

**MOLTEN SALT ASSISTED SELF-ASSEMBLY
PROCESS: SYNTHESIS OF MESOPOROUS
TRANSITION METAL OXIDE THIN FILMS
AND CdSe SENSITIZED TiO₂ PHOTOANODES**

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By
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ABSTRACT

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Fabrication of mesoporous transition metal oxide thin films are important for the development of many energy related technologies. Molten salt-assisted-self-assembly (MASA) method, that has simple stages such as preparation of a clear solution of the precursors in water or ethanol, coating of this solution on a substrate as a thin film, and calcination of the film at an elevated temperature is a simple and useful method to fabricate mesoporous thin films. In this thesis, mesoporous transition metal oxides thin films and CdSe sensitized TiO₂ photoanodes have been fabricated using MASA approach and characterized using multi-analytical techniques. In the first part of the thesis, CdSe/TiO₂ thin films were synthesized by reacting mesoporous CdTiO₃ thin film under a H₂Se gas atmosphere. Many synthesis parameters were optimized in the synthesis of mesoporous CdTiO₃ thin films. The film thickness, calcination temperature, and H₂Se reaction condition have been changed to determine the optimum synthesis conditions for an efficient photoanode of a quantum dot sensitized solar cell (QDSSC). However, the reactivity of CdTiO₃ towards to H₂Se gas is low and selenium forms as a side product upon H₂Se reaction. For the reactivity problem, mesoporous CdO-SiO₂ (denoted as meso-CdO-SiO₂) thin films were synthesized to increase the CdSe nanoparticle

population, as the sensitizer in the CdSe sensitized TiO₂ photoanode. However, The meso-CdSe-SiO₂ thin films are not active in solar cells because of an insulating nature of silica.

Second part of the thesis involves infiltration of MASA solution (precursors of salt-surfactant and a polymerizing agent, such as Si(OCH₃)₄ or Ti(OC₄H₉)₄) into the pore of prefabricated films (using P25) of mesoporous titania (denoted as meso-P25). In latter steps, the above films were calcined and then reacted under H₂Se to obtain the photoanodes (denoted meso-CdSe-SiO₂-P25 and meso-CdSe-TiO₂-P25). The synthesis conditions were optimized by changing the synthesis parameters (such as precursor concentrations, calcination, and H₂Se reaction temperatures) and using XRD, FTIR, Raman, ²⁹Si-MAS-NMR, EXAFS, XANES, SEM, TEM, N₂-sorption techniques. However, formation of a meso-CdO-SiO₂ thin film, on top of the meso-P25 film, was observed upon using a concentrated MASA solution in the infiltration step. Therefore, multiple loading method has been established to increase the CdSe-SiO₂ layer in the pores of meso-P25 using diluter MASA solutions. Also, the H₂Se reaction conditions were optimized by controlling the reaction atmosphere and temperature. Effects of silica amount in the CdO-SiO₂ system on the photoanode has been examined by measuring the I-V curves, of the solar cells fabricated using our photoanodes.

In the last part of the thesis, the MASA method has been adopted for the synthesis of mesoporous transition metal oxides thin films. Firstly, mesoporous iron oxide film has been synthesized using MASA approach and characterized using above analytical tools. The thermal and structural properties of the [Fe(H₂O)₆](NO₃)₃/surfactants (10-lauryl ether and CTAB) mesophases have been investigated for the synthesis of a well-ordered iron oxide films. Effects of calcination temperature, on the crystallinity, and porosity of mesoporous Fe₂O₃, have been demonstrated by using TEM, SEM, XRD, and N₂ sorption techniques. Later, other mesoporous transition metal oxides (such as ZnO, CuO, NiO, Co₃O₄ and Mn₂O₃) have been synthesized using the MASA approach. The transition metal salts ([Zn(H₂O)₆](NO₃)₂, [Cu(H₂O)₆](NO₃)₂, [Ni(H₂O)₆](NO₃)₂, [Co(H₂O)₆](NO₃)₂, [Mn(H₂O)₆](NO₃)₂)-surfactant mesophases have been used as the starting liquid crystalline materials that can be calcined at high temperatures (above 300 °C) to

obtain the thin films. The synthesized mesoporous metal oxide thin films were characterized by using above analytical tools.



Keywords: Mesoporous Materials, Lyotropic Liquid Crystals, Molten-Salt-Assisted-Self-Assembly, Mesoporous Thin Films, Quantum Dot Sensitized Solar Cell.

ÖZET

ERİYİK TUZ YARDIMLI KENDİLİĞİNDEN OLUŞMA (EYKO) YÖNTEMİ: MEZOGÖZENEKLİ GEÇİŞ METAL OKSİT İNCE FİLMLERİN VE CdSe DUYARLI TiO₂ FOTO-ANOTLARIN SENTEZİ

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Mezogözenekli geçiş metal oksitlerinin üretilmesi birçok enerji ile ilgili teknolojilerin gelişmesinde önemlidir. Eriyik tuz yardımcı kendiliğinden oluşma (EYKO) metodu, birkaç basit aşamadan oluşur, bunlar başlangıç malzemelerinin (uygun tuz, yüzeyaktifler, setiltirimetilamonyum bromür, (CTAB) ve 10-löril eter, C₁₂H₂₅(OCH₂CH₂)₁₀OH, ve su veya etanol) şeffaf çözeltisinin hazırlaması, bu çözeltinin herhangi bir alttaşa kapladıktan sonra yakılmasını içerir.

Mezogözenekli geçiş metal oksit ince filmleri ve CdSe TiO₂ foto-anotları, EYKO metodu ile üretildi ve birçok analitik teknik ile karakterize edildi. Tezin ilk bölümünde, CdSe/TiO₂ ince filmi, mezogözenekli CdTiO₃ ile H₂Se gazının reaksiyona girmesi sonucu üretildi. Sentez basamakları her aşamada optimize edildi. Film kalınlığı, yakma sıcaklığı ve H₂Se tepkime ortamı optimum koşulları bulmak için değiştirildi ve kuantum nokta duyarlı güneş pilleri üzerindeki etkisi incelendi. Fakat, mezogözenekli CdTiO₃ ile H₂Se gazının tepkimesinin verimsiz olduğu belirlendi ve ayrıca, metalik selenyum yan ürünü olduğu belirlendi. Verimlilik probleminden dolayı, mezogözenekli CdO-SiO₂ (meso-CdO-SiO₂ olarak adlandırıldı) ince filmleri, CdSe duyarlı TiO₂ foto-anodunda daha çok duyarlı CdSe

nanoparçacıkları oluşturmak için, sentezlendi. Fakat bu filmler silikanın yalıtkan olmasından dolayı güneş pilleri için uygun değildir.

Tezin ikinci kısmı, başlangıç MASA çözeltisinin, (uygun tuz, yüzeyaktifler (CTAB ve 10-lörlil eter) etanol ve silika kaynağı $\text{Si}(\text{OCH}_3)_4$ veya titania kaynağı $\text{Ti}(\text{OC}_4\text{H}_9)_4$) önceden hazırlanmış mezogözenekli TiO_2 (meso-P25 olarak adlandırıldı) filmine eklenmesini içerir. Sonraki aşamalarda, filmler yakılır ve H_2Se tepkimesi sonucu foto-anotlar elde edildi. Sentez parametreleri optimize edildi ve elde edilen bu malzemeler XRD, FTIR, Raman, ^{29}Si -MAS-NMR, EXAFS, XANES, SEM, TEM, N_2 -sorplama teknikleri kullanılarak karakterize edildi. Başlangıçta yoğun çözelti kullanması, meso-P25 filminin içerisini homojen kaplarken, üzerinde de yalıtkan CdO-SiO_2 filmini oluştuğu gözlemlendi. Dolayısıyla, meso-P25 filminin boşlukları içerisine yeterli CdSe-SiO_2 film tabakası oluşturmak için seyreltik çözelti kullanıldı ve birkaç yükleme ile hedefe ulaşıldı. H_2Se reaksiyon ortamı ve tepkime sıcaklığı optimize edildi. Ayrıca, CdO-SiO_2 film tabakasındaki silika miktarı sistematik azaltılarak incelendi.

Üçüncü kısımda ise EYKO metodu mezogözenekli geçiş metal oksit ince filmlerini sentezlemek için uyarlandı. İlk olarak, mezogözenekli demir oksit ince filmleri EYKO metot ile sentezlendi ve yukarıdaki teknikler kullanılarak karakterize edildi. $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_3$ ve CTAB ve 10-lörlil eter sisteminin termal ve yapısal özellikleri daha düzenli mezogözenekli Fe_2O_3 filmi elde edebilmek için incelendi. Yakma sıcaklığının, kristalleşme ve gözenekli yapı üzerindeki etkisi TEM, SEM, XRD and N_2 sorplama teknikleri ile detaylı şekilde incelendi. Sonra, diğer mezogözenekli geçiş metal oksitleri (ZnO , CuO , NiO , Co_3O_4 and Mn_2O_3) EYKO metot kullanılarak sentezlendi. Başlangıçta bilinen geçiş metali nitrat tuzları ($[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$) ve yüzey aktif arafazları kullanıldı. Sıvı kristal arafaz oluştuktan sonra farklı sıcaklıkta yakılarak ince filmler elde edildi. Sentezlenen mezogözenekli geçiş metal oksit ince filmlerini, yukarıdaki analitik teknikler kullanılarak karakterize edildi.

Anahtar Sözcükler: mezogözenekli malzemeler, sıvı arafazlar, eriyik tuz yardımcı kendiliğinden oluşma, mezogözenekli ince filmler, kuantum nokta duyarlı güneş pili.

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List of Abbreviations

IUPAC: International Union of Pure and Applied Chemistry

FTIR: Fourier Transform Infrared Spectroscopy

EXAFS: Near Edge X-Ray Absorption Fine Structure

XANES: X-Ray Absorption Near Edge Structure

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

BET: Brunauer-Emmett-Teller

JCPDS: Joint Committee on Powder Diffraction Standards

NMR: Nuclear Magnetic Resonance

LLCT: Lyotropic Liquid Crystalline Templating

EISA: Evaporation Induced Self-Assembly

MASA: Molten Salt Assisted Self-Assembly

QDSSC: Quantum Dot Sensitized Solar Cell

PEC: Photoelectrochemical Cell

PCE: Power Conversion Efficiency

Chapter 1

Introduction

1.1 Sol-Gel Process

Many materials have been synthesized starting from solution phase (*sol*), where the gelation (*gel*) takes place by the formation of polymeric network of precursor species over time. Using *sol-gel* method, aerogels, xerogels, films, fibers and size controlled nanoparticles have been fabricated in the last three decades [1]. In the gelation, the hydrolysis and condensation (alcoxolation, oxolation) take place by nucleophilic substitution (S_N) reactions, schematically shown in **Figure 1.1**. Inorganic precursors can be metal alkoxides ($M(OR)_x$) and metal salts (MA) of chloride, acetate, and nitrate. The reactivity of precursors depends on electronegativity of OR groups and oxidation state of the metal center [2]. The hydrolysis and condensation can be controlled by choosing optimum alkoxides or metal salts, pH, [1] where different morphologies can be synthesized. Titania [3] and silica [4] are synthesized from their alkoxides by sol-gel process, because of their instability towards hydrolysis and condensation. Titanium alkoxides ($Ti(OR)_4$ [3], R can be ethyl, propyl, isopropyl, or butyl) or titanium chloride ($TiCl_4$ [5]) are usually used as titanium precursors and silicon alkoxides ($Si(OC_nH_{2n+1})_4$ [1]) are usually used as a silica precursor.

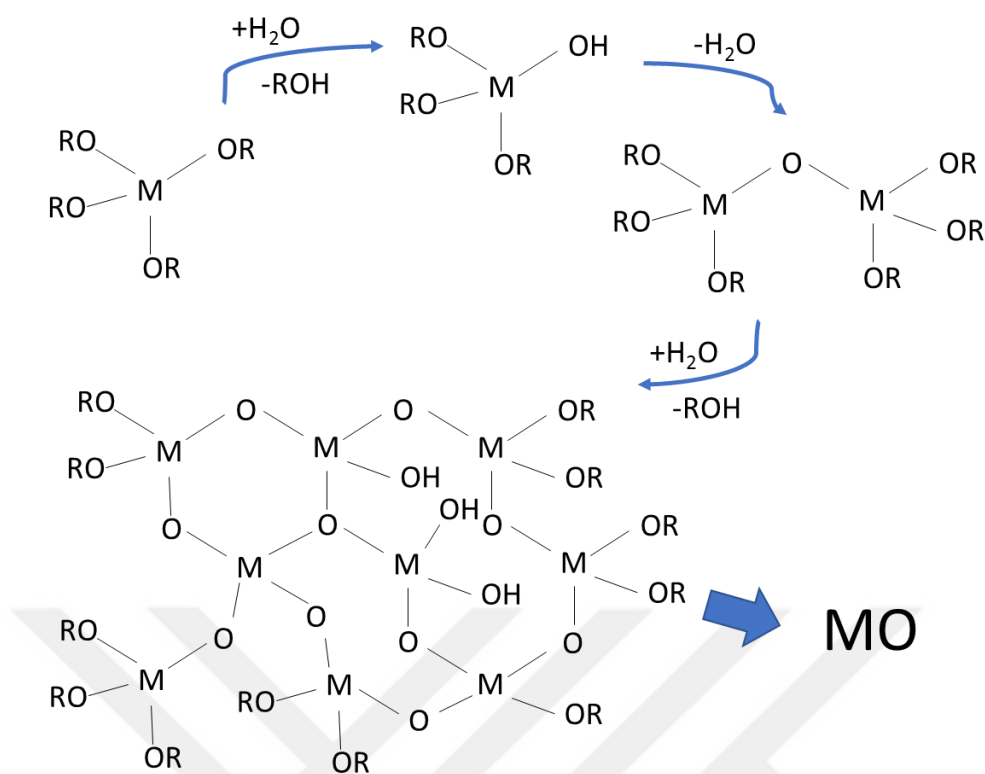


Figure 1.1. Hydrolysis and condensation of inorganic precursors.

The condensation precursors of inorganic precursors have been investigated by spectroscopic techniques [6] (such as FTIR, Raman, NMR [7]). There are many spectroscopic changes during gelation and solidification stages. Also, other techniques (XRD and electron microscopy) are helpful to understand the formation mechanism of the products. For instance, **Figure 1.2** shows a set of ^{29}Si NMR [8] spectra at different times during the condensation of methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS) and tetraethoxysilane (TEOS). In each spectrum, while different chemical shifts are observed, relative ratios of Q_2 , Q_3 and Q_4 peaks (Q_0 , Q_1 , Q_2 , Q_3 , Q_4 are used to represent of silicon atoms surrounded by 0, 1, 2, 3 or 4 siloxane bridges) show changes over time [8]. The changes are useful to evaluate the formation mechanism of each samples. The final product of TEOS has peaks at around -91 ppm that originates from Q_2 species, around -100 ppm from Q_3 and around -109 ppm from Q_4 , where the Q_3 and Q_4 peaks have the higher intensity, due to surface hydroxide and bulk silicas.

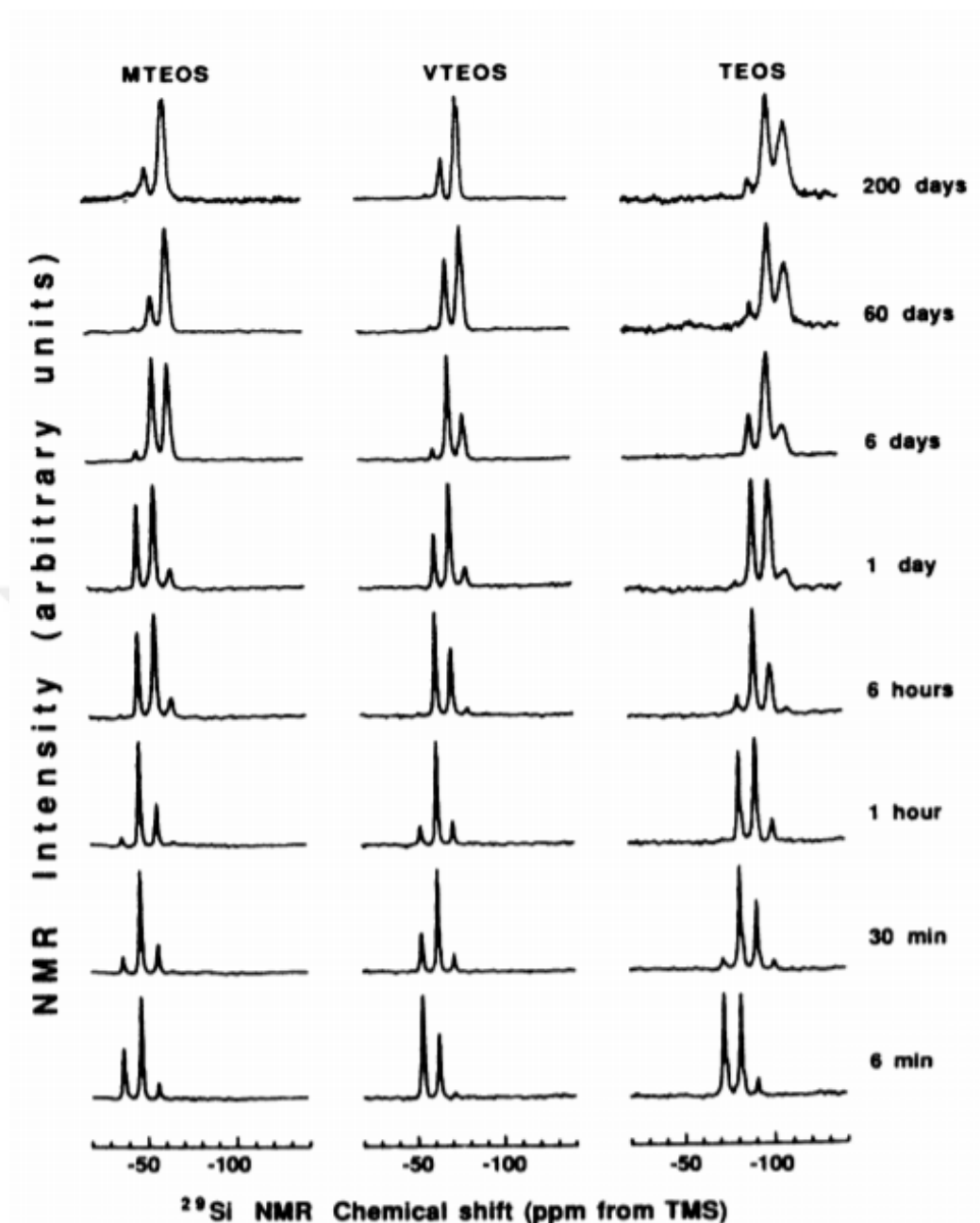


Figure 1.2.¹ ^{29}Si NMR spectral changes over time during the condensation of methyltriethoxysilane (MTEOS), vinyltriethoxysilane (VTEOS) and tetraethoxysilane (TEOS).

¹ Reprinted from Physical Review A, Vol. 41, Devreux, F; Boilot, J P; Chaput, F; Lecomte, "Sol-gel Condensation of Rapidly Hydrolyzed Silicon Alkoxides: A joint ^{29}Si NMR and Small-angle X-ray Scattering Study." 6901- 6909, (1990), with permission from American Physical Society.

