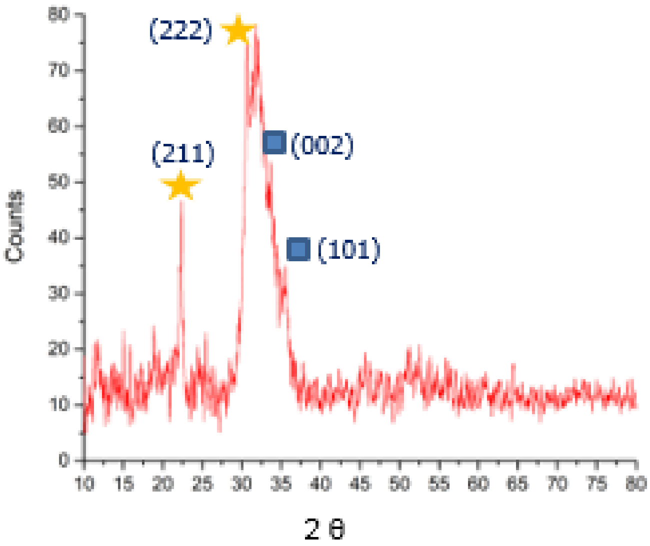

Figure 5.10 : XRD pattern of USP synthesized IZO at 600°C.

Figure 5.11 demonstrates the XRD pattern of IZO nanoparticles synthesized by USP method at 700ºC. It can be seen that these samples have matching peaks with In2O3 XRD results and ZnO XRD results from Xpert softwares index.

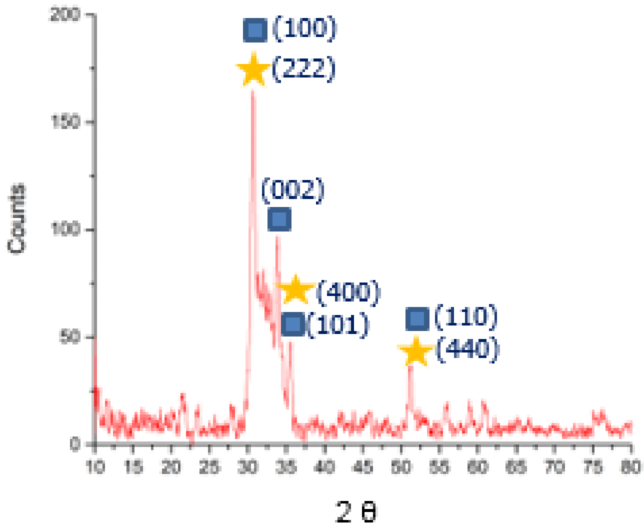

Figure 5.11 : XRD pattern of USP synthesized IZO at 700°C.

Figure 5.12 demonstrates the XRD pattern of indium doped zinc oxide thin films studied by Murali and his colleagues in literature. Main 2θ values of their study are located at 38°, 32°, 30° and 58°. The peaks marked with a star represent the peaks which are not included by pure ZnO nanoparticles. Therefore, 33°, 38° and 52 ° locations for 2θ values are critical. It can be seen that these 2θ values are also exist in the XRD results of this study. From this, it can be said that IZO production via Sol-Gel method and USP method is possible.

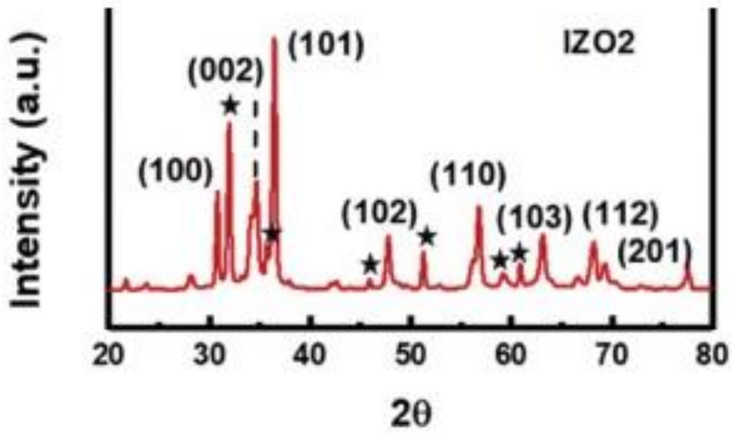

Figure 5.12 : XRD pattern of IZO nanoparticles from literature [34].