1.2 Mesoporous Materials

Recently, surface of materials and interface between two different materials have become important, because in all chemical process, mass and electron transport take place at the surface and/or in the interfaces materials and determine the effectiveness of the material. At the interface, two-materials transfer electron or mass to each other, therefore the amount of interface is critical. One way to increase the interface of the materials is by increasing the surface area and porosity of materials. High surface area is needed for an effective electron transfer and porous structure is necessary for an efficient mass transport. Therefore, porous materials are important for material efficiency for various chemical and electrochemical processes.

Porous materials have been classified by IUPAC depending on the pore size: microporous materials have pore size lower than 2 nm, mesoporous materials fall between 2 and 50 nm, and macroporous materials have pores larger than 50 nm [9]. The materials with smaller pores have higher surface area. Depending on application of the materials, a different pore size may be needed. For instance, for a gas separation, microporous materials are essential [10] and for photovoltaics, mesoporous materials are essential [11]. Therefore, synthesis of porous materials is still an important and emerging field.

Kresge *et al.* has introduced the first examples of mesoporous materials [12] in 1992. Mesoporous silica (MCM-41, MCM-48 and MCM-50 are labels for 2D hexagonal, cubic, and lamella, respectively) had been synthesized by controlling polymerization of tetramethylorthosilicate (TMOS) in an aqueous surfactant (hexadecyltrimethylammonium bromide ion (CTAB)) media. The sol-gel process takes place in a confined space among the micella species in above conditions. After this pioneering study, a lyotropic liquid crystalline templating (LLCT) method for the synthesis of mesoporous silica has been introduced in 1995 by Attard *et al.* [13].

1.3 Lyotropic Liquid Crystals Templating Method

Before going into the LLCT method, it would be useful to describe the liquid crystalline mesophase in terms of structure and composition. Some of the primary phases of matter are solid, liquid, gas, and liquid crystal (LC). The LC phase is considered to be the 4th phase of matter. The LC phase is observed between solid and liquid phases in terms of rigidity, viscosity, and orientation of matter, see **Figure 1.3**. Solids have ordered structures but there is no order in liquid phase. The molecules or micelles (self-assembled collection of surfactant molecules, typically 50-150 molecules) in the LC have some degree of order, due to long organic chains. Usually, the LC phase is observed in long chains organic molecules with certain geometry and surfactants that have both hydrophobic and hydrophilic groups, attached to each other.

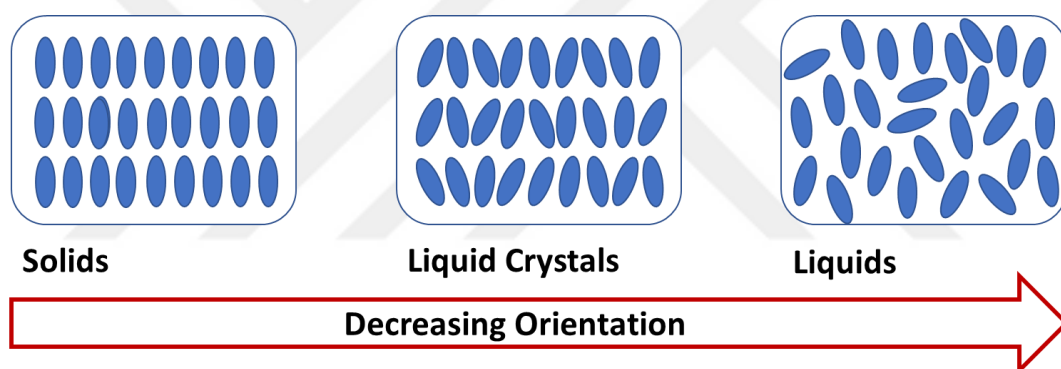


Figure 1.3. Illustration of orientational order in solids, liquid crystals and liquids.

Liquid crystals are divided into two categories; thermotropic liquid crystal (TLC) and lyotropic liquid crystal (LLC). The order in the TLCs are only temperature dependent. However, the order in the LLC phases depend on both composition and temperature. Structure of the LLC phase changes with the composition, such as surfactant/solvent ratio as well as temperature of the media. The surfactant molecules contain a polar head group and apolar chain. Interaction like van der Waals, hydrogen bonding, and dipole-dipole with the solvent determines the assembly of surfactant molecules. Surfactants form micelles by self-assembly if the surfactant concentration is above a critical concentration, known as critical micelle concentration (CMC) in an aqueous media. Further increase of the surfactant concentration may lead to form LLC mesophases. **Figure 1.4** shows a phase diagram

of CTAB, one of the charged surfactant, in water, where CMC1 is critical micelle concentration for spherical micelles, CMC2 is critical micelle concentration for rod-like micelles. By increasing the surfactant concentration in water, the LLC phase appears as lamellar, hexagonal, or cubic mesostructure. The LLC phase is very dynamic and the assembly of micelles (lamellar, hexagonal, or cubic phases) can be controlled easily to determine optimum conditions of surfactant/solvent systems for a desired mesostructure. Surfactants can be triblock co-polymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) like pluronics or oligo(ethylene oxide) type molecules, like 10 lauryl ether ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, denoted as $\text{C}_{12}\text{EO}_{10}$).

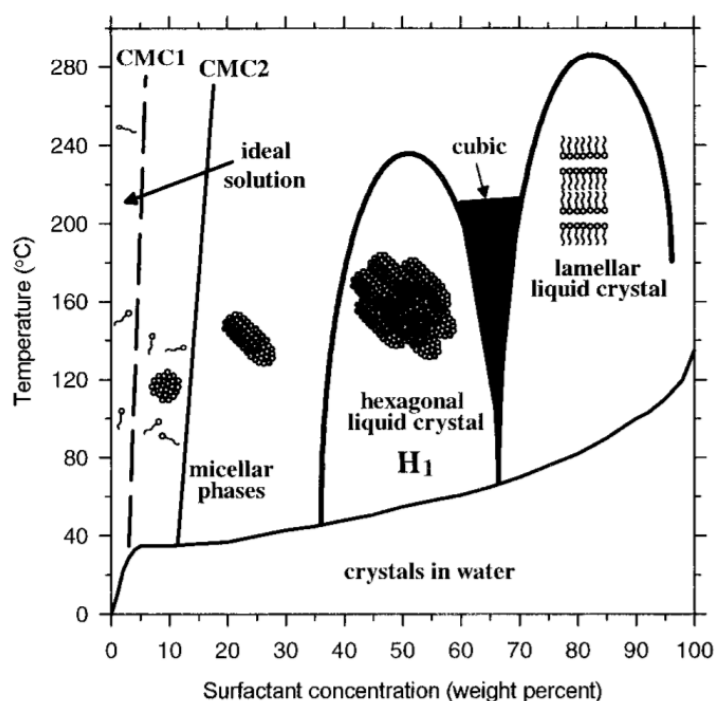


Figure 1.4. The phase diagram of CTAB in water. (CMC1: critical micelle concentration for spherical micelles, CMC2: critical micelle concentration for rod-like micelles)².

² Reprinted from Chemistry of Materials, Vol 8, Raman, N. K.; Anderson, M.T. and Brinker C. J. "Template-Based Approaches to the Preparation of Amorphous, Nanoporous Silicas." 1682-1701, (1996), with permission from American Chemistry Society.

The second component of the LLC phase can be water, ionic liquids, electrolytes, and salts. They have different effects on the LLC phase and could be useful for the synthesis of porous materials through LLCT approach.

Attard *et al* introduced the synthesis of mesoporous silica using LLCT approach [13]. The silica precursor (tetraethoxysilane, TEOS) and water with a high surfactant concentration have been used for synthesis of mesoporous silica. In this study, by controlling the hydrolysis and condensation of the silica precursor in a C₁₂EO₈, TEOS and water LLC media, monoliths and thin films of highly uniform mesoporous silica with a 3 nm pore size were synthesized in 1995 [13].

Later, LLC has been applied to synthesize many different mesoporous materials. For instance, mesoporous metal films (Pt [14], Sn [15]) and Pt/Ru [16] alloys) were synthesized by electrodeposition and also mesoporous Ni/Co alloy [17] and Ni particles [18] were fabricated by electroless deposition. Some metal oxides (TiO₂, ZrO₂, Al₂O₃, Nb₂O₅, Ta₂O₅, WO₃, HfO₂, SnO₂) and mixed oxides (SiAlO₃, SiTiO₃, ZrTiO₃, Al₂TiO₃, ZrW₂O₈) have also been synthesized [5] using LLCT method. Also, some semiconducting solids (CdS, ZnS and CdSe) has been synthesized in the LLC mesophase by reacting their metal salts by hydrogen sulfides and selenide gases [19], [20].

In all these synthesis approaches, the hydrolysis and condensation of inorganic precursor are controlled in either micella solution or LLC phase of surfactants. In a latter step either calcination or extraction methods have been employed to obtain the mesoporous materials. The surfactants were used as a sacrificial agent to form porous network of materials. In all these approaches, surfactant weight (>30 % w/w) was kept high to control the porosity in the final product. Low inorganic precursor amounts could be problematic in the formation of porous materials with solid amorphous or crystalline pore walls, because the volume shrinkage of metal precursors (such as salts) is huge when they are converted to their oxides or sulfides or selenides to form solid films.

In another lyotropic liquid crystalline system, nonionic surfactant and transition metal salts (such as [Co(H₂O)₆](NO₃)₂, [Ni(H₂O)₆](NO₃)₂, [Zn(H₂O)₆](NO₃)₂, and [Cd(H₂O)₄](NO₃)₂) were used as a surfactant and solvent, respectively, to form the

LLC phase [21]. Inorganic metal precursor was kept high with a transition metal precursor weight of up to 60% (w/w) in these salt-surfactant LLC mesophases. Effects of different non-ionic surfactants [22] and effects of counter ions of transition metal salts [23] on the liquid crystalline mesophase of transition-metal salt-surfactant have been investigated. The salt- surfactant system might be useful for eliminating the effects of volume shrinkage and therefore might be used to form solid films of metal oxides and chalcogenides. So far, mesostructured metal sulfide films (CdS and $\text{Cd}_{1-x}\text{Zn}_x\text{S}$) were synthesized using cadmium salt-surfactant LLC mesophase [24]. Before we go into details of salt-surfactants systems as a template, it is better to follow the chronological progress in mesoporous material synthesis in the literature to make it easy to understand the importance of salt-surfactant systems for the synthesis of porous thin films and monoliths.

1.4 Evaporation Induced Self- Assembly (EISA) Method

Evaporation induced self-assembly (EISA) method has been developed from lyotropic liquid crystalline templating to fabricate materials, easily and fast [25]. The mixture of inorganic precursor, surfactant and solvent are used as a clear solution. The di-block or tri-block copolymer have been used as surfactants with an easily evaporating solvent in this process [26]. **Figure 1.5** shows schematic representation of the EISA process, where the micelles are formed above CMC during the solvent evaporation; the surfactants and inorganic precursors are assembled together by the help of weak interactions, like hydrogen bonding, dipole-dipole interaction and van der Waals interaction. The highly ordered mesostructured thin films are formed by condensation of the inorganic precursors and thermal treatments. Adjusting the inorganic precursors, surfactant, humidity, and pH, various morphologies of silica [27], [28] have already been synthesized.

It is possible to prepare crystalline, crack-free, ultrathin mesoporous metal oxide films using EISA process [29]. Mesoporous crystalline WO_3 , CeO_2 [29], TiO_2 , Al_2O_3 [30], SrTiO_3 , CoTiO_3 [31] FeO_x [32] thin films have been produced by using the EISA process. The film thickness is controlled by the evaporation rate of the volatile solvent and the concentration of the ingredients [33]. Dip coating is a preferable method to coat the substrate in this process. The final step of EISA

process is to remove surfactants by either burning the coated substrate at high temperature or washing it with a proper solvent.

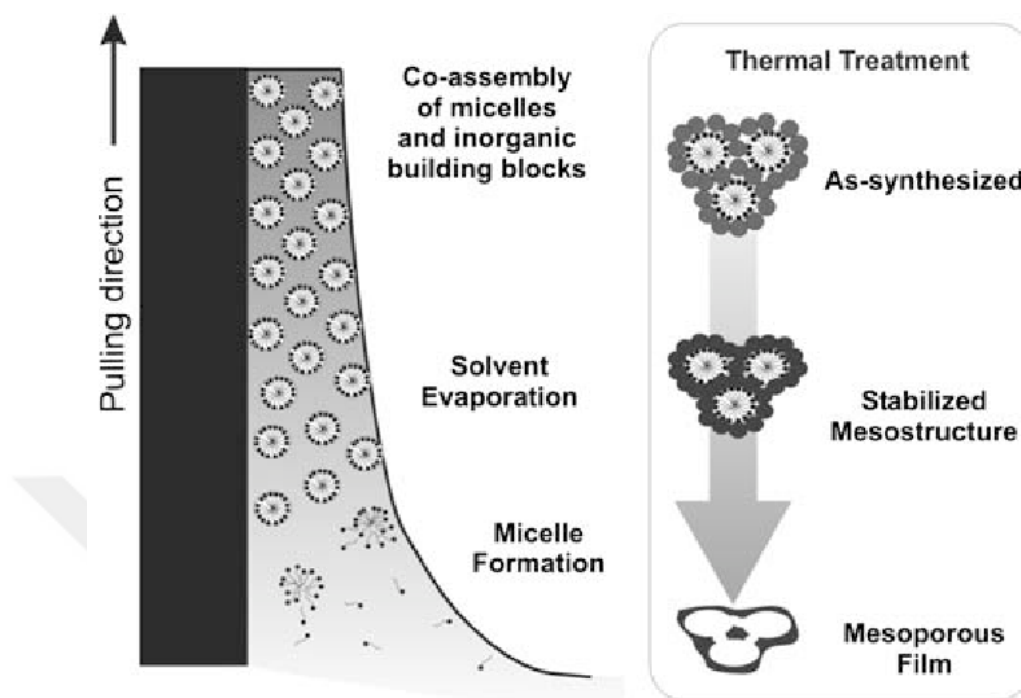


Figure 1.5. Schematic presentation of evaporation induced self-assembly process³.

The initial concentration of inorganic precursors in a EISA process is low. There is huge volume (or density) difference between especially metal nitrate salts and metal oxides. The high temperature treatment might destroy mesostructured films during the calcination step. The condensation of the precursors also takes long time, up to 1-2 weeks. For this reason, it is very hard to synthesize ordered mesoporous transition metal oxides by using the EISA (also known as a soft templating) method.

³ Reprinted from Advanced Materials, Brinker, J. C.; Lu, Y.; Sellinger, A.; Fan, H. "Evaporation-Induced-Self-Assembly: Nanostructures Made Easy." 579- 585, (1999), with permission from John Wiley and Sons.

1.5 Nano-casting or Hard-Templating Methods

Nano-casting is a hard-templating method to produce mesoporous materials using an ordered mesoporous material to replicate its porosity [5]. Highly ordered mesoporous materials are important for gas separation [10], catalysis [11] and many other applications. The synthesis of ordered mesoporous materials involve three steps in nano-casting. Firstly, a suitable (in terms of pore size) hard template are infiltrated with metal precursors. The fully filled mesoporous templates are calcined at an optimum temperature to form metal oxides in the templates. Later, etching removes the templates using a proper solvent. Mesoporous silica and mesoporous carbon are commonly used as hard templates. CeO_2 , Co_3O_4 , Fe_2O_3 , MnO_2 , NiO and In_2O_3 has been produced using hexagonally channeled mesoporous silica (SBA-15) [34] or bicontinuous cubic mesostructured silica (KIT-6) [35]. Ordered mesoporous CuO are fabricated using both silica and carbon templating [36].

Hard-templating is a more complicated method than soft templating method, but it could be more applicable than soft templating for certain cases, such as synthesis of ordered metal oxides. However, each step of the nano-casting process has problems. The infiltration of metal precursor into pores of hard templates is not easy because the pores are not large enough for penetration of metal precursors throughout the pores of templates. The decomposition of metal salts can be close to their melting point that may create problems both in the infiltration and calcination processes. Lastly, etching hard-template using some chemical (HF or NaOH for silica) may damage metal oxide on the pore-walls of the template and it may cause a collapse the pores in the final product.

However, the EISA and nano casting methods are the commonly used two methods to fabricate mesoporous materials in forms of powders and thin films. These method is not applicable for all materials and there is still a demand for another more universal method for certain technologically important materials. The new method(s) should be easy, cheap, and applicable for scaling up [37]. Molten salt assisted self-assembly (MASA) could be an applicable method for the synthesis of some of these materials in powder and thin film forms.

1.6 Molten Salt Assisted Self-Assembly (MASA) Method

The LLC mesophase of transition metal salts with oligo(ethylene oxide) [21] has been introduced to the literature by Dag's group in 2001. The transition metal salts/surfactant mole ratio has been increased up to 8 by adding ionic surfactants to the media [38]. Also, the roles of inorganic and organic additives on the assembly of surfactants and the morphology of silica [39], [40] have been studied. These studies form the bases of MASA process, where two surfactants and two solvents are needed. Using MASA process, mesoporous metal titanates (CdTiO_3 , Zn_2TiO_4 [41], CoTiO_3 , MnTiO_3 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [42]), metal sulfide-titania (CdS-TiO_2 , ZnS-TiO_2 [41]), metal selenide-titania (CdSe-TiO_2 , ZnSe-TiO_2 [41]) thin films and mesoporous metal oxides-silica (CdO-SiO_2 , ZnO-SiO_2 [43]) thin films have been synthesized. Recently, mesoporous lithium metal oxides (LiMn_2O_4 and LiCoO_2) thin films have been successfully synthesized using MASA process [44]. MASA is a process that uses salts in their molten phase as a solvent and a metal ion source for metal oxides [41], [43]. In the titanates and silicates, titanium(IV) tetrabutoxide (TTB) and TEOS, as the polymerizing agents, and two surfactants, CTAB and $\text{C}_{12}\text{EO}_{10}$, as templating agents, were used in the MASA process. The MASA solution is a clear solution of all the ingredients that solidify into mesostructured film upon spin coating over any substrate and ready for calcination to convert into mesoporous thin films. Further reaction under a mixture of H_2Se and N_2 gasses produces mesoporous CdSe modified titania or silica (denoted as meso- CdSe-TiO_2 in the titania case and meso- CdSe-SiO_2 in the silica case) depending on the polymerization agent, TBB or TEOS, respectively. **Figure 1.6** shows schematic presentation of the MASA process.