XRD results of synthesized In_2O_3, ZnO and IZO nanoparticles with Sol-Gel and ultrasonic spray pyrolysis (USP) methods have matching characterstic peaks with In_2O_3 with the card number of ICDD 03-065-3170 and ZnO with the card number of ICDD 01-075-1533 from the comparison made in Xpert softwares index. Moreover, the peaks of studied samples are matching with the XRD patterns taken from the literature. Process temperature, acidic catalisor addition and process type have some effects on the quality of peaks. However, this could be optimized by changing characterization process parameters.

5.2 Results of SEM-EDS analysis

In order to compare results according to the achievement of the production composite particles, SEM images of the ZnO and In_2O_3 particles are given below. Figure 5.13 demonstrates SEM images of the ZnO particles which were synthesized by USP technique at 600ºC, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed roughly the spherical shapes. Highest magnification (x50.000) enables to investigate the nanoparticles. It can be seen that there are some nanoparticles formed and some of them agglomerated. Particle sizes of zinc oxide nanoparticles are ranging between 500-680 nm.

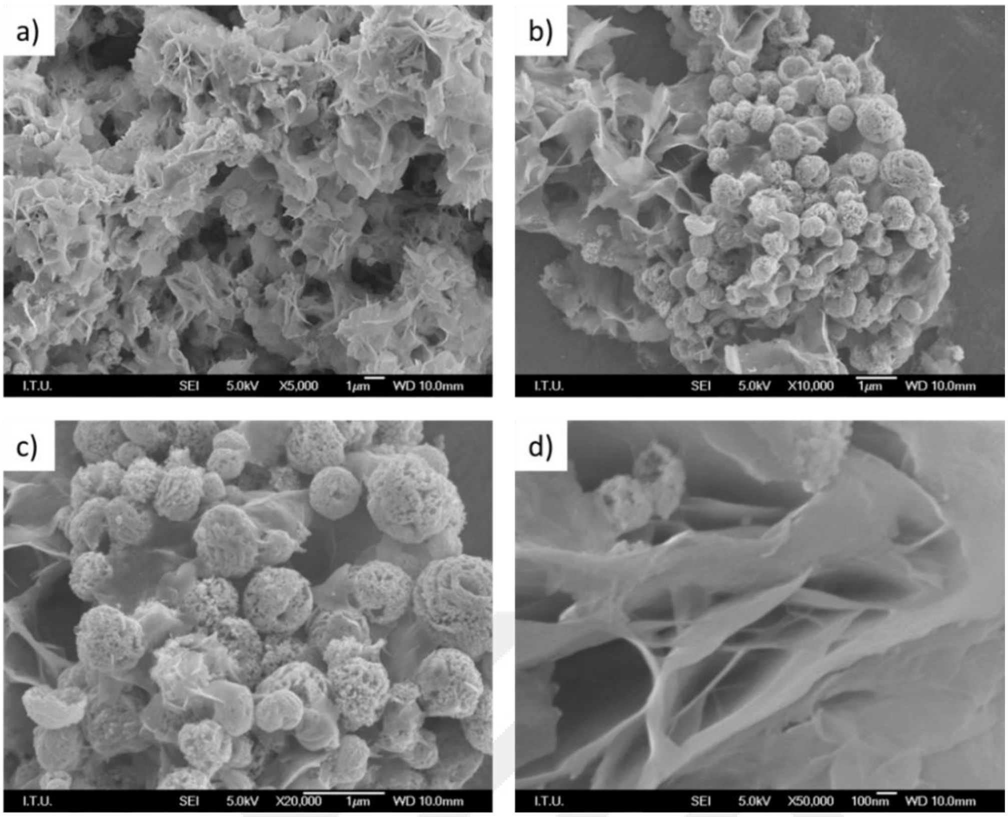

Figure 5.13 : SEM images of ZnO nanoparticles synthesized by USP at 600°C.

Figure 5.14 demonstrates SEM images of the In_2O_3 particles which were synthesized by USP technique at 600ºC, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed perfect spherical shapes. Particle sizes of USP synthesized indium oxide particles are between 100-300 nm mostly.

Figure 5.15 demonstrates SEM images of the IZO samples derived from collected from the particles in the distilled water which were synthesized by USP technique at 600ºC, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed roughly spherical shapes. Also, the size of the particles are in the nanoscale. Particle sizes are ranging between 300-500 nm.

Figure 5.16 demonstrates SEM images of the IZO samples derived from collected from the particles in the distilled water which were synthesized by USP technique at 700ºC, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed roughly spherical shapes. Also, the size of the particles are in the nanoscale. Particle sizes are ranging between 100-600 nm.

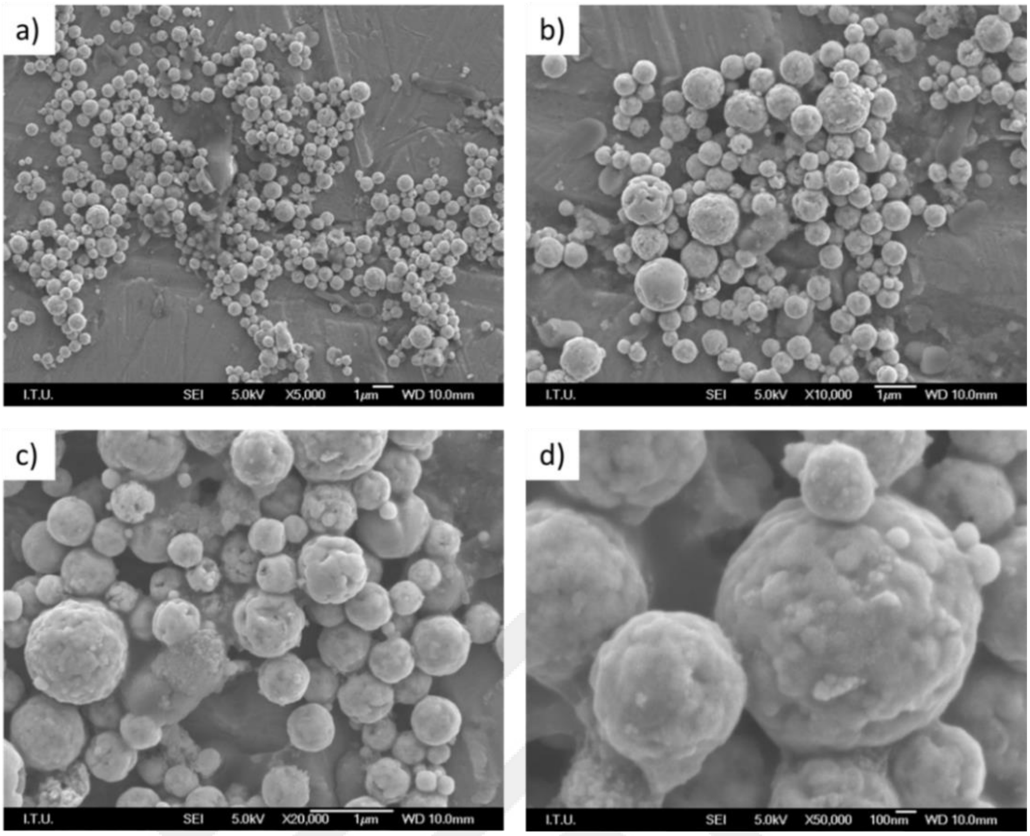

Figure 5.14 : SEM images of In_2O_3 nanoparticles synthesized by USP at 600°C.