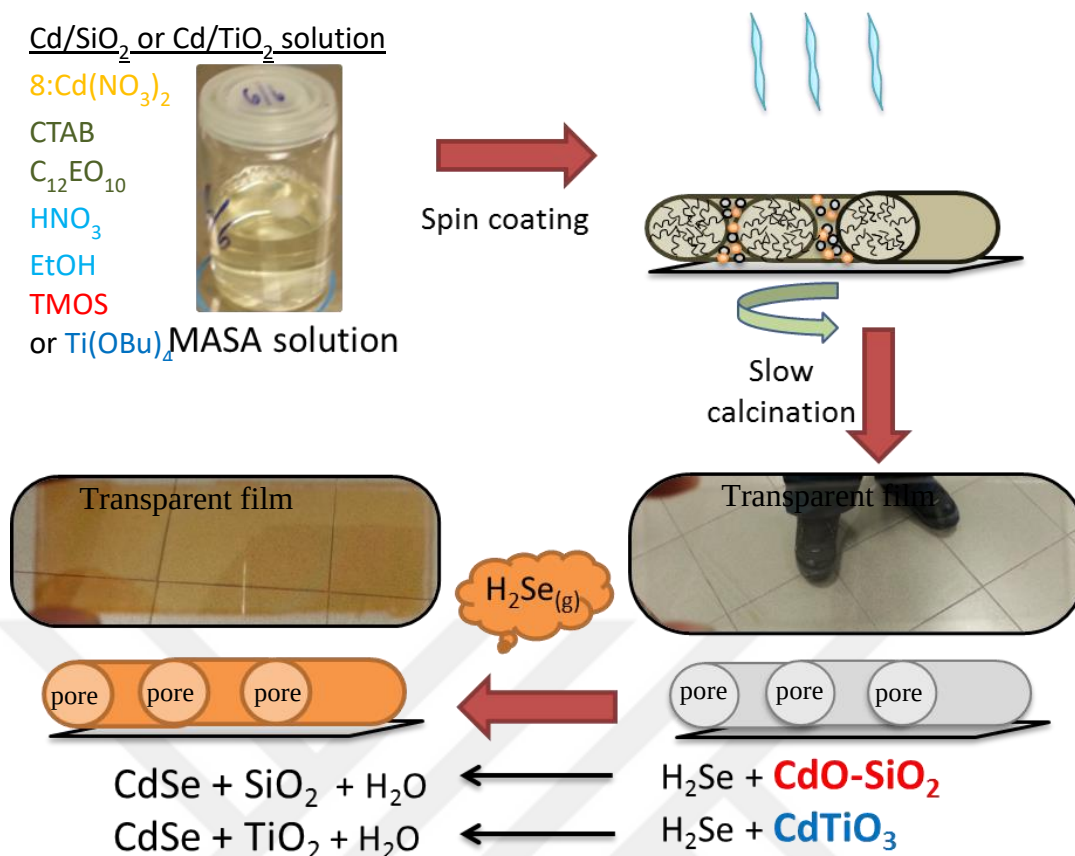


Figure 1.6. Schematic presentation of the MASA process and further H_2Se treatments.

1.7 Designing Porous Materials for Quantum Dot Sensitized Solar Cells

Renewable energy is an emerging field to meet the energy need of the world. Wind, solar, biomass, geothermal and hydroelectric are sources of renewable energy. The annual amount of solar energy is much more than any other sources. The energy supplied by the Sun to the Earth is around 10^{24} joules per year and its approximately 10000 times more than the global population recently annual consumes. [45] If a small percentage of the solar energy is converted to electricity, it will be sufficient for the demand of humanity. There is a efficient material demand for the energy conversion process. However, fabrication of these materials need to be easy and cheap to compete with the current energy sources, such as fossil fuels.

The spectrum of solar radiation is shown in Figure 1.7 [46]. Most of the radiation is in the energy range between 1.1 and 3.0 eV. A suitable material to harvest the solar light should be in this region. The optimum materials should also have a suitable band gap for harvesting solar cells. The band gaps of some metal oxides and metal sulfides are shown in **Figure 1.8**, respectively [47]. The energy level of metal sulfides is higher than its oxides.

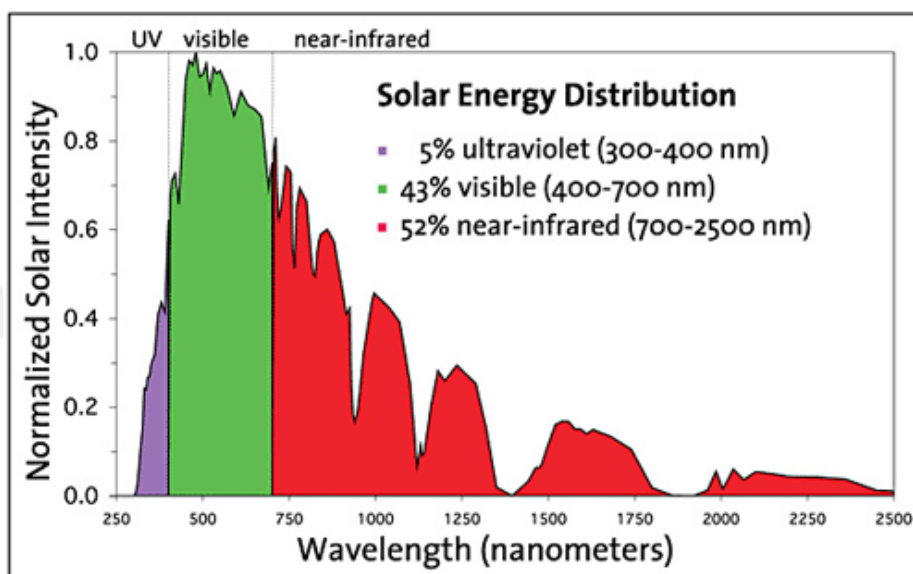


Figure 1.7. The spectrum of solar radiation⁴.

The solar energy has been harvested to electricity through solar cells and to chemical energy through photoelectrochemical (PEC) cells [45]. **Figure 1.9** (a) shows a diagram of solar cell producing electricity from solar light. Solar light separates an electron-hole pair from each other at anode side and then the electron is transferred from anode to cathode side and recombined with the hole through a chemical reaction to produce electricity. **Figure 1.9** (b) shows a diagram of PEC cell, producing chemical energy through the photo-cleavage of water. Again, solar energy produces an electron and a hole and they split water to hydrogen and oxygen as a source of chemical energy. The important parameter for both cells is band gap of the anode and cathode materials.

⁴ Reprinted from In Tech, Biernat, Krzysztof; Malinowski, Artur; Gnat, Malwina "The possibility of Future Biofuels Production Using Waste Carbon Dioxide and Solar Energy, Biofuels-Economy" 2013 with permission from In Tech.

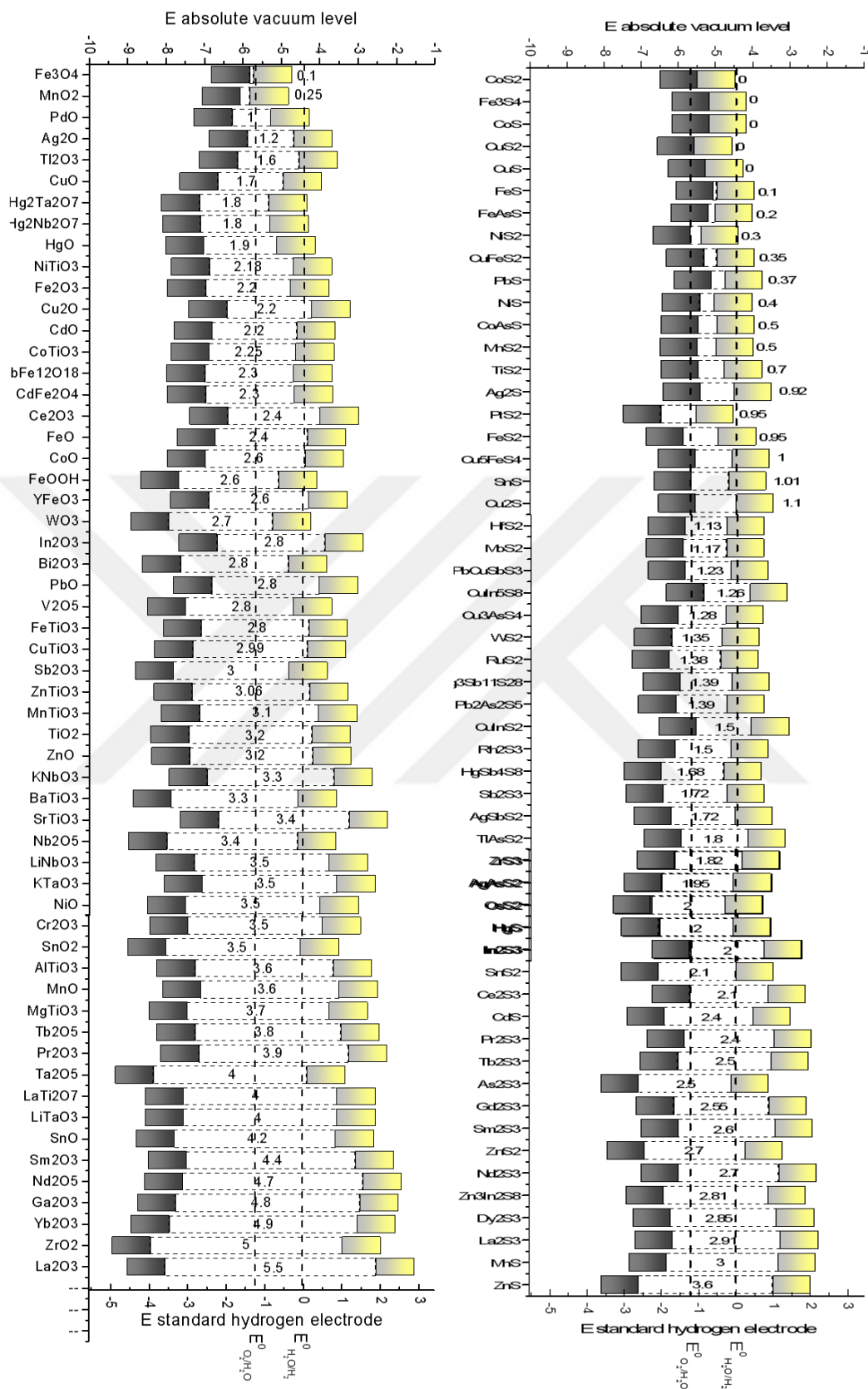


Figure 1.8. The band gaps of some metal oxides (left) and metal sulfides (right).

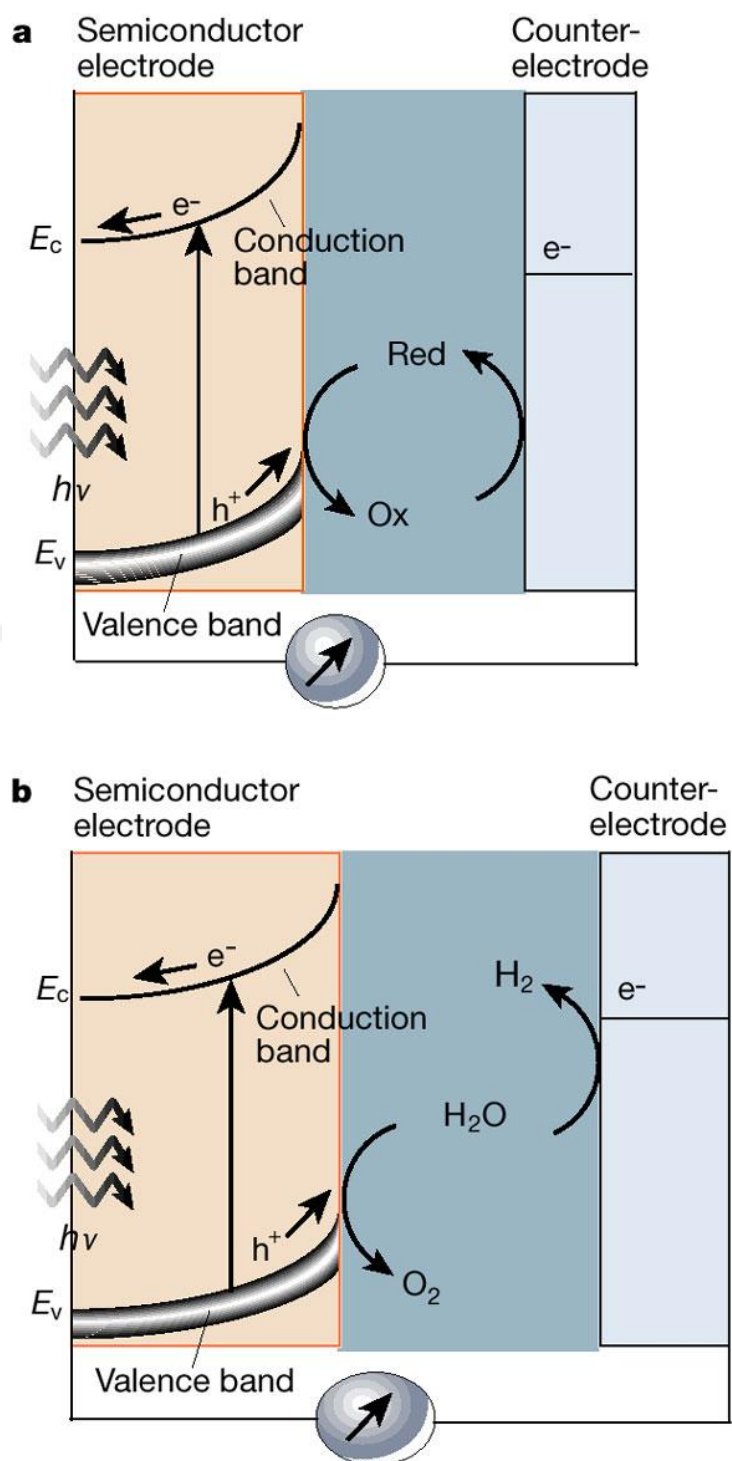


Figure 1.9. Schematic diagrams of the cells, (a) producing electricity from solar light and (b) producing chemical energy through the photo-cleavage of water⁵.

⁵ Reprinted from Nature, Gratzel, M "Photoelectrochemical Cells" 328-344, (2001), with permission from Nature Publishing Group.

1.8 Solar Cell Parameters

The current generated by a solar cell is expressed in **equation 1** [48].

$$I = I_{SC} - I_{o1} (e^{qV/kT} - 1) - I_{o2} (e^{qV/2kT} - 1) \quad \text{eq.1}$$

The dark saturation currents (I_{o1} , I_{o2}) are related to material properties, the solar cell structure and other limiting factors, coming from the operation conditions. **Figure 1.10** shows simple solar cell circuit model, where diode 1 represents the recombination current in the quasi-neutral regions ($\propto e^{qV/kT}$), while diode 2 represents recombination in the depletion region ($\propto e^{qV/2kT}$). The problems, coming from electron transport resistance, charge transfer resistance, charge recombination rate, and series resistance are defined as decreasing parameters in **equation 1**, [48]. The short-circuit current (I_{SC}) is ideal current source, produced by the photoanode under 1 sun condition.

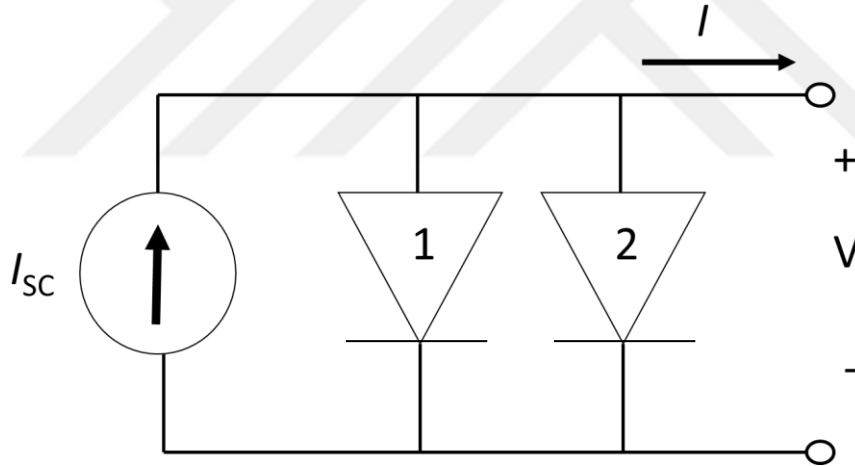


Figure 1.10. Simple solar cell circuit model.

Figure 1.11 shows a characteristic $I - V$ curve of a solar cell. The most important parameter of a solar cell is power conversion efficiency (PCE), η , is determined by dividing a produced power ($V_{MP} \cdot I_{MP}$) by the incident power [48]. The other important parameters are I_{SC} , short current at 0 V, and V_{OC} , open circuit voltage. The last parameter is filling factor (FF), obtained from the curve ($FF = V_{MP} \cdot I_{MP} / V_{OC} \cdot I_{SC}$) [48]. FF is always less than 1 but is between 0.5 and 0.7 for a typical ODSSC [49].

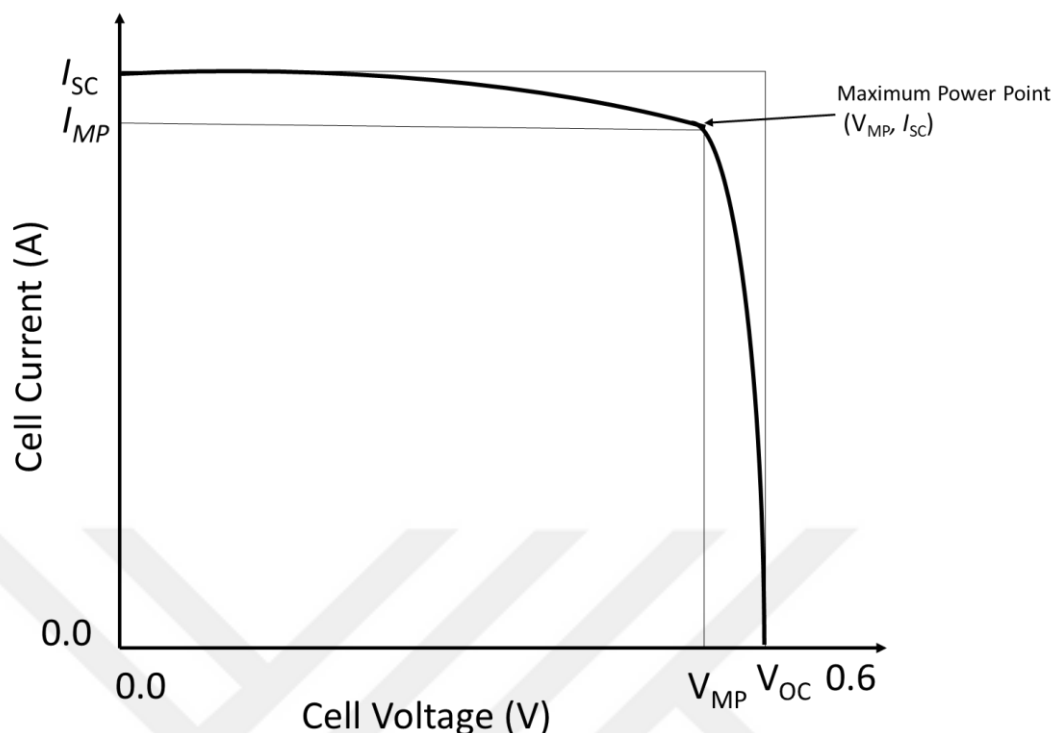


Figure 1.11. A characteristic $I - V$ curve of a solar cell

1.9 Titania Based Solar Cells

Titania is a good alternative to silicon based solar cells because of easy and cheap fabrication [45]. Titania is a catalytically active material and transfers electrons easily. Titania nanoparticles [50], [51], nanosheets [52], nanorods [53], nanotubes [54], [55] with high surface area has been synthesized using different techniques (such as sol-gel, sonochemical, hydrothermal methods) for above purposes..

Titania is an n-type semiconductor with a band gap of 3.03 eV for rutile phase and 3.20 eV for anatase phase [56]. These are not suitable band gaps to directly harvest solar energy, therefore a sensitizer is needed to first absorb the solar light to activate the titania. Although there are some studies to make titania to be used as visible light absorber, still it is an emerging field [57]. Dye-sensitized solar cell (DSSC) and quantum dot-sensitized solar cell (QDSSC) are two common cells. In the DSSCs, dyes are used as an absorber for solar light due to suitable electronic energy levels and strong light absorption coefficients [58]. The assembly of titania, modified using a dye, as an anode, iodine/iodide based electrolyte and a platinum counter electrode

construct the cell. The power conversion efficiency (PCE) of a DSSCs nowadays reaches up to 13% [59]. In the QDSSCs, quantum dots (PbS [60], CdS [61], CdSe [62], CuInS₂ [63] or mixed CdSe-ZnS [64]) are used as the absorber, because the band gap of these particles are tunable with their particle size [65]. The assembly of titania loaded with quantum dot nanoparticles, sulfide/polysulfide based electrolyte [66] and copper (I) sulfide counter electrode [67] construct the QDSSCs. The PCE of a QDSSC reaches up to 11% [68]. Although the efficiency of QDSSCs is lower than DSSCs, the advantage of QDSSCs overweigh the advantages of DSSCs in terms of long term stability and also to high temperature because dye molecules decompose at high temperature and have low long-term stability.