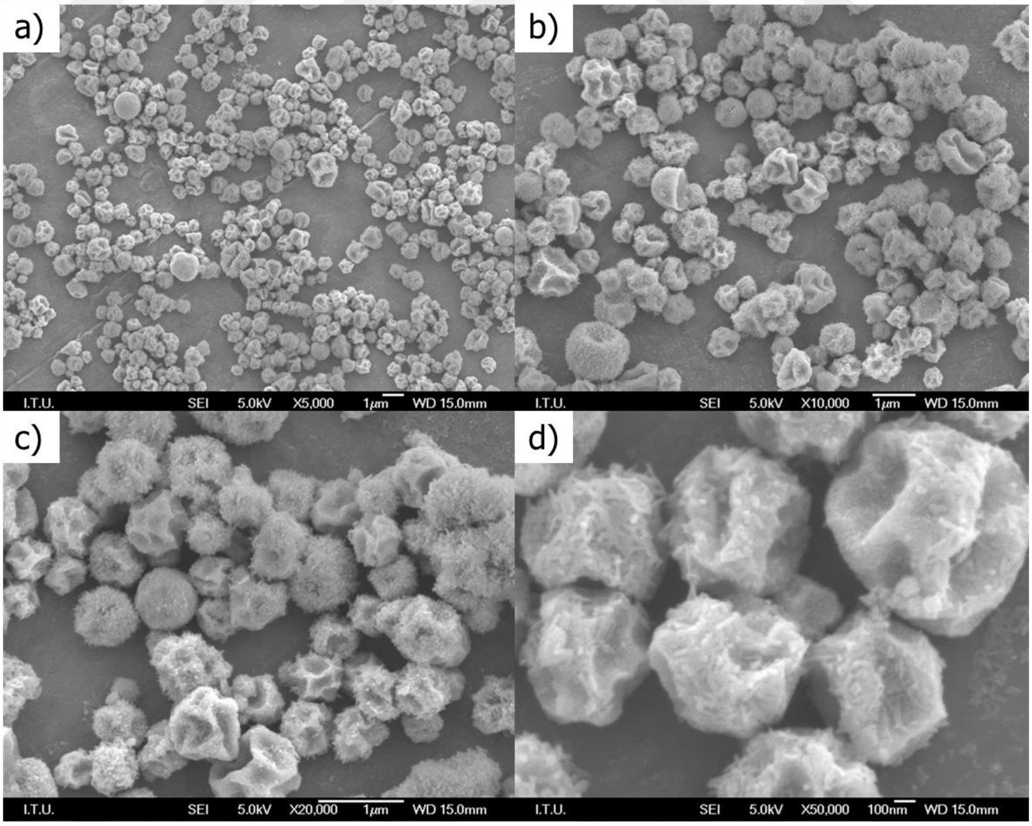

Figure 5.15 : SEM images of IZO particles synthesized by USP at 600°C.

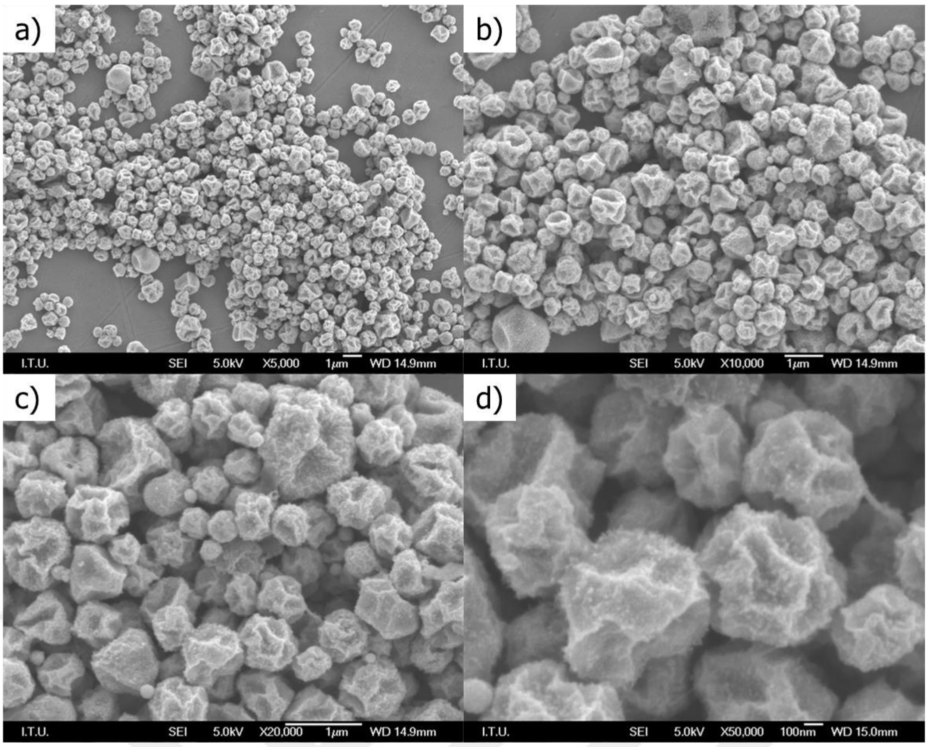

Figure 5.16 : SEM images of In_2O_3 nanoparticles synthesized by USP at 700°C.

Table 5.1 shows the EDS results of the nanoparticles produced by USP method. As it can be seen from the table, there are not any other impurity elements that could be contamined by the nitrate salt or environment exist.

Table 5.1 : EDS results of nanoparticles synthesized via USP.

Spectrum	O	Zn	In
Zinc Oxide USP	39.12%	60.88%	
Indium Oxide USP	41.33%		58.66%
IZO USP (600 ºC)	33.33%	17.21%	49.47%
IZO USP (700 ºC)	30.90%	17.24%	51.86%

Figure 5.17 demonstrates SEM images of the In_2O_3 particles which were synthesized by Sol-Gel technique with 600°C calcination temperature and without acidic catalisor addition. Morphologies are investigated under x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed spherical shapes. Also, there is not vital agglomeration of the particles. Particle sizes of the synthesized particles are ranging between 30-100 nm.

Figure 5.18 demonstrates SEM images of the In_2O_3 particles which were synthesized by citric acid as an acidic catalisor addition Sol-Gel technique with 600°C calcination. Samples are investigated under x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have showed roughly spherical shapes. Also, agglomeration of the particles can be seen easily from the figure. Particle sizes of synthesized nanoparticles are between 200-400 nm.

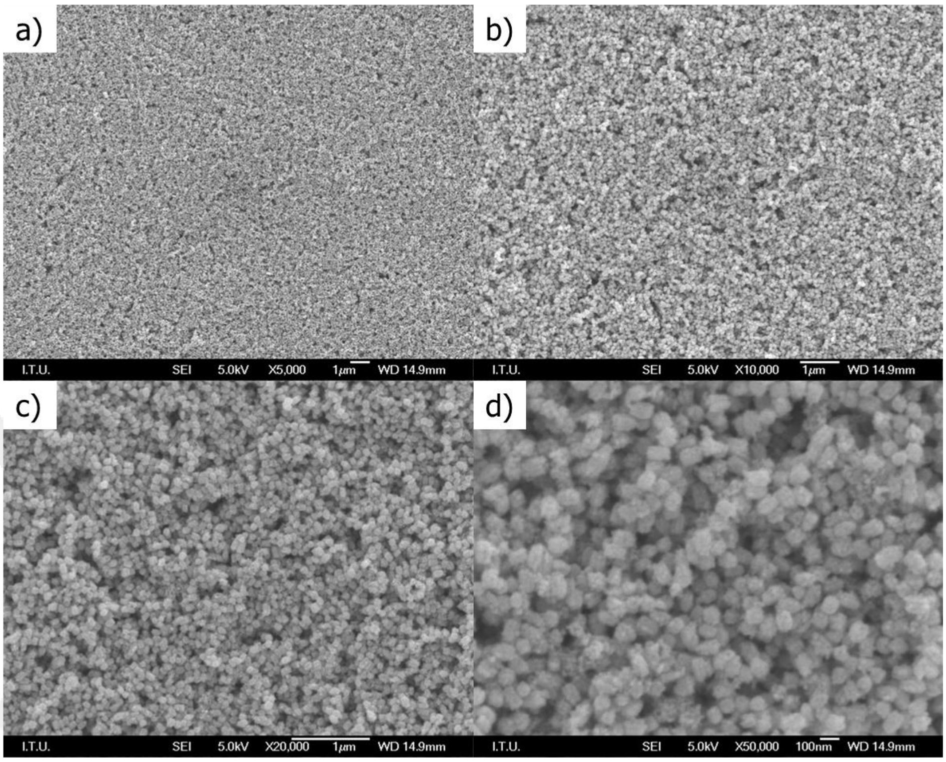

Figure 5.17 : SEM images of In_2O_3 nanoparticles by Sol-Gel with 600°C calcination.

Figure 5.19 demonstrates SEM images of the IZO particles which were synthesized by citric acid added Sol-Gel technique and analyzed before calcination, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have not showed spherical shapes. Also, agglomeration of the particles can be seen from the figure. Particle sizes are ranging between 700-1300 nm due to the agglomeration.

Figure 5.20 demonstrates SEM images of the IZO particles which were synthesized by citric acid added Sol-Gel technique with calcination at 600°C, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have not showed spherical shapes. Morphologies of synthesized particles have existed as flat like structure. However, agglomeration of the particles is less than the ones without calcination. It could be seen that the nanoparticle formation has occured. Particle sizes are ranging between 200-400 nm.