Titania, modified by quantum dots harvests the solar light. Firstly, solar light is absorbed by the QDs in which the electrons are excited from valence band (VB) of sensitizer to conduction band (CB) of sensitizers. Excited electrons are transferred to conduction band of titania which is lower in energy than that of CB of sensitizer. Then the collected electrons are transferred to cathode electrode through titania and fluorine doped tin oxide (FTO) glass and connecting Cu wire. An electrochemical process take place on the cathode surface between the electrode and electrolyte and then the reduced chemicals regenerate the oxidized quantum dot back on the anode, resulting in combining the electron and hole back to generate the photo-current, named harvesting solar light [69]. **Figure 1.12** shows the pathway of electron in QDSSC. The reactions that take place in the pathway are also shown in **Figure 1.12**.

There are predicted and unpredicted problems in the QDSSCs and they all affect the efficiency of the cells. All components of the cells, anode, cathode, and electrolyte are needed to be optimized [69]. Sulfide/polysulfide is not an optimum electrolyte for the QDSSCs and copper (I) sulfide may not be optimum as the cathode. The synthesis of photo-anode is still another essential part of obtaining high efficiency.

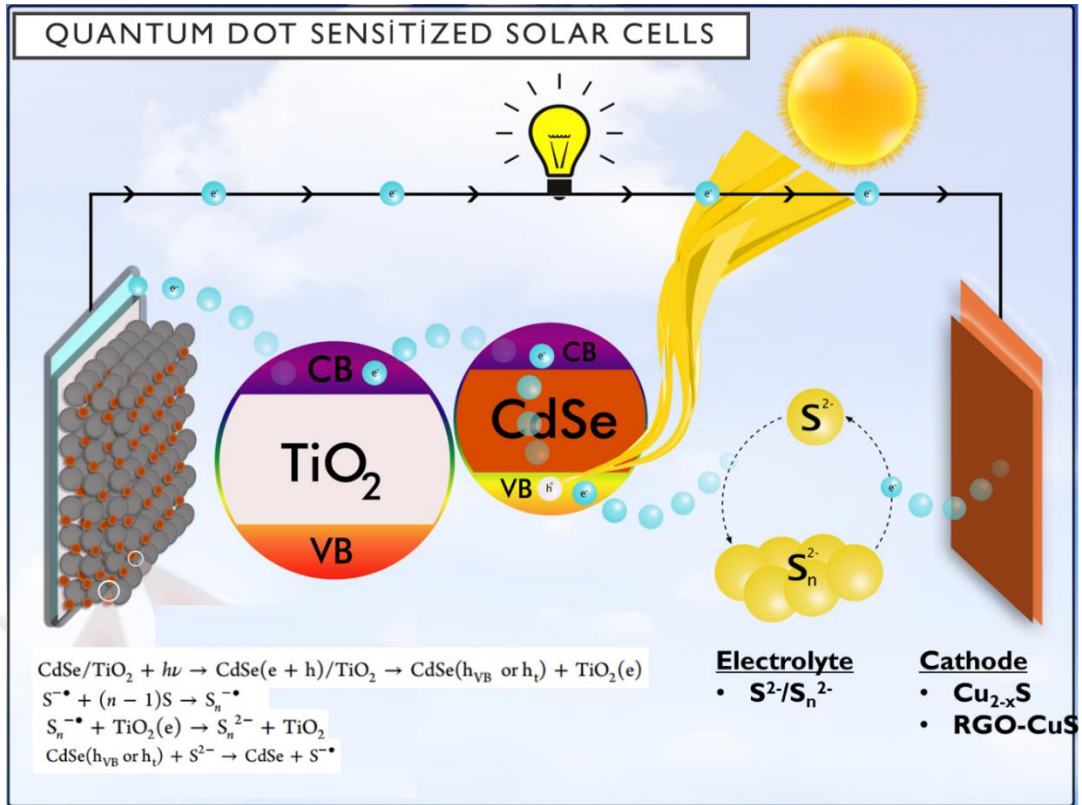


Figure 1.12. Schematic presentation of electron pathway in quantum dot sensitized solar cells

1.10 Synthesis of Photo-anode Electrode for a Quantum Dot Solar Cell (QDSC)

For a high efficiency, each component of the solar cells needs to be fully characterized to identify the issues causing low efficiency. For example, only the photo-anode of the QDSSCs has been investigated last two decades. One of the main problem of the anode is how to effectively anchor the sensitizers on the titania nanoparticles. One of a commonly used method is *in-situ* synthesis of quantum particles in the pores of titania. For this purpose, in successive ionic layer adsorption and reaction (SILAR) [70], [71] and chemical bath deposition [72] have been developed; the semiconductor nanoparticles are directly synthesized over the titania nanoparticles. The SILAR method consist of number of dipping titania electrode (fabricated by doctor-blade coating and annealing at 450 °C) into cadmium ions solution and then into selenium ion solution to form CdSe nanoparticles. After each dipping, the surface of titania coated with the corresponding ions that react with the

counter ion in the next dipping step are washed several times to remove excess amounts from the surface of the electrode. The other commonly used method is electrophoretic deposition, (ED), [73]; involves two steps, in the first step nanoparticles are synthesized and then infiltrated into titania particles in the second step. In ED, quantum dot particles are formed in solution phase and then inserted into titania mesopores by the help of high external voltage. **Figure 1.13** shows schematic representation of different synthesis methods of photoanode of QDSSCs.

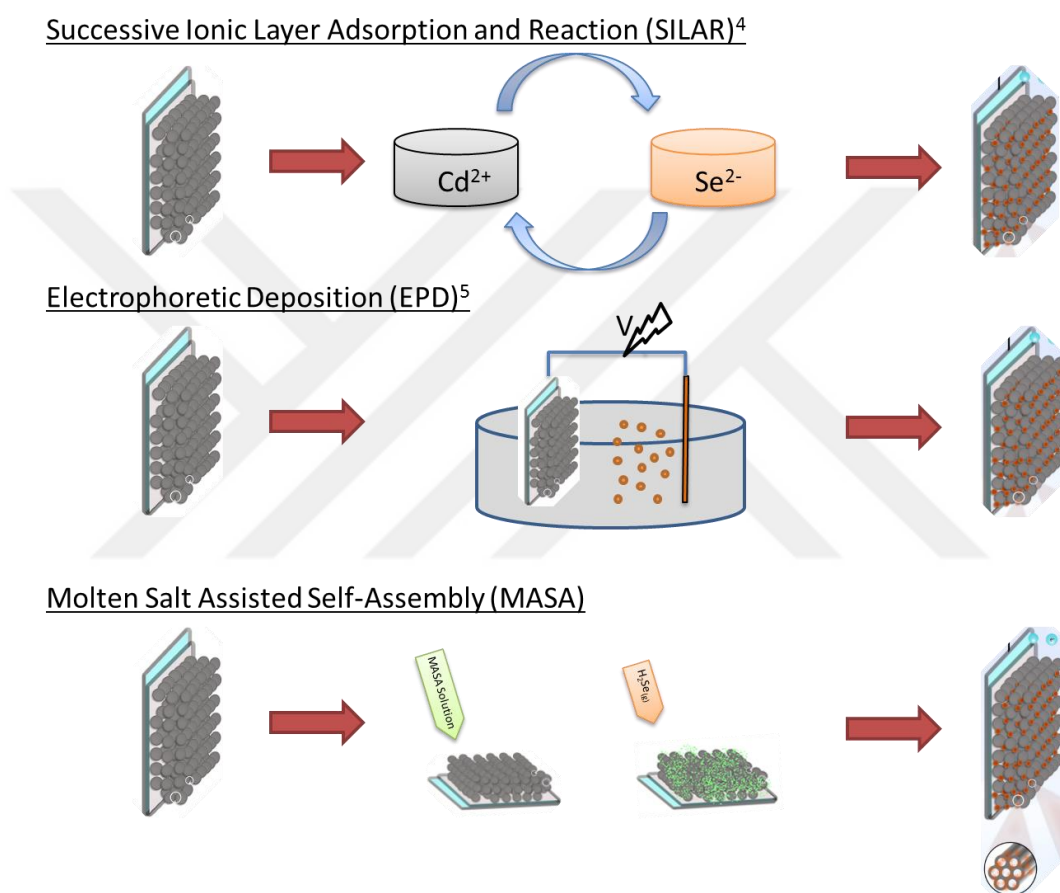


Figure 1.13. Schematic presentation of different synthesis method of photoanode of QDSSCs.

Synthesis of the nanoparticles and coating steps are not well controlled in the SILAR method, so where and when the nanoparticles are formed and whether the titania particles fully coated are still unknown. Each dipping might block the pores of titania and next coating steps become unnecessary or result in the formation of useless nanoparticles coating on the external surface. In the ED method, applying high voltage to the nanoparticle solution causes unwanted reactions and also the penetration of 3 nm particles into pores formed by 20-30 titania nanoparticles is not

easy; they could not diffuse through the film down to the bottom. If the bottom of these electrodes is white after CdSe loading with ED, it indicates diffusion problems. Therefore, cheap and new methods are needed for an effective sensitization of the titania film electrodes.

This thesis contains three syntheses with a goal of developing a general synthesis method for efficient QDSSCs. In the first part of the thesis, CdSe/TiO₂ and CdSe/SiO₂ thin films that were synthesized by reacting mesoporous CdTiO₃ and CdO/SiO₂ thin films (prepared using MASA method) under a H₂Se gas atmosphere. Effects of the synthesis parameters (film thickness, calcination temperature, and H₂Se reaction condition) on solar cell performance were investigated. Second part involves adaptation of the MASA method for the modification of mesoporous titania films (prepared using Aeroxide® P25, 20-25 nm commercial TiO₂ nanoparticles, denoted as meso-P25) by meso-CdSe/SiO₂ to make a solar active material. In this approach, the MASA solution was infiltrated into the meso-P25, followed by calcination, and H₂Se reaction for an *in-situ* synthesis of the CdSe sensitizer. The materials were characterized in each step of the preparation to elucidate the likely problems of the new synthesis method for the fabrication of photoanodes of the QDSSCs. Last part of the thesis, using MASA approach, many different mesoporous transition metal oxides thin films (such as ZnO, CuO, NiO, Co₃O₄, Fe₂O₃, and Mn₂O₃) have been synthesized and characterized by using analytical tools.

Chapter 2

Materials

2.1 Materials

All chemicals and solvents were used without any further treatment.

Surfactants, 10-lauryl ether ($C_{12}EO_{10}$, $CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$, $M_w = 626.9$ g/mol, Aldrich) and cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}N(CH_3)_3Br$, $M_w = 364.45$ g/mol, Aldrich).

Cadmium(II) nitrate tetrahydrate ($[Cd(H_2O)_4](NO_3)_2$ 99%, Aldrich), zinc(II) nitrate hexahydrate ($[Zn(H_2O)_6](NO_3)_2$ 98%, Aldrich), copper(II) nitrate pentahydrate ($[Cu(H_2O)_5](NO_3)_2$, Aldrich), nickel(II) nitrate hexahydrate ($[Ni(H_2O)_6](NO_3)_2$, 98%, Aldrich), cobalt(II) nitrate hexahydrate ($[Co(H_2O)_6](NO_3)_2$, 98%, Aldrich), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99%, Aldrich), manganese(II) nitrate tetrahydrate ($[Mn(H_2O)_4](NO_3)_2$, 98%, Aldrich) are used without further purification.

Titanium tetrabutoxide ($Ti(OC_4H_9)_4$, %98, Aldrich), tetramethyl ortho-silicate (TMOS, %99, Aldrich) are used as polymerizing agents.

Hydrogen selenide (H_2Se , 99.99%, Air Products), hydrogen sulfide (H_2S , 99.5%, Aldrich) and sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 98%, Aldrich) are used without a treatment.

Ethanol (C₂H₅OH, 99.9%, Aldrich), hydrochloric acid (HCl, %37, Reidel-de Haën), hydrofluoric acid (HF, 40-45%, Aldrich), nitric acid (HNO₃, %65, Reidel-de Haën), polyethylenimine, branched (designated as PEI, MW = 25000 g/mol) and sulfur (S₈, 99.5%, Aldrich) are used as purchased.

Titania (TiO₂, Aeroxide® P25, 20-25 nm commercial TiO₂ nanoparticles, Aldrich), Triton® X-100 (Aldrich), fluorine doped tin oxide coated glass slide (FTO, Aldrich) are used.

2.2 Synthesis of Materials

2.2.1 Synthesis of Meso-Cadmium Titanate Thin Films

A mixture of required amounts of [Cd(H₂O)₄](NO₃)₂ (0.985 g), CTAB (0.29 g), C₁₂EO₁₀ (0.50 g) and ethanol (5.0 ml) was vigorously stirred for 15 min to obtain a clear solution (see **Table 2.1** for details of the amounts of the ingredients for other mole ratio of Cd(II)/Ti(IV)). Then, a concentrated HNO₃ (0.50 g) was added to the above solution and stirred for another 10 min. Finally, titanium (IV) butoxide (n-butyl) (Ti(OBu)₄) (1.080 g) was added to the mixture and stirred for additional 5 min.

The mole ratios of Cd ²⁺ / Ti ⁴⁺	Cd(NO ₃) ₂ (g)	CTAB (g)	C ₁₂ EO ₁₀ (g)	EtOH (ml)	HNO ₃ (g)	Ti(OBu) ₄ (g)
2/2	0.493	0.291	0.500	5.0	0.500	0.540
2/4	0.493					1.080
2/6	0.493					1.620
2/8	0.493					2.160
4/6	0.985	0.291	0.500	5.0	0.500	1.080
6/6	0.985					1.620

Table 2.1. The amount of the ingredients of a cadmium titanate film

Before spin coating over a substrate, the above solution must be homogenous and clear. A few drops of the above solution were put on a substrate using the spin coater

and spun for 20 s at 1000 rpm. The substrate can be a glass, quartz, Si wafer or FTO coated glass depending on characterization techniques. The coated substrates were placed in an oven at 80 °C to prevent a salt leach out and were calcined up to different temperature (above 300 °C) with 1 °C/min increments and kept 1 hour at that temperature.

2.2.2 Synthesis of Mesoporous-Cadmium Oxide-Silica (meso-CdO-SiO₂) Thin Films

A mixture of required amounts of [Cd(H₂O)₄](NO₃)₂ (1.970 g), CTAB (0.291 g), C₁₂EO₁₀ (0.500 g) and ethanol (5.0 ml) was vigorously stirred for 15 min to obtain a clear solution. Then, a concentrated HNO₃ (0.05 g) was added to the above solution and stirred for another 10 min. Finally, tetra methyl ortho silicate (TMOS) (0.85 gr) was added to the mixture and stirred for additional 5 min.

Before spin coating over a substrate, the above solution must be homogenous and clear. A few drops of the above solution were put on a substrate using the spin coater and spun for 20 s at 1000 rpm. A substrate can be a glass, quartz, Si wafer or FTO coated glass depending on characterization techniques. The coated substrates were placed in an oven at 80 °C and were calcined up to different temperature (above 300 °C) with 1 °C/min increments.

2.2.3 Preparation of Mesoporous Titania Films (meso-P25)

For the thicker films, doctor blade technique was used to obtain meso-P25 film over an any substrate (such as FTO or glass). 0.2 gr of titania (P25) was mixed with 12 drops of acetic acid, 1 drop of Triton-100, 0.6 ml of water, and 0.6 ml of ethanol in a vial and stirred overnight. The mixture was sonicated for 30 min. It becomes a paste that was spread over half of the 2x1 cm FTO glass. The sample was calcined at 450 °C for 1 h, denoted as meso-P25.

2.2.4 Synthesis of Mesoporous Cadmium Oxide-Silica-Titania (meso-CdO-SiO₂-P25) Films

0.291 g of CTAB and 0.500 g of C₁₂EO₁₀ were dissolved in a 5 ml ethanol. For the other compositions, all the ingredients are same but different amount (1, 3, 5 or 10 ml) of ethanol was used. Then, 1.970 g of [Cd(H₂O)₄](NO₃)₂ and 0.05 g of concentrated HNO₃ were added to the solution and the solution was stirred for 10 min. 0.85 g of TMOS was added the above solution at once and stirred until the solution is homogenous and clear (see **Table 2.2** for details of the amounts of the ingredients for other mole ratio of Cd/Si). The meso-P25 film was placed over the spin coater, and 1-2 ml of the above solution was put over the meso-P25 film and spin coated at 1000 rpm for 30 s. The coated substrates were placed in an oven at 80 °C and calcined up to 450 °C with 1 °C/min increments.

The mole ratios of Cd/ Si	Cd(NO ₃) ₂ (g)	CTAB (g)	C ₁₂ EO ₁₀ (g)	EtOH (ml)	HNO ₃ (g)	TMOS (g)
8/7	1.971	0.291	0.500	5.0	0.005	0.850
8/5	1.971					0.607
8/3	1.971					0.364
8/1	1.971					0.121
8/1	1.971					0

Table 2.2. The amount of the ingredients for the production of meso-CdO-SiO₂-P25 film

2.2.5 Synthesis of Mesoporous CdSe-TiO₂, Mesoporous CdSe-SiO₂, and Mesoporous CdSe-SiO₂-P25 Films

The calcined meso-CdTiO₃, meso-CdO-SiO₂ or CdO-SiO₂-P25 films was placed into a homemade vacuum chamber (see **Figure 2.1**), designed for an H₂Se reaction. The chamber was evacuated to less than ~1 torr for a few minutes before exposing the sample to a H₂Se atmosphere. 100 Torr of H₂Se gas was added to the reaction chamber and the reaction was carried out for 30 min at 100 °C. The reaction was also conducted under different conditions (such as in vacuum (~1 torr), in N₂ (~

300 torr), in N_2 (~ 760 torr) or in air (~ 760 torr)) and temperatures (such as RT, 100 °C, or 200 °C). After the reaction, the chamber was evacuated by pumping the unreacted H_2Se gas. The gas was sent to CdO-loaded silica and then to the atmosphere through the fume hood.

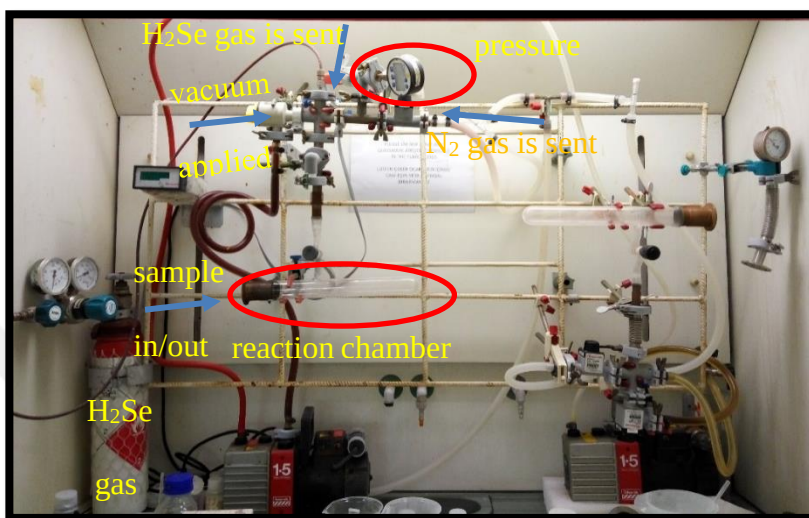


Figure 2.1. Photograph of a fume hood, placed a homemade reaction chamber.