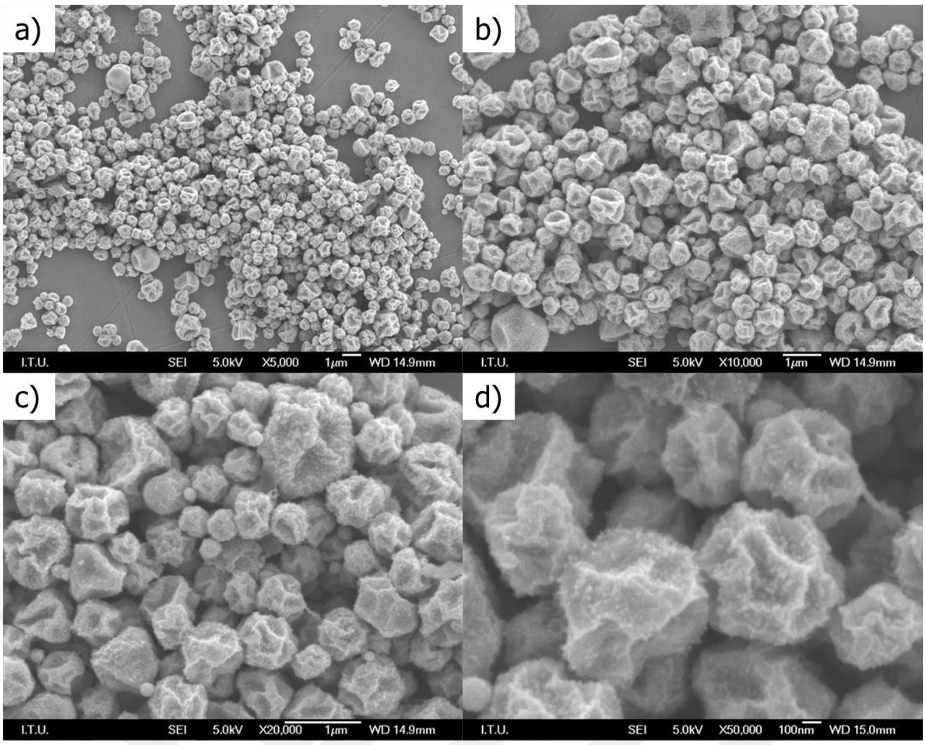

Figure 5.18 : SEM images of IZO nanoparticles by acidic catalisor added Sol-Gel with 600°C calcination.

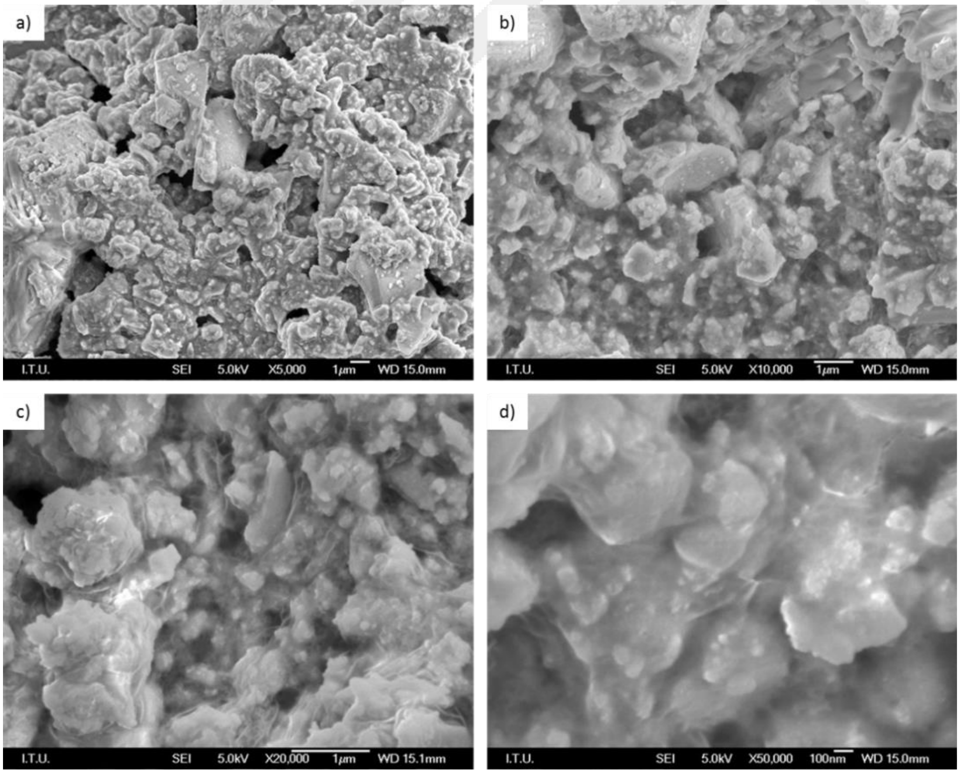

Figure 5.19 : SEM images of IZO nanoparticles by Sol-Gel before calcination.

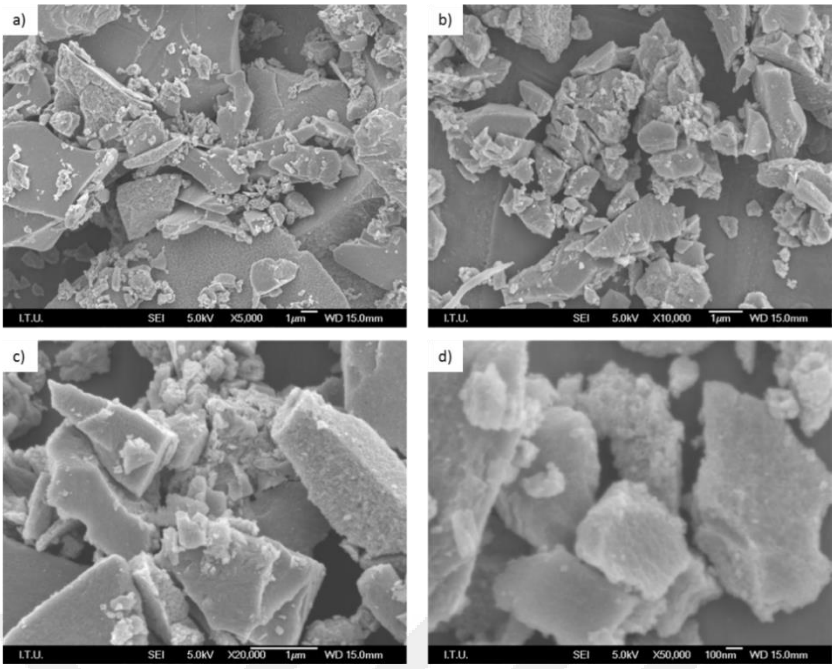

Figure 5.20 : SEM images of IZO nanoparticles by Sol-Gel and 600°C calcination.

Figure 5.21 demonstrates SEM images of the IZO particles which were synthesized by citric acid added Sol-Gel technique with calcination at 700°C, with x5.000, x10.000, x20.000 and x50.000 magnifications. According to these images, they have not showed spherical shapes. Morphologies of the particles are seen generally as flat like structured. Particle sizes are ranging between 50-200 nm. Moreover, IZO nanoparticle sizes are smaller than non-calcinated and calcinated at 600°C samples.

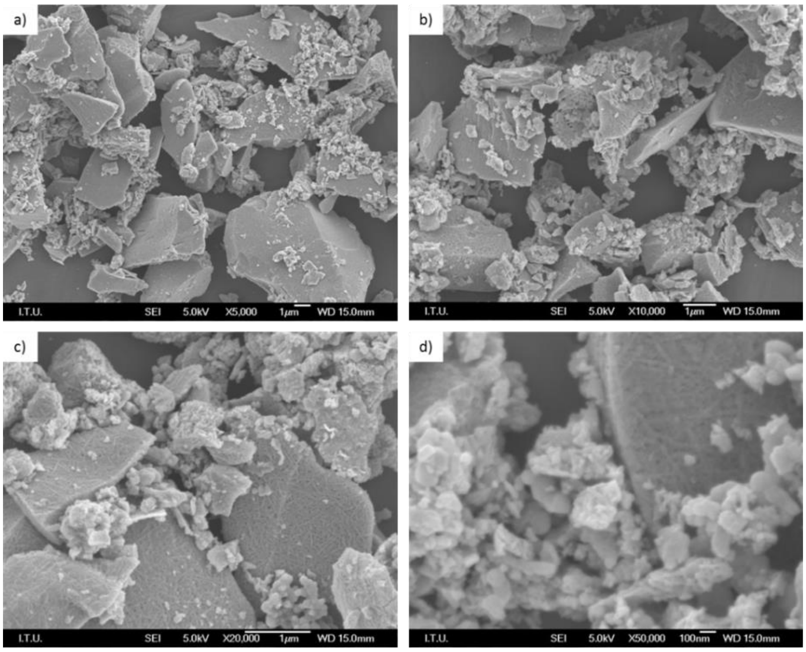

Figure 5.21 : SEM images of IZO nanoparticles by Sol-Gel and 700°C calcination.

Table 5.2 shows the EDS results of the nanoparticles produced by Sol-Gel method. As it can be seen from the table, there are not any other impurity elements that could be contamined from the nitrate salt or environment, exist.

Table 5.2 : EDS results of IZO nanoparticles synthesized via sol-gel.

Spectrum	O	Zn	In
In_2O_3 Sol-Gel non citric acid added	24.33%		75.67%
In_2O_3 Sol-Gel non citric acid added	25.77%		74.23%
IZO Sol-Gel (Non-calcinated)	49.15%	15.97%	34.88%
IZO Sol-Gel (600°C Calcinated)	24.73%	25.31%	49.96%
IZO Sol-Gel (700°C Calcinated)	23.28%	27.36%	49.37%

5.3 Results of Raman Spectrometer Analysis

Figure 5.22 demonstrates the results of RAMAN analysis for IZO nanocomposite particles synthesized by Sol-Gel method and then calcinated at 700°C. The peaks having the highest intensity have been located at 137.2, 312.6, 501.3 and 632.9 cm^{-1} Raman shifts. The result of Raman spectrometry is compatible with the results found in literature.