2.2.6 Preparation of the Electrodes and Installation of the QDSSC

The photoanode electrode (meso-CdSe-SiO₂-P25 or meso-CdSe-TiO₂) was dipped into 0.1 M S^{2-} aqueous solution (prepared by $Na_2S \cdot 9H_2O$) for 30 s, rinsed with ethanol, and then dipped into 0.1 M Zn(II) aqueous solution (prepared using $[Zn(H_2O)_6](NO_3)_2$) for 30 s. This process was repeated three times to coat all surfaces with ZnS nanoparticles. The counter electrode (CE) was prepared by cleaning brass with 1 M HCl for 5 min at 70 °C and reacted with a 0.1 M $Na_2S \cdot 9H_2O$ aqueous solution. The electrolyte solution was prepared using appropriate amount of $Na_2S \cdot 9H_2O$ and elemental sulfur (S_8) in 10 ml of water to ensure 2 M S^{2-} and 2 M S in the solution.

The anode electrode and CE were sandwiched using a spacer (Parafilm). The electrolyte (S^{2-}/S) solution was infiltrated between the electrodes and the electrodes were clamped with a paper clip.

2.2.7 Synthesis of Mesoporous Transition Metal Oxides Thin Films

0.291 g of CTAB and 0.500 g of C₁₂EO₁₀ were dissolved in a 5 ml of ethanol. For each composition, all ingredients are same but different transition metal precursor was used. Then, 1.900 g of [Zn(H₂O)₆](NO₃)₂, or 1.776 g of [Cu(H₂O)₅](NO₃)₂, or 1.857 g of [Ni(H₂O)₆](NO₃)₂, or 1.853 g of [Co(H₂O)₆](NO₃)₂, or 2.580 g of Fe(NO₃)₃·9H₂O was added to the solution and the solution was stirred for 10 min.

Before spin coating over a substrate, the above solution must be homogenous and clear. A few drops of the above solution were put on a substrate using the spin coater and spun for 20 s at 1000 rpm. The substrate can be a glass, quartz, Si wafer or FTO coated glass depending on characterization techniques. The coated substrates were placed in an oven at desired temperature and were calcined up to different temperature (above 300 °C) for 2 h.

2.3 Equipment

2.3.1 X-Ray Diffraction (XRD)

A Rigaku Miniflex diffractometer equipped with a Cu K α ($\lambda = 1.5405 \text{ \AA}$) X-rays source operating at 30 kV/15 mA and a Scintillator NaI (T1) detector with a Be window was used for small angle (1°-5°, 2 θ measurements for the gels on glass microscope slides.

Two diffractometers, Rigaku Miniflex diffractometer and Pananalytical Multi-Purpose X-ray diffractometer (equipped with a Cu K α (1.5405 $\text{\AA}$) X-rays source operating at 45 kV/40 mA), were used for wide angle (10°-80°, 2 θ) XRD measurements of powder samples.

2.3.2 Infrared Spectroscopy

A Bruker Tensor 27 model FT-IR spectrometer was used for FT-IR spectra. A DigiTect™ DLATGS detector was used with a resolution of 4 cm⁻¹ and 64 scans in 400-4000 cm⁻¹ range for all samples. Samples were prepared as pellets mixing in

KBr (2% w/w) or spin coated on IR transparent Si (100) wafers depending on phase of the samples.

A Bruker Alpha Platinum ATR-IR spectrometer was used for ATR-IR spectra with a resolution of 4 cm^{-1} and 64 scans in 400-4000 cm^{-1} range. The spectra were measured after adding a few drops of solution on the diamond ATR crystal.

2.3.3 Ultraviolet (UV)-Visible Absorption Spectroscopy

A Varian Cary 5, double beam spectrophotometer, was used for the UV-Vis spectra with a 100 nm/min speed and a resolution of 2 nm over a UV-visible wavelength range from 200 nm to 800 nm in absorbance mode. The substrates were glass, quartz or fluorine doped tin oxide (FTO) so when we observed the absorption of the samples, the glass, quartz or FTO was used as a reference depending the substrates to eliminates error coming from different substrates.

2.3.4 X-Ray Absorption Spectroscopy

The EXAFS and XANES measurement were carried under the I-20160351 EC project number using P65 beamline between October 08th and 10th, 2016 at DESY, Germany. The reference samples (CdO, CdSe, CdTiO₃) were first recorded in both XANES and EXAFS regions of the spectra. Due to sample limitations, most measurements were carried in florescence mode. For Cd-K edge (26720 eV), the measurements were performed between 26500 – 27500 eV and for Se-K edge (12666 eV), the measurement were performed between 12600 – 13600 eV.

The collected data were further analyzed using Athena software.

2.3.5 ²⁹Si Nuclear Magnetic Resonance (NMR) Spectroscopy

A Bruker Superconducting FT.NMR spectrometer Avance TM 300 MHz WB spectrometer with a 7-mm double channel Bruker probe-head was used at room temperature for ²⁹Si MAS spectra.

2.3.6 Raman Spectroscopy

A LabRam Model confocal Raman microscope with a 300-mm focal length was used for the micro Raman spectra. The spectrometer is equipped with both HeNe laser operated at 20 mW, polarized 500:1 with a wavelength of 632.817 nm, and dipole-pumped solid-state laser operated at 50 mW, polarized 100:1 with a wavelength of 532.1 nm, and a 1024 x 256 element CCD camera. The signal collected is transmitted via a fiber optic cable into a spectrometer with 600 or 1800 g/mm gratings. The sample on a silicon wafer were placed at the desired point manually.

2.3.7 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

Zeiss EVO-40 SEM microscope, operated at 20 kV with a Bruker AXS XFlash EDS detector 4010 attached to the same microscope were used for imaging and elemental analysis. Carbon adhesive tabs were used to attach the samples on the silicon wafer or on FTO to the aluminum sample holders.

2.3.8 Transmission Electron Microscope (TEM)

A FEI Technai G2 F30, operated at 200 kV was used for the TEM images.

The samples were prepared by using the following procedure; the MASA solution was spin coated on glass substrate at 5000 rpm, after calcination, the film was scraped and then dispersed in 10 ml ethanol solution using a sonicator for 30 min. If the samples are not calcined, the samples were dissolved in ethanol and dispersed by shaking because sonication can crystallize the samples. The dispersed solution was put on a holey carbon film on 200 mesh copper grids for TEM measurements and then heated under powerful light to evaporate ethanol.

Further TEM analysis was done using Digital Micrograph 3.6.5 software.

2.3.9 Polarized Optic Microscope (POM)

A ZEISS Axio Scope A1 Polarizing Optical Microscope was used in transmittance mode with 20X optic lens, between crossed polarizers for the POM images of the gels on microscope slides.

2.3.10 Solar Simulator

An AM 1.5 solar Simulator equipped with a 300 W Xenon lamp (Model no. 81172, Oriel) was used solar performance measurements. The intensity of generated light was adjusted to 1000 W/m^2 by using a reference Si photodiode. A Keithley model 2400 digital source meter was used to measure the generated photocurrent by applying an external bias to the cell.

Chapter 3

Result and Discussion

3.1 Synthesis of Mesoporous Thin Films

Recently, mesoporous cadmium titanate and cadmium oxide-silica thin films have been synthesized using molten salt assisted self-assembly (MASA) method [41] [43]. In these two groups of materials, all the ingredients ($\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CTAB, $\text{C}_{12}\text{EO}_{10}$, EtOH) are same, except the polymerization agents $\text{Ti}(\text{OBu})_4$ versus TMOS, in the cadmium titanate and cadmium oxide coated silica, respectively. H_2Se reaction of the cadmium titanate yields cadmium selenide-titanate (denoted as meso- CdSe-TiO_2) thin films and of cadmium oxide-silica yields cadmium selenide-silica (denoted as meso- CdSe-SiO_2) thin films. The cadmium selenide-titania couples are important in solar cells so the synthesis conditions of the films were optimized using their solar cell performance.

3.1.1 Synthesis of Mesoporous CdTiO_3 and Its Solar Cell Performance

The synthesis pathway of mesoporous CdTiO_3 thin films and mesoporous CdSe-TiO_2 thin films are shown in **Figure 1.6**. Synthesis conditions (such as spin coating rate, calcination temperature and H_2Se reaction conditions) of both thin films are important and need to be investigated for an effective thin film electrode. Therefore, the synthesis conditions were investigated step by step in the following sections.

3.1.1.1 Effects of Film Thickness on Solar Cell Performance

The thickness of the meso-CdSe-TiO₂ thin films is important to make a well performing solar cell. Thicker films contain more absorber (CdSe) and absorb more solar light therefore, display better QDSSC performance. The spin coating rate directly affect thickness of the thin films. Decreasing the spin coating rate increases the thickness of thin films. The films were prepared using spin coating rate, revolution per minute, (RPM) of 500, 1000, 1500 and 2000 RPM to find optimum 1-layer thickness of the thin films. In **Table 3.1**, there are solar cell parameters of the meso-CdSe-TiO₂ films with 4 different thicknesses. It is expected that the highest efficiency should be observed from the thickest film, coated at 500 RPM. However, the film is too thick so it has some cracks. The cracks form during calcination of initial film and they cause low efficiency and filling factor (FF), due to shorts in the cells. However, the solar cell parameters of the film, coated at 1000 RPM are better than the other thickness (see **Figure 3.1**). Therefore, we determined the optimum spin coating rate is 1000 RPM.

Rate Per Minute (RPM) of Spin Coating	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	$\eta\%$
500 RPM	0,708	0,145	0,26	0,027
1000 RPM	0,565	0,550	0,68	0,211
1500 RPM	0,661	0,533	0,58	0,206
2000 RPM	0,440	0,517	0,60	0,136

Table 3.1. Summary of solar cells parameters for the samples with different spin coating rate (500 RPM, 1000 RPM, 1500 RPM and 2000 RPM).

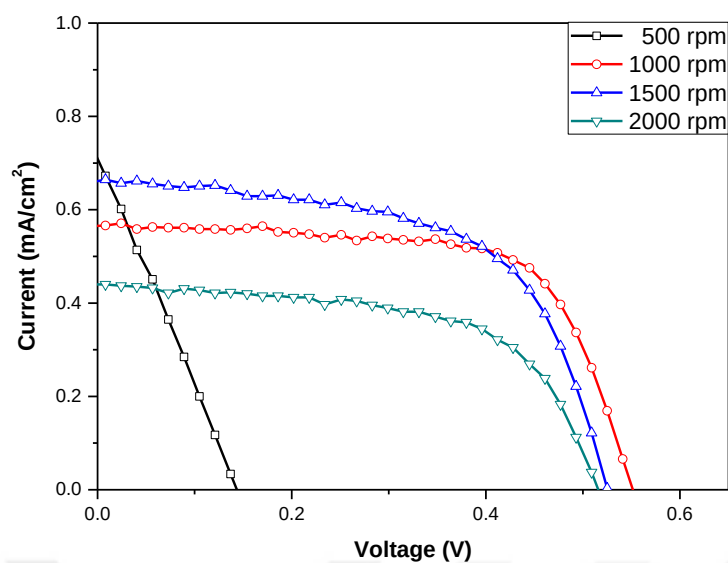


Figure 3.1. *I*-*V* Curves of the samples with different spin coating rate (500, 1000, 1500, 2000 RPM).

The real thickness of the thin films, coated at 1000 RPM, was determined using SEM images of the scraped films and it is found to be around 400 nm. **Figure 3.2** shows uniformity of the thin film and its thickness.

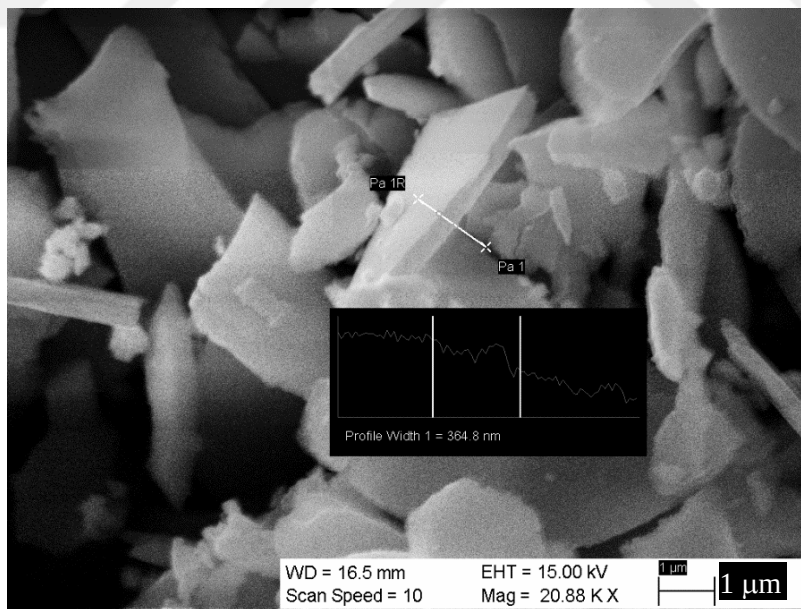


Figure 3.2. SEM images of the meso-CdSe-TiO₂ film coated at 1000 RPM.

3.1.1.2 Effects of Calcination Temperature on Solar Cell Performance

The fresh solution contains $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CTAB, $\text{C}_{12}\text{EO}_{10}$, EtOH and $\text{Ti}(\text{OBu})_4$ and it is denoted as a MASA solution. Coating the MASA solution over a substrate and calcination at 450 °C produces mesoporous cadmium titanate (meso- CdTiO_3) thin film. The calcination process has been probed using FTIR spectroscopy. The spectra from fresh sample to cadmium titanate provide some information about the formation of the thin films. Thermal behaviors of the nitrate FTIR peaks have been the topic of many studies using different transition metal salt:surfactants systems [74], [75]. Free nitrate ion has a single absorption peak at 1360 cm^{-1} , due to its asymmetric stretching mode. Nitrate ions can bind to surface of titania and/or cadmium of cadmium titanate. It could bind as a monodentate, bidentate or bridged ligand and cause a splitting on the doubly degenerate asymmetric stretching mode of nitrate ion. Two peaks are observed due to coordination of nitrate to a metal center, at around 1300 cm^{-1} and $1450\text{--}1550\text{ cm}^{-1}$ [74]. The intense peaks at 1300 and 1450 cm^{-1} at lower temperatures are due to nitrate ion coordinated to $\text{Cd}(\text{II})$ ions and the weak peak at around 1550 cm^{-1} is due to nitrate ion coordinated to titania species. Also, the amount of nitrate in the samples can be determined from the area under the nitrate peaks. The coated sample over a Si substrate was monitored using FT-IR spectroscopy to follow the spectral changes during heat treatment, calcination. Clearly, some nitrates bind to titania even at 30 °C and they remain until 270 °C. Most of the nitrates were decomposed around 170 °C and almost all at 300 °C. The surfactant peaks, due to $\nu\text{-CH}$, between 2800 and 3000 cm^{-1} disappeared at 300 °C because they were burned out to form films at higher temperature. To sum up, 300 °C is the critical temperature to remove all nitrate species and surfactants to form cadmium titanate, denoted as meso- CdTiO_3 .

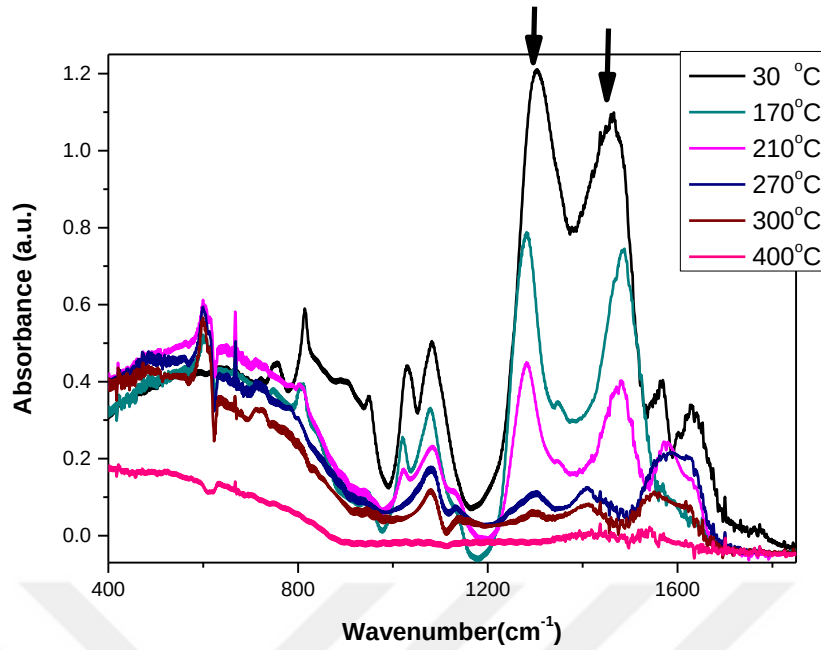


Figure 3.3. FT-IR spectral changes of the meso-CdTiO₃ film over silicon, prepared from the MASA solution, during calcination (RT to 400 °C).

The meso-CdTiO₃ films have been synthesized at various calcination temperature and reacted with H₂Se gas in a homemade vacuum chamber (see **Figure 2.1**). Normalized Raman spectra of the films, synthesized from cadmium titanate calcined at different temperatures are shown in **Figure 3.4**. If the spectra are normalized using CdSe peak, at around 206 cm⁻¹, it is found that the intensity of Se(0) peak, at around 240 cm⁻¹, decreased with increasing calcination temperature of cadmium titanate (see more discussion in the next section).

Crystallinity of the samples also affect the solar cell performance. Therefore, the cell performances of the films, prepared at different calcination temperatures were also recorded and the summary of cell parameters are given in **Table 3.2**. The *I*-*V* curves of the samples are shown in **Figure 3.5** and the samples calcined at 450 °C, 500 °C and 550 °C show a good cell behavior. Power conversion efficiency (PCE) was increased with calcination temperature up to 500 °C and started to decrease after 500 °C. The reason of increase of PCE could be a better crystallinity of cadmium titanate films that increase the efficiency. The reason for the decrease of PCE over 500 °C could be a collapse of the pores that affect badly the efficiency [41]. Therefore, the

optimum calcination temperature of the formation of cadmium titanate is found to be 500 °C.

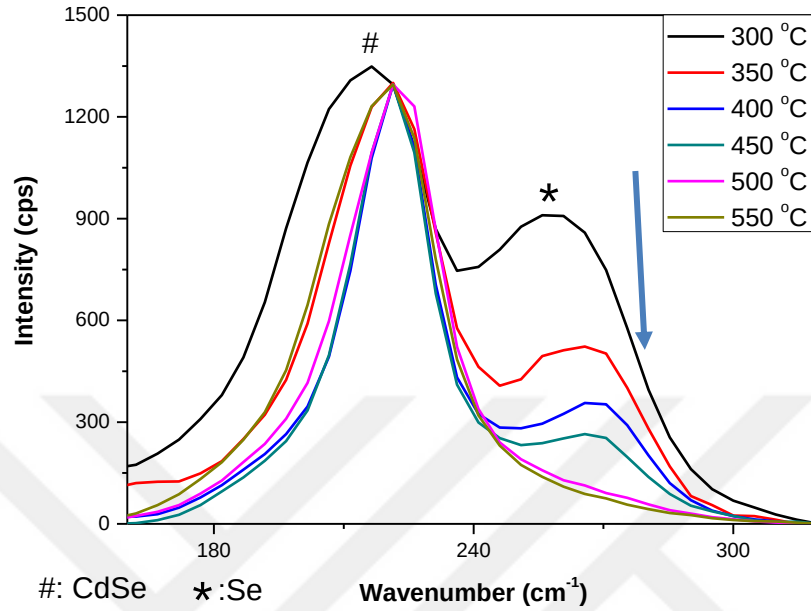


Figure 3.4. Normalized Raman spectra of meso-CdSe-TiO₂, synthesized from the meso-CdTiO₃ calcined different temperature.

Calcination Temperature Cd/Ti=4/6	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	$\eta\%$
300 °C	0,039	0,097	0,28	0,001
350 °C	0,034	0,436	0,15	0,002
400 °C	0,109	0,388	0,38	0,016
450 °C	1,126	0,533	0,58	0,347
500 °C	1,384	0,582	0,61	0,490
550 °C	1,183	0,566	0,64	0,431
600 °C	0,821	0,566	0,46	0,216
650 °C	0,361	0,517	0,40	0,075

Table 3.2. Summary of solar cells parameters of meso-CdSe-TiO₂, synthesized from meso-CdTiO₃ films calcined at different temperatures.

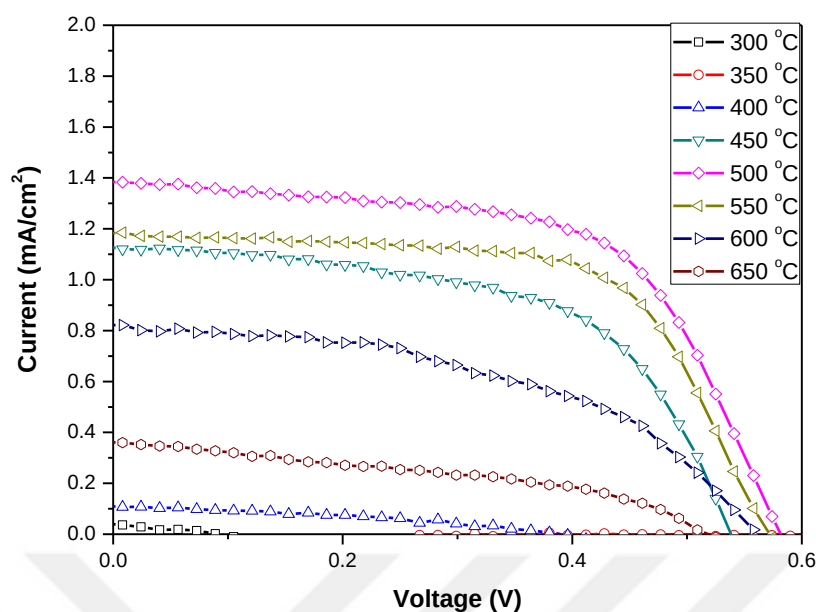


Figure 3.5. *I-V* curves of meso-CdSe-TiO₂, synthesized from the meso-CdTiO₃ films calcined at different temperatures.

3.1.1.3 The Reactivity of Mesoporous Cadmium Titanate Under H₂Se Gas

The reactivity of meso-CdTiO₃ towards H₂Se should be high enough to obtain sufficient amount of CdSe. Here, to enhance CdSe formation and minimize the formation of selenium byproducts (such as Se metal and selenium oxides) the reaction conditions have been optimized. To find the origin of metallic selenium formation, the titania system has been chosen, because the Se (0) formation in the titania system is much more than in the silica system.

Firstly, the mole ratio of cadmium to titanium was changed to understand the effect of titania on the formation of CdSe and Se. **Figure 3.6** (a) displays the Raman spectra of the samples, prepared using different Cd(II) amounts with respect to a fixed and reasonable amount of titanium precursor. The CdSe peak, observed at around 206 cm⁻¹, increases with increasing cadmium salt amount in the MASA solution, while the Se (0) peak, observed at around 250 cm⁻¹, remained the same. The Raman results showed that increasing cadmium amount only affects the amount of CdSe and not metallic selenide. The Raman spectra of samples, prepared using different titanium

mole ratio with respect to a fixed and low Cd(II) are shown in **Figure 3.6(b)**. The intensity ratio of the CdSe peak to the Se peak decreased with increasing titanium amount and showed that the amount of excess titanium, likely on the pore surface and accessible by H₂Se gas, promotes the formation of selenide.

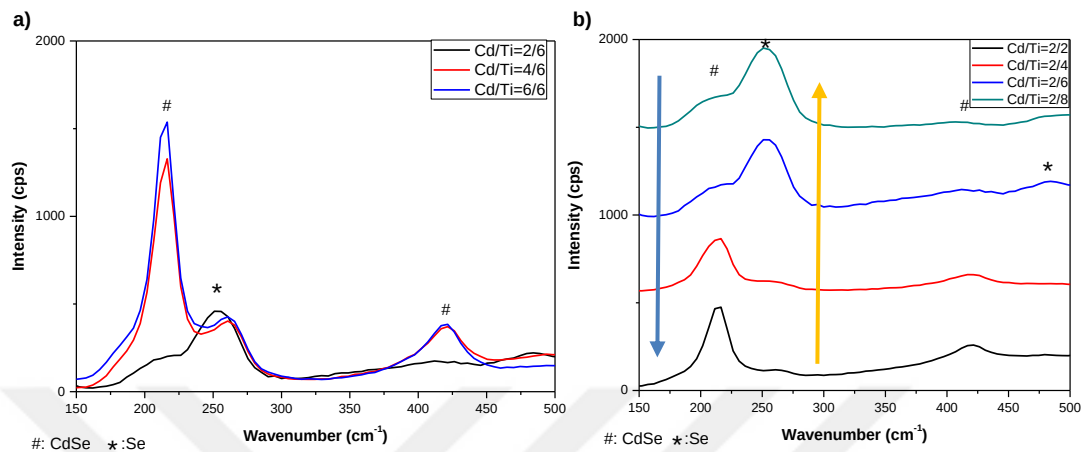


Figure 3.6. Raman spectra of meso-CdTiO₃ films, prepared by changing the concentration of (a) Cd(II)/C₁₂EO₁₀ and (b) titania/C₁₂EO₁₀ mole ratio.

In the presence of excess titanium, the metallic Se formation is enhanced. Therefore, the procedure was adopted to eliminate the formation of selenium. **Figure 3.7 (a)** shows the Raman spectra of the H₂Se reaction product of pure titania (without cadmium) and metallic Se, for comparison. It is found out that the formation of selenium is independent from the presence of cadmium. The UV-Vis absorption spectrum of this sample was also recorded (see **Figure 3.7 (b)**) to obtain the absorption spectrum of selenium. The Se absorption spectrum is like the spectrum of CdSe. Therefore, the source of absorption, in the 350-600 nm region, is not only CdSe particles; one must be very careful from an intense absorption in this region, the strong absorption is not necessarily means, it is originated from the photoactive species. Note that Se (0) species absorb solar light but inactive in the photovoltaic action and therefore and it will negatively affect the active in solar cell performance.

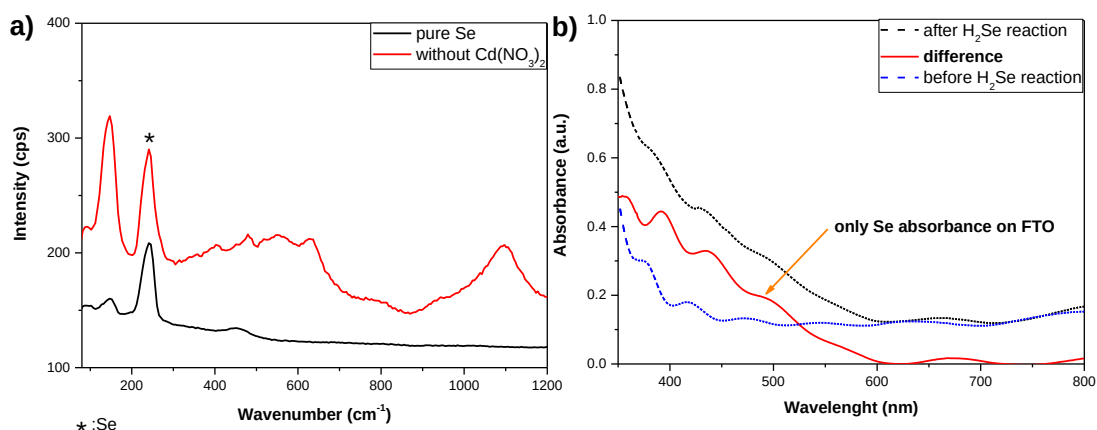


Figure 3.7. (a) Raman and (b) UV-Vis spectra of mesoporous titania films after H₂Se reaction (titanium mole ratio 8 without cadmium).

The existence of oxygen in the H₂Se reaction chamber was also examined to determine the origin of the Se (0) formation. The reason of this examination is what causes the oxidation of selenide (Se²⁻) to selenium (Se). This helps to understand the mechanism of the Se formation. Oxygen may behave as an oxidizing agent in the chamber. The amount of oxygen was changed to elucidate the role of oxygen on the formation of selenium. Three different conditions were set up; for low amount of oxygen, N₂ (~760 torr) was used in the reaction chamber; for middle amount of oxygen, vacuum (~1 torr) was used in the reaction chamber; for high amount of oxygen, air (~760 torr) was used in the reaction chamber. The partial pressure of oxygen in each condition increases. ($p_{O_2, \text{in air}} > p_{O_2, \text{in vacuum}} > p_{O_2, \text{in N}_2}$). **Figure 3.8** (a) shows normalized Raman spectra of the samples, reacted under above 3 different conditions. The CdSe peak was not observed in **Figure 3.8** (a) as we expect. **Figure 3.8** (a) shows that the intensity of selenium peak increases by increasing the amount of oxygen in the reaction chamber. Also, the UV-Vis absorption spectra of the samples reacted under the same conditions were also recorded (**Figure 3.8** (b)). **Figure 3.8** (b) shows the absorption due to presence of Se (0) and the amount of Se that increases with increasing the amount of oxygen. Therefore, the absorption of the samples, including cadmium and titania, originate from both CdSe and Se (0) particles. To sum up, the formation of selenide is related to the amount of oxygen in the reaction chamber. Oxygen is reduced, while selenide is oxidized.

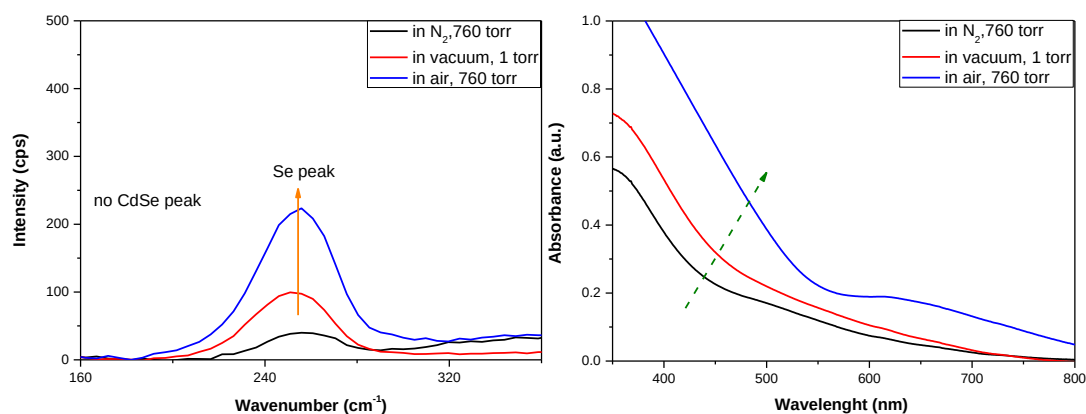


Figure 3.8. (a) Raman and (b) UV-Vis spectra of titania species without cadmium after H₂Se under different conditions (in N₂ 760 torr, in vacuum and in air). The arrow shows the direction of change.

The effect of reaction temperature on the formation of metallic selenium was also examined. Previous H₂Se reactions were carried at 100°C and the formation of metallic selenium using pure titania was carried at room temperature (RT) in different amount of oxygen (vacuum, N₂, and air) to understand the effect of reaction temperature. Photograph of the products at 100°C and RT after H₂Se reaction are shown in **Figure 3.9**. The Raman spectra and UV-Vis absorption spectra of the products, reacted H₂Se at RT, were also recorded. The formation of selenium could not be observed at RT. Therefore, the amount of metallic selenium is higher at high the reaction temperatures.

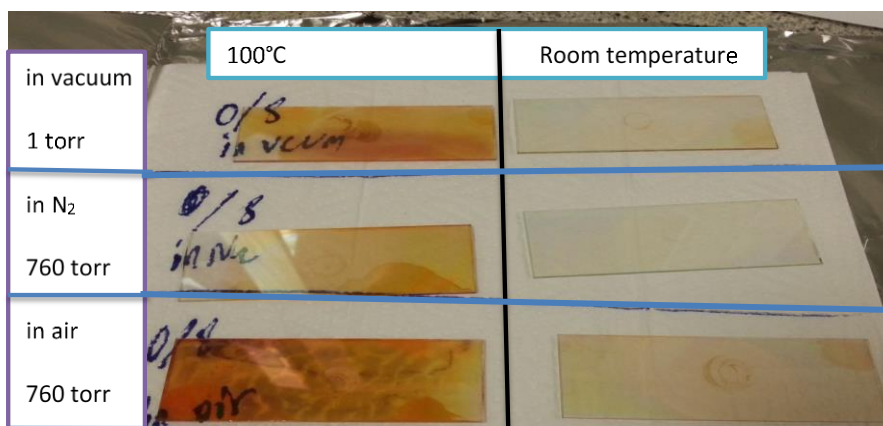
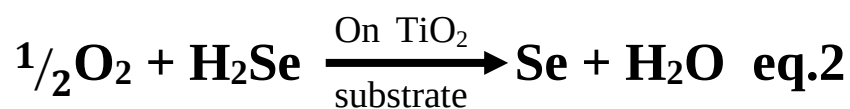


Figure 3.9. Photograph of the products after H₂Se reaction under different amount of oxygen (in vacuum, in N₂, in air) at 100 °C (left side) and RT (right side).

To sum up, the formation of selenium is dependent on the amount of titania, oxygen, and reaction temperature and not dependent to cadmium amount. The following chemical equation that likely explain these observation is given below in **equation 2**.



Oxygen behaves as an oxidizing agent in the reaction and when the amount of oxygen increases, the formation of selenium is enhanced. The role of titania might be that it catalyzes the reaction by transferring the electron from selenide to oxygen. Thus, selenium and water form after the reaction. However, there is still missing reaction steps to fully elucidate the formation of metallic selenium.

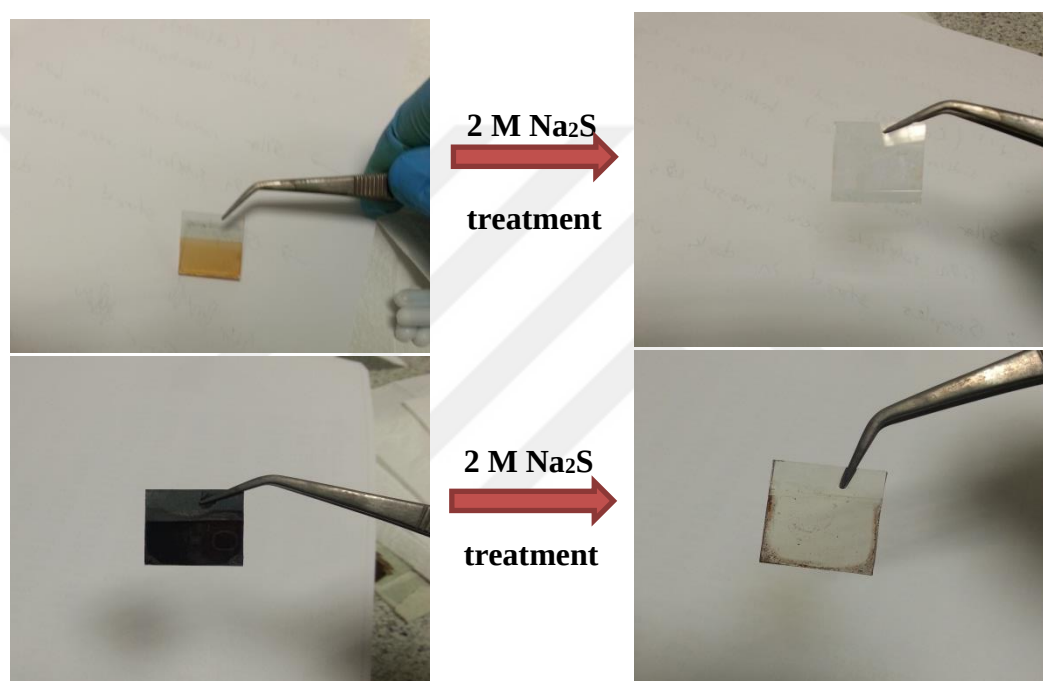


Figure 3.10. Photographs of the samples before (left side) and after (right side) 2 M Na₂S treatment. Both samples were prepared without adding cadmium nitrate heated up 100°C (up) and extra heat up to 450°C after the H₂Se reaction (down).

Removing metallic selenium from the films is more important than understanding how it forms. To remove selenium, the samples were treated by using 2 M Na₂S solution. It is known that sulfide react with selenium to form water soluble sulfur-selenium anionic species. **Figure 3.10** shows that the samples before and after sulfide treatment were in different color, the dark color originates from the metallic

selenium. Therefore, metallic selenium can be washed out from the films using 2 M Na_2S solution.

In the construction process of QDSSCs, sulfide solution is used first in the passivation of the surface by ZnS nanoparticles and as well as an electrolyte during the solar cell measurements. These two steps also help to remove metallic selenium from the photoanode of QDSSCs, but it may contaminate the electrolyte solution with selenium species and negatively affect the solar cell performance.

Therefore, one of the major problem of meso- CdTiO_3 film is its reactivity with H_2Se . The reaction is not efficient enough to convert all cadmium titanate to cadmium selenide and titania. However, cadmium oxide is more reactive than cadmium titanate. The calcination product of the MASA solution of silica precursor, however, forms cadmium oxide over silica walls [43]. The H_2Se reactivity of meso- CdTiO_3 and meso- CdO-SiO_2 were examined. **Figure 3.11** shows the XRD patterns of H_2Se reaction products of meso- CdTiO_3 and meso- CdO-SiO_2 under similar conditions. It is obvious that cadmium oxide on silica is very reactive to H_2Se reaction and can be an alternative material for the solar cells. Therefore, the silica system needs to be further analyzed to determine conditions for the fabrication of quantum dot sensitized solar cells using silica precursors in place of titania precursor.