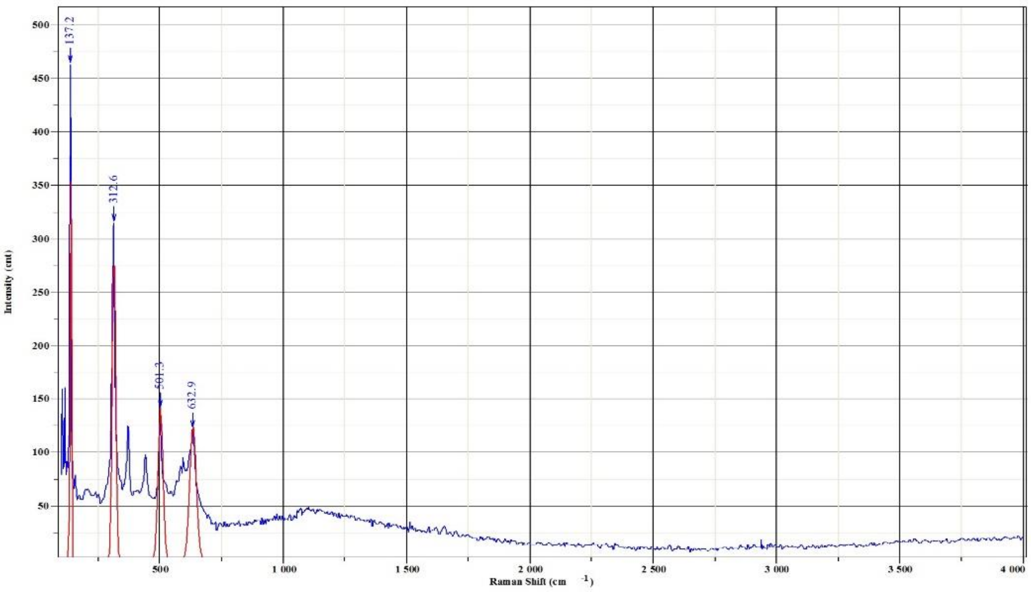

Figure 5.22 : Raman spectrometer analysis of IZO synthesized by sol-gel and calcinated at 700°C.

6. CONCLUSION

- Indium Zinc Oxide (IZO) nano-composite particles have been synthesized by USP and Sol-Gel methods.
- In order to synthesize IZO particles via USP technique, 0,1 M indium nitrate and zinc nitrate solution has been used. Reactions in the furnace have taken 3 hours at 600°C.
- In order to synthesize IZO particles via Sol-Gel technique, 0,1 M indium nitrate and zinc nitrate hexahydrate solution has been used.
- Calcination temperatures of the IZO particles which are produced by Sol-Gel have been determined by DSC-TGA analysis. According to the results of the analysis no mass change has observed over 600°C. So that, calcination tempearatures have been determined as 600°C and 700°C.
- Particles synthesized via Sol-Gel method have lower particle sizes (50-200 nm) than the particles synthesized by USP (100-600 nm).
- Particles synthesized by USP have more spherical particle structure than the ones synthesized by Sol-Gel.
- Higher calcination temperature for the particles synthesized by Sol-Gel method, leads formation of the particles having smaller particle size. IZO nanparticles calcinated at 600°C have particle sizes ranging between 200-400 nm and IZO nanoparticles calcinated at 700°C have particle sizes ranging between 50-200 nm.
- Particle sizes of IZO nanoparticles produced by USP with process temperature of 600°C are 300-500 nm. However, the ones processed at 700°C have particle sizes of 100-600 nm. From this result, it can be said that smaller IZO nanoparticles can be synthesized by higher process temperatures of USP, but with higher particle size distributions.
- Particle sizes of Sol-Gel synthesized In_2O_3 nanoparticles differ according to acidic catalisor addition before gelation process. Samples that are processed with citric acid as an acidic catalisor have higher particle sizes (200-400 nm) while acidic catalisor free samples have lower particle sizes (30-100 nm)

- XRD results of IZO nanoparticles includes both the zinc oxide and the indium oxide peaks. Since synthesized IZO nanoparticles contain both zinc oxide and indium oxide, it can be said that the process is successful in making composite.
- XRD peaks of produced samples are matching with In_2O_3 having the card number of ICDD 03-065-3170 and, ZnO having the card number of ICDD 01-075-1533 from Xpert softwares index.
- XRD and Raman analysis results have been compared with the literature. According to the literature, it could be said that the particles synthesized by these methods are compatible with the literature.
- From the EDS results of both Sol-Gel and USP methods, it could be understood that there are not any impurity exists in synthesized particles chemical compositions.
- In order to increase the yield of the USP method, longer time could be given for the synthesis.
- In order to investigate the efficiency of synthesized particles, photocatalytic activity of them could be investigated in further researches.
- Effects of graphene addition could be investigated in the future studies.

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