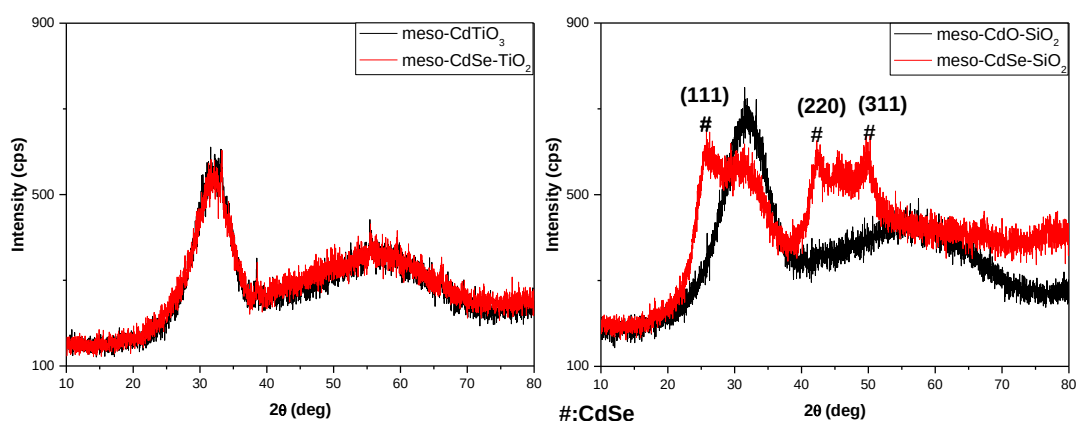


Figure 3.11. XRD patterns of meso- CdTiO_3 and meso- CdO-SiO_2 reacted with H_2Se under similar conditions.

3.1.2 Synthesis of Mesoporous CdO-SiO₂ and CdSe-SiO₂ Thin Films

Mesoporous cadmium oxide-silica (meso-CdO-SiO₂) thin film has been synthesized and characterized that the pore walls are made up of 1.6 nm CdO layer on silica [43]. After H₂Se reaction and etching the silica, CdSe nanoflakes has been obtained as a mesoporous CdSe [43]. The formation of cadmium oxide over silica was detected in the FT-IR spectrum of meso-CdO-SiO₂. **Figure 3.12** shows a set of FTIR spectra of a sample of MASA solution coated over a silicon wafer and heated at different temperatures. The nitrate peaks disappear with heating at elevated temperatures. The spectral changes are like that of the titania system. Only nitrate species are the ones coordinated to the Cd(II) species, therefore only peaks at 1300 and 1450 cm⁻¹ are observed. In later stages (higher temperatures) the nitrates coordinated to CdO surface sides are also observed at 1570 cm⁻¹. The silica related peaks at around 1200 cm⁻¹ gradually shifts to 960 cm⁻¹ with heating, showing the formation of Cd-O-Si type interface species, likely on the pore walls of meso-CdO-SiO₂ films.

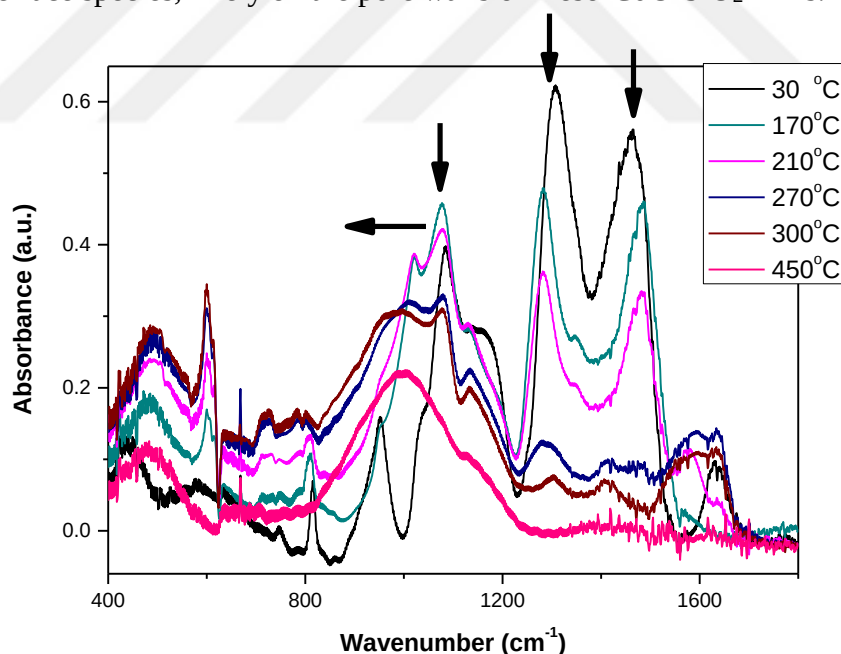


Figure 3.12. FT-IR spectra of MASA solution coated over Si wafer, including silica with heating.

The meso-CdO-SiO₂ silica thin films were reacted with H₂Se to form mesoporous cadmium selenide-silica (denoted as meso-CdSe-SiO₂). The reaction proceeds all the way to the CdO-SiO₂ interface and breaks the Cd-O-Si bonds to form CdSe and HO-Si(O)_x, as evidenced from the FT-IR spectra (see **Figure 3.13**). After the

reaction, cadmium selenide was formed and the ν -Cd-O-Si peak shifted to a higher energy, where the spectrum looks like the spectrum of pure silica, the pure silica has two peaks around 1050 and 1150 cm^{-1} .

The interface between cadmium oxide and silica has also been investigated using ^{29}Si MAS-NMR spectra (see **Figure 3.14**). **Figure 3.14** shows that no cadmium silicate peak around -80 ppm [76] remains upon H_2Se reaction, only peaks are due to pure silica, observed at around -100, -110 ppm. After the reaction, pure silica peaks (Q_2 , Q_3 , Q_4) were observed that all the peaks, related to the interfaces species, disappeared. All these results show that cadmium oxide silica layer is converted to cadmium selenide and silica layer.

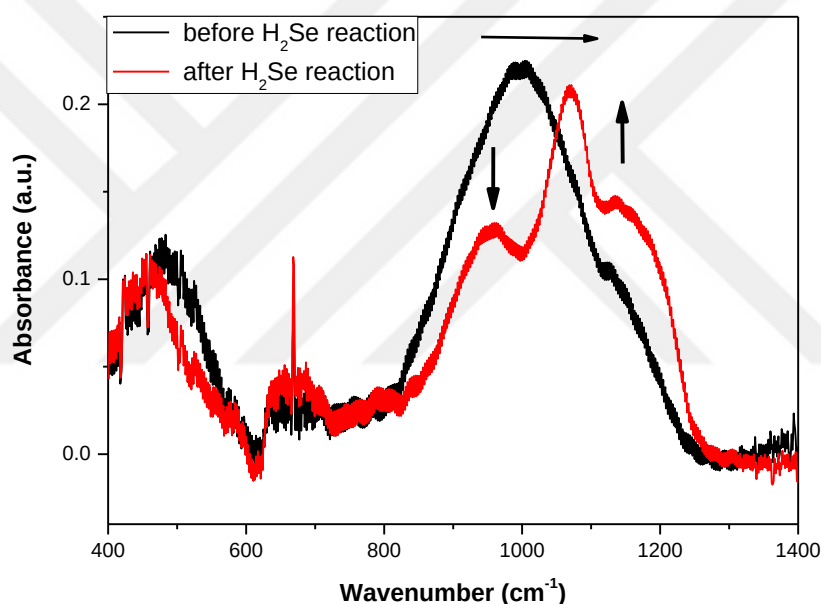


Figure 3.13. FT-IR Spectra of the meso-CdO-SiO₂ films prepared with silica before and after H_2Se reaction.

However, meso-CdSe-SiO₂ thin films, and it is, cannot be used in solar cells because silica is an insulator. Silica samples are more reactive with H_2Se gas than titania sample, therefore the silica samples may be used in solar cells with some modification. Titania is good materials for electron transfer and need to be sensitized to absorb solar light. The combination silica system and titania nanoparticles might be good material solution for the QDSSCs.

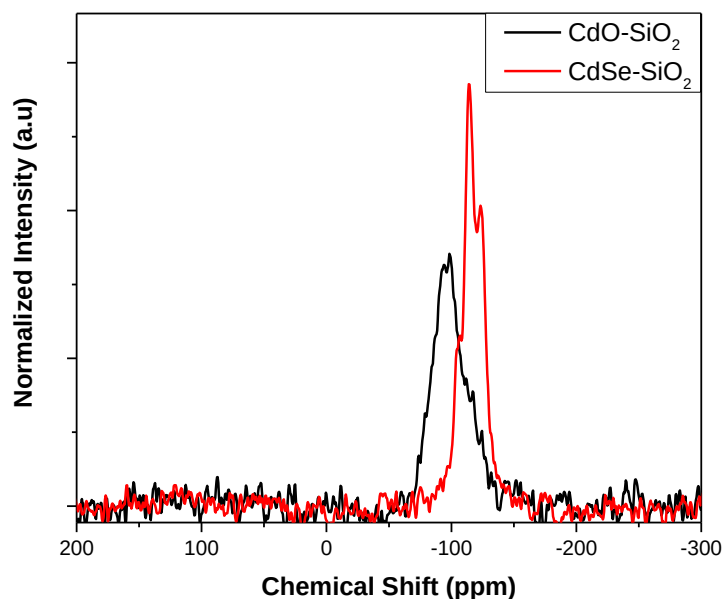


Figure 3.14. ^{29}Si MAS-NMR spectra of the meso- CdO-SiO_2 films before and after H_2Se reaction.

3.2 Infiltration and Mesophase Formation of MASA Solution in TiO_2 Films

To develop a new and simple method for a CdSe sensitized photoanode, the MASA solution, prepared using cadmium nitrate, two surfactants ($\text{C}_{12}\text{EO}_{10}$ CTAB), ethanol and TMOS, is infiltrated into titania film that was fabricated from TiO_2 (P25) nanoparticles (denoted as meso-P25). Previously, the MASA solutions (titania and silica) that were coated on glass substrates produced a uniform mesoporous metal titanate [41] and metal oxide-silica films [43], respectively. However, the behavior of the MASA solution in pores of meso-P25 film, obtained from titania paste, might be different because the confined space among TiO_2 nanoparticles affects the formation of the gelation and products. Cadmium selenide particles, in the silica films, might be formed on titania nanoparticles but it is difficult to characterize them well. The interface of cadmium selenide-silica and titania and the behavior of the solution in the porosity of meso-P25 is important to develop a more efficient solar cell material. The infiltrated MASA solution using both silica and titania MASA solutions in meso-P25 was investigated and characterized step by step.

3.2.1 Infiltration of MASA Solution to meso-P25 Films

How much MASA solution could be infiltrated into the titania paste was questioned to solve possible problems of the infiltration into meso-P25. First question could be to answer whether the MASA solution is coated over meso-P25 or infiltrated through down to the bottom of meso-P25 film. If the MASA solution does not infiltrate down to the bottom of the film, the H_2Se reaction will not produce cadmium selenide at the bottom of the film and the film will remain white on the other side. This decreases the solar efficiency of the electrode because solar light is exposed from the bottom side and absence of CdSe at the bottom of the film will reduce the amount of light absorption and thus overall solar efficiency. Second possible problem could be that a film (meso-CdO-SiO₂ or meso-CdTiO₃) formation at the top surface of the meso-P25 film. This film can block the diffusion of the electrolyte into meso-P25 film. To address this problem, the MASA solutions were prepared with different viscosity. Increasing the amount of solvent (ethanol) increases the viscosity of the MASA solution. The samples were prepared using 4 different ethanol (1, 3, 5, 10 ml) amounts and a same composition of the MASA solution. After infiltration of the above solution into meso-P25 and calcination at 450 °C, the samples were characterized by X-ray diffraction. **Figure 3.15** (a) shows the XRD patterns of meso-P25 (bottom), coated with CdO-SiO₂ with decreasing the amount of ethanol (bottom to top). A broad feature gradually increases with decreasing ethanol amount in the initial MASA solution, including an increasing the amount of CdO in and over the meso-P25. The H_2Se reaction, at suitable conditions, converts CdO to CdSe. The more concentrated solution formed more CdSe on the TiO₂ surface (see **Figure 3.15** (b)) and it also looks darker. The broad diffraction lines, marked with #, originate from the zinc blend CdSe nanoparticles and could be indexed to (111), (220), and (311) planes from low angle to high angle, respectively.

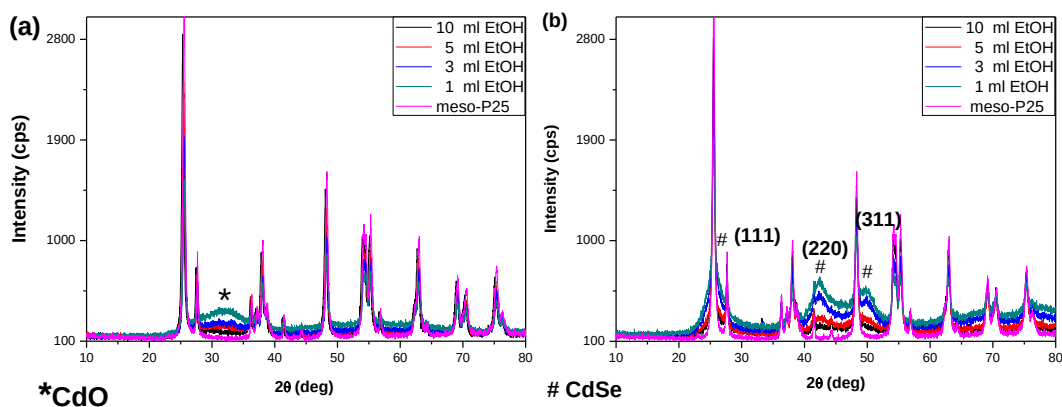


Figure 3.15. XRD patterns of meso-P25 films, loaded with solutions prepared with different amounts of ethanol (a) before reaction and (b) after H_2Se reaction.

Also, FT-IR spectra of the same calcined samples show an increasing intensity trend at around 1000 cm^{-1} with increasing the amount of infiltrated solution. The spectra in **Figure 3.16** are normalized to TiO_2 peak at around 660 cm^{-1} . The absorption peak at around 990 cm^{-1} due to ν Si-O-Cd mode increases with increasing the concentrated of solution (see **Figure 3.16** (a)). The Si-O bond is sensitive to its neighboring atom. The infiltration and calcination process in the silica precursor formed 1.6 nm thin cadmium oxide layer on silica layer (pore-walls) [43]. Upon H_2Se reaction, the Si-O-Cd interface species on the pore walls are converted to Si-O-H and CdSe and the peak due to Si-O is shifted to higher energy, see **Figure 3.16** (b). As shown in **Figure 3.16** (b), all CdO domains were converted to CdSe after the reaction. However, the sample prepared using 1 ml ethanol was needed a more reaction time than the other samples. Both XRD patterns and FT-IR spectra show that the samples are quite still reactive under the H_2Se gas.

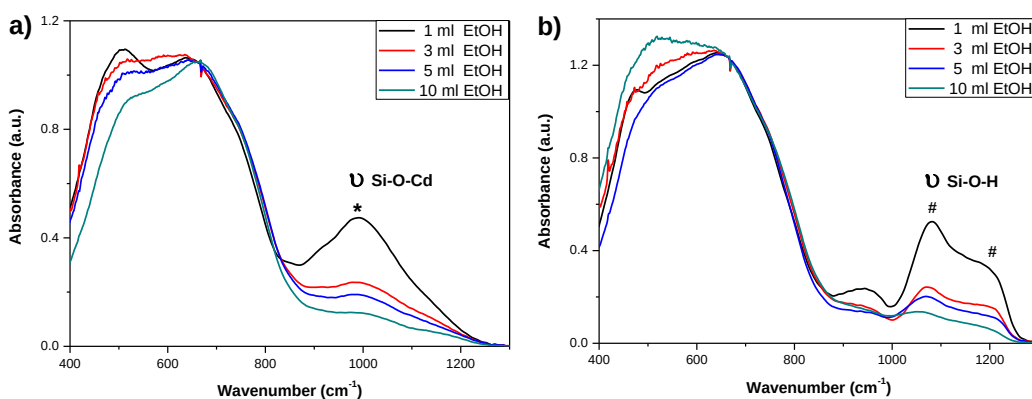


Figure 3.16. FT-IR Spectra of meso-P25 films, loaded with solutions prepared with different amount of ethanol (a) before reaction and (b) after H_2Se reaction.

Effects of viscosity of the infiltrated MASA solution on pore size distribution of titania were also investigated using N_2 sorption measurements. In **Figure 3.17**, N_2 sorption isotherms and BJH pore size distribution plot of the desorption branch of the bared titania and titania with loading using different ethanol solution are shown. With decreasing the amount of ethanol and increasing the concentration of the solution, the pore size of titania decreased and became more uniform, because of effective coating of the meso-P25 internal surface. The average pore size of the bared titania is about 30 nm. However, after coating with the MASA solution and calcination, it decreased down to 20 nm. It means that the coating layer is around 5 nm on each side of titania pore.

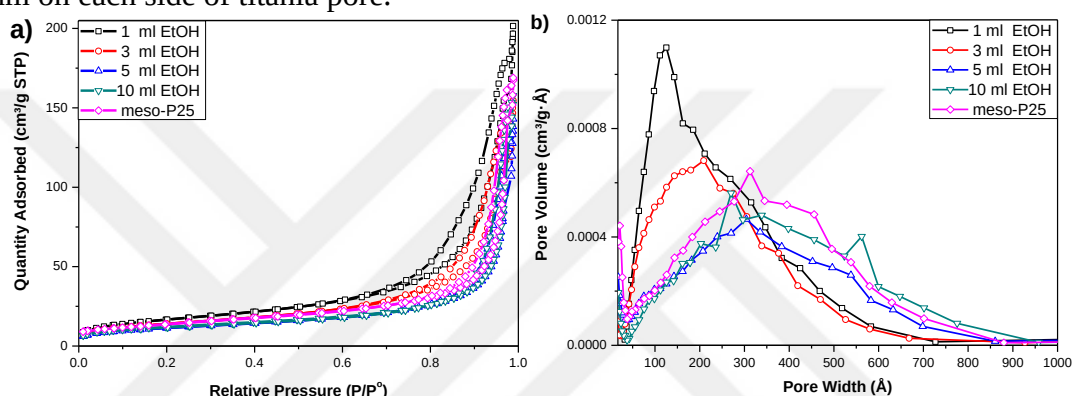


Figure 3.17. Linear N_2 (77K) (a) isotherms and (b) BJH desorption pore size distributions of meso-P25 films, loaded with solutions prepared with different amount of ethanol before the reaction.

Infiltration of MASA solution down to the bottom of the film was investigated. After the H_2Se reaction, if cadmium selenide, which is dark brown colored compound is not formed at the bottom of the film, the backside of the film should be white, which is the color of bared titania. **Figure 3.18** shows backside of the prepared photo anodes, which are loaded using different amount of ethanol in the MASA solution. There is no indication (white color) of bared titania and all the films were coated with CdSe nanoparticles.

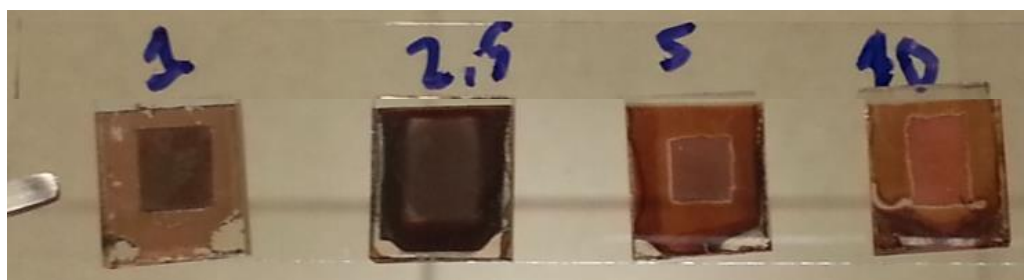


Figure 3.18. Photograph of backside of photo anodes, loaded using different amount of ethanol after H_2Se reaction on FTO glass substrate.

Second problem is the film formation at the top of meso-P25 films and it can block for the diffusion of electrolytes during solar cell performance measurements. To elucidate the above issues, the cadmium oxide-silica films were also investigated by scanning electron microscopy (SEM), because the morphology of titania nanoparticles and the films formed from the MASA solution are different from each other. **Figure 3.19** shows the SEM images of the films, loaded using solutions prepared with different amounts of ethanol. The yellow circles show the film morphology. No film formation was observed over the titania film loaded with 5 ml ethanol and 10 ml ethanol and only pure titania morphology was observed. The film formation at the top of the titania started to be visible in the samples, prepared using 3 ml ethanol. It is clear from the images that the films were formed at the top of the samples prepared using 1 ml ethanol solution.

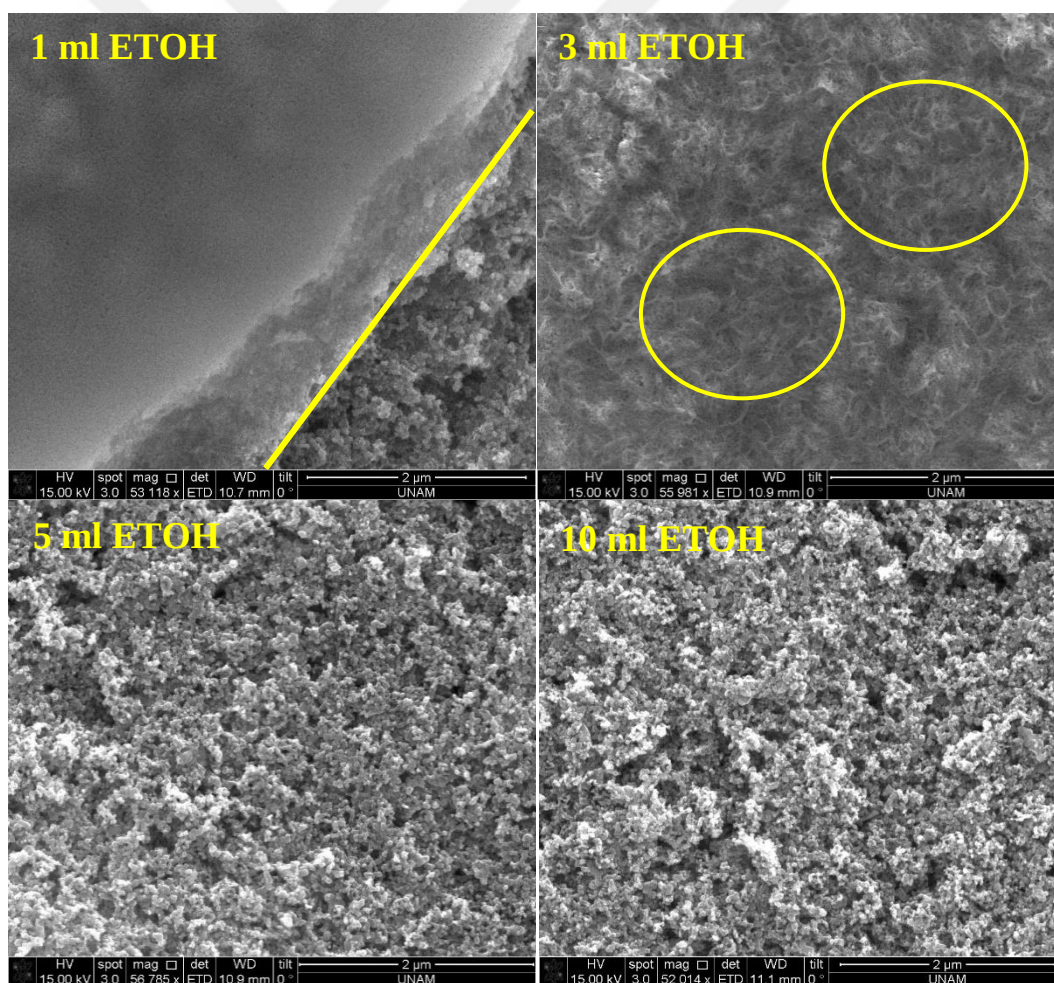


Figure 3.19. SEM images of films, loaded using solutions prepared with different amounts of ethanol. The yellow circles show the film morphology.

Also, the cross section of the samples was investigated to be sure that the MASA solution is infiltrated homogeneously into meso-P25 film, throughout from top to bottom. **Figure 3.20** shows cross section SEM images and EDS spectra of the samples prepared using 5 ml (top) and 1 ml (bottom) EtOH. The yellow line shows the places, where the EDS data were collected. The sample prepared using 5 ml EtOH homogeneously coated the titania film, from bottom of the film to top of the film. The black line and red line show the amount of silicon and cadmium, respectively, and the cadmium and silicon amounts are similar and same throughout the film, indicating the homogeneous coating of the internal surface of meso-P25. However, the images and EDS data of the sample, prepared using 1 ml EtOH showed a homogeneously coated meso-P25 from bottom to top of titania films and above of meso-P25 films, a cadmium oxide-silica film layer was observed. To sum up, the SEM images of both cross section and surface shows that the sample prepared using 1 ml ethanol solution has a cadmium oxide-silica film layer and it can block the diffusion of electrode and behave as an insulating layer over the photoanodes.

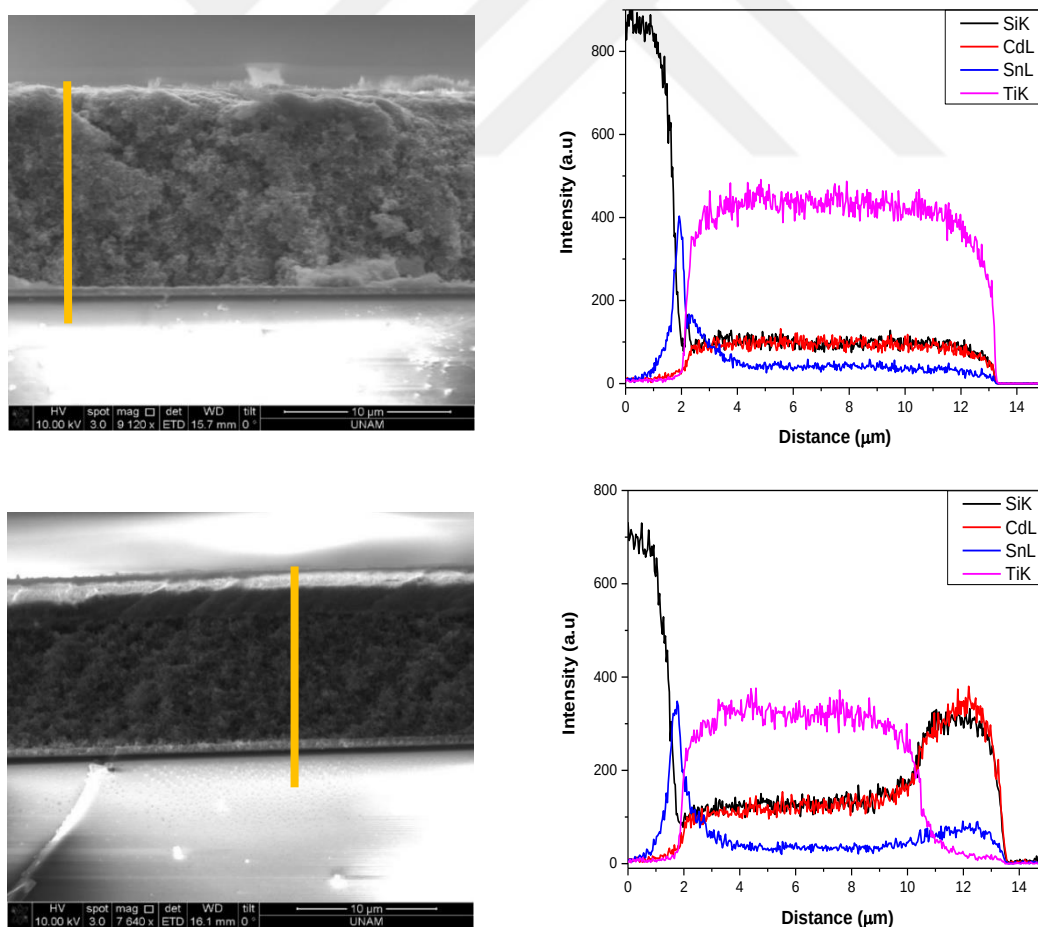


Figure 3.20. Cross section SEM images and EDS spectra of the samples prepared with 5 ml (top) and 1 ml (bottom) EtOH. The yellow line shows the places, which EDS were collected.

After the calcination, the observation of a film formation means that before the calcination, at the top of titania, the mesostructured film was formed. To detect mesostructured film formation over meso-P25 films, after infiltration of MASA solution, a small angle XRD measurements was performed. Firstly, the MASA solutions prepared using different amounts of ethanol were spin coated on glass substrate to see mesostructured formation as a reference and then were spin coated over meso-P25. In **Figure 3.21** (a), the diffraction line at around 1.7° , 2θ , is due to mesostructured film on glass. **Figure 3.21** (b) shows that all infiltrated MASA solutions, except 10 ml ethanol solution, formed a XRD detectable mesostructured film over the meso-P25 film. However, after the calcination, the films were only observed over meso-P25 film from the 1 ml and 3 ml ethanol solutions. This shows that the mesostructured film in the fresh sample, obtained from the 5 ml ethanol solution, is likely too thin that the heat treatment makes the gel-like mesostructured film to diffuse into the pores of meso-P25 films. The temperature dependent changes in the XRD pattern of mesostructured film are shown **Figure 3.22** (a). The diffraction, at around 1.7° , disappeared at 200°C , because the high temperature treatment destroyed the orientation in the mesoscale and created a disorder in the film. The critical temperature is around 150°C to investigate the thermal behavior of the mesostructured film over the meso-P25. **Figure 3.22** (b, c, and d) show that the mesostructured film at the top surface of meso-P25 was remained in the samples, prepared using 1 and 3 ml ethanol solutions. These observations well correlated with the observations in the SEM images. The mesostructured film layer, at the top of surface of meso-P25, is likely to be sucked into the pores by shrinking and melting during thermal treatment. To sum up, the thickness of the mesostructured film over meso-P25 films determines the film formation at the top of meso-P25 films.

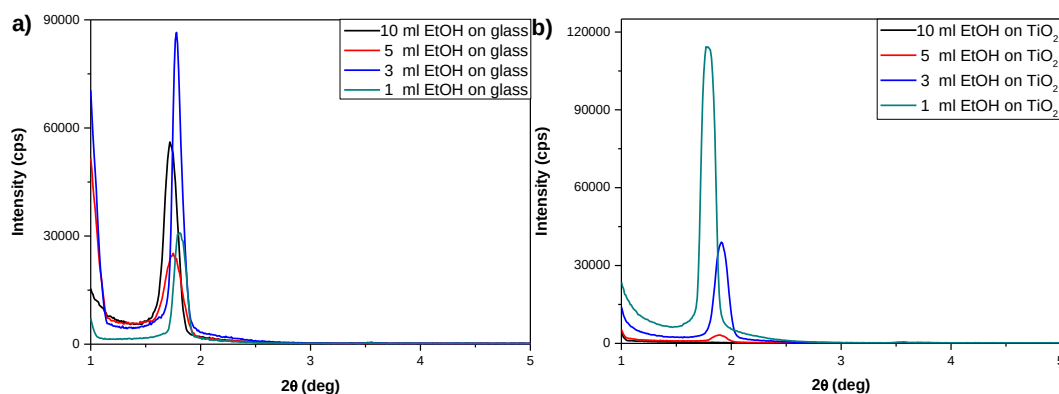


Figure 3.21. Small angle XRD patterns of MASA solutions, prepared using different amounts of ethanol, upon spin coating on (a) glass substrate, and (b) meso-P25 film.

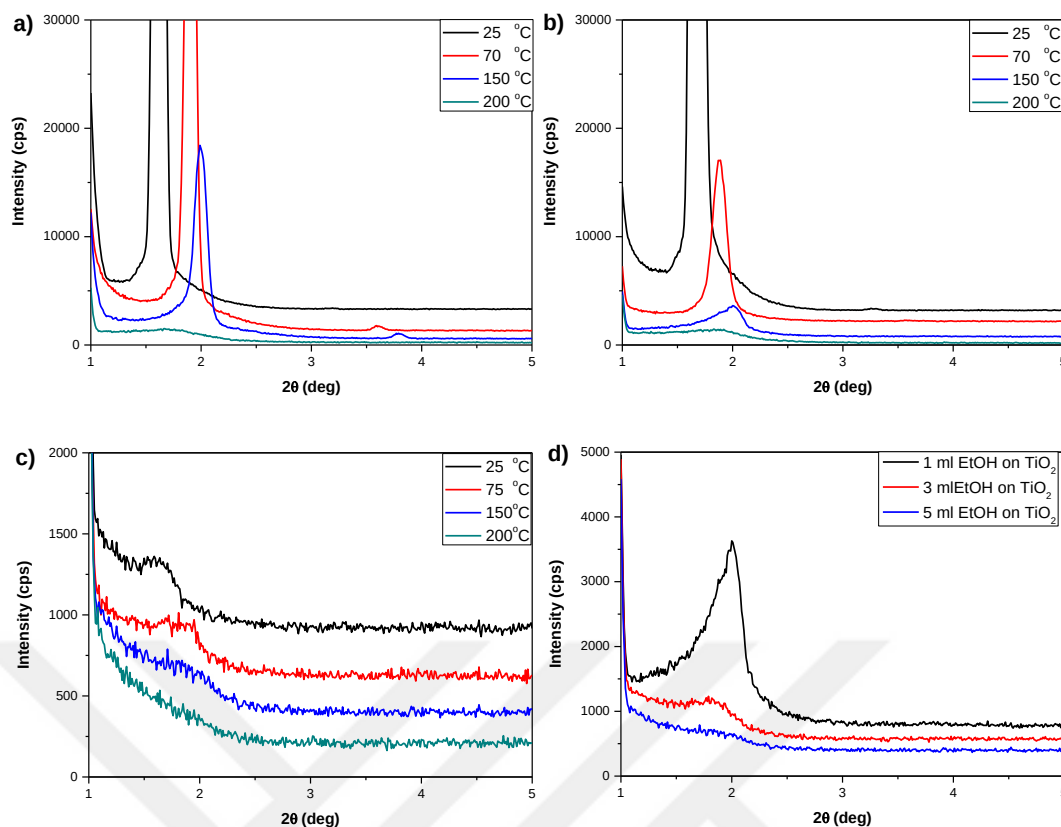


Figure 3.22. Temperature dependent changes in the small angle XRD patterns of the MASA solutions (a) coated over glass substrate using 1 ml ethanol solution, and coated over meso-P25 using (b) 1 ml ethanol solution, and (c) 5 ml ethanol solution and (d) XRD patterns of meso-P25 at 150 °C, coated using 1, 3, and 5 ml ethanol solutions.

A set of photoanodes were prepared as described above and reacted under H_2Se gas to investigate the role of infiltrating different MASA solutions on the overall efficiency of solar cells. In **Figure 3.23**, I - V curves of the photoanodes, loaded using different amount of ethanol MASA solutions are shown. The trend in **Figure 3.23** shows that solar cell performance of the anodes increases with increasing ethanol in the solution, however the best performance was observed from the electrodes, prepared using 5 ml ethanol solution. Further increasing ethanol (10 ml) in the solution reduces the cell performance. These observations are reasonable, because at low ethanol concentration a mesostructured film forms over the anode and it is not very active. Over 5 ml ethanol, the internal surface coating of meso-P25 is uniform but, increasing ethanol in the solution reduces the infiltrated Cd (II) amount and as a result the number of CdSe sensitizers in the meso-P25 film. The efficiency of the solar cell, obtained from 1 ml ethanol solution is dramatic, because the mesoporous cadmium selenide-silica film covers the photoanode and behaves as an insulator. To sum up, all above characterizations (XRD, FTIR, SEM and solar cell

performance) show that the MASA solution should be prepared using 5 ml ethanol and then infiltrated into meso-P25 for an efficient solar cell.

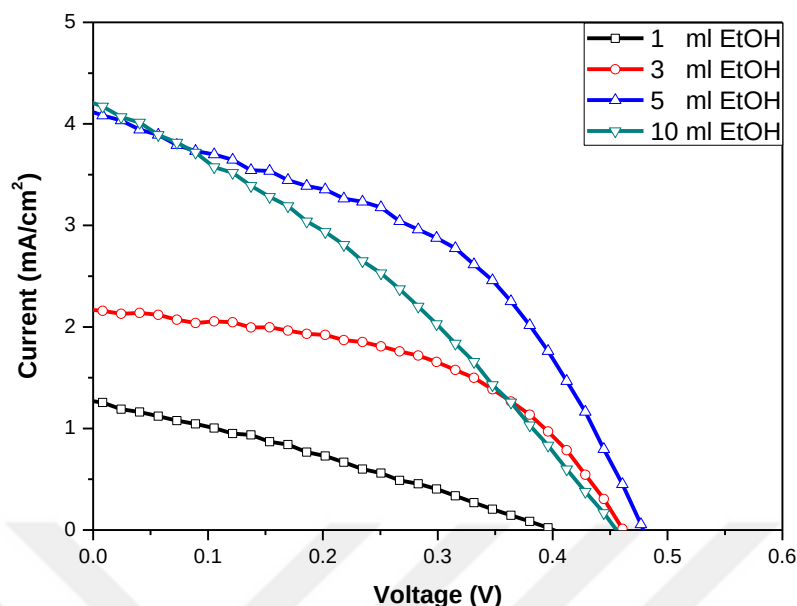


Figure 3.23. *I-V* Curves of the photoanodes, prepared using different MASA solutions (same composition, different amount of ethanol)

The film samples prepared using 5 ml ethanol solution were further characterized by using ^{29}Si MAS-NMR and TEM to better understand the silica system. **Figure 3.24** shows the ^{29}Si MAS-NMR spectra of a sample before (black line) and after (red line) H_2Se reaction. After the reaction, pure silica peaks (Q_2 , Q_3 , Q_4) were observed and all the peaks related to $\text{Si}(\text{OSi})_{4-x}(\text{OCd})_x$ sites ($x=2,3$ or 4) were disappeared, indicating a complete conversion of CdO to CdSe . **Figure 3.25** shows a set of TEM images of a meso- $\text{CdO-SiO}_2\text{-P25}$ before and after H_2Se reaction. Yellow lines show borders of the crystalline titania nanoparticles (P25 domains). The coated cadmium oxide-silica layer is visible over titania particles. After H_2Se reaction, nanoparticles were formed with a typical particles size of around 3 nm and they are homogenously distributed over the titania particles. No bare titania was observed in the images. The presence of bare titania may cause a shortcut for the transfer of photo generated electrons from bare titania to the electrolyte. Although there is an insulating silica layer between the CdSe nanoparticles and titania, the CdSe particles are close enough to titania to transfer excited electrons from conduction band of CdSe to conduction band of TiO_2 . **Figure 3.26** shows *I-V* Curves of the photoanodes, prepared using same MASA solutions (same composition, 5 ml of ethanol). The PCE of the efficient cell is about 2.2%, I_{sc} of 8 mA/cm^2 , V_{oc} of 0.58 V and FF of 0.47.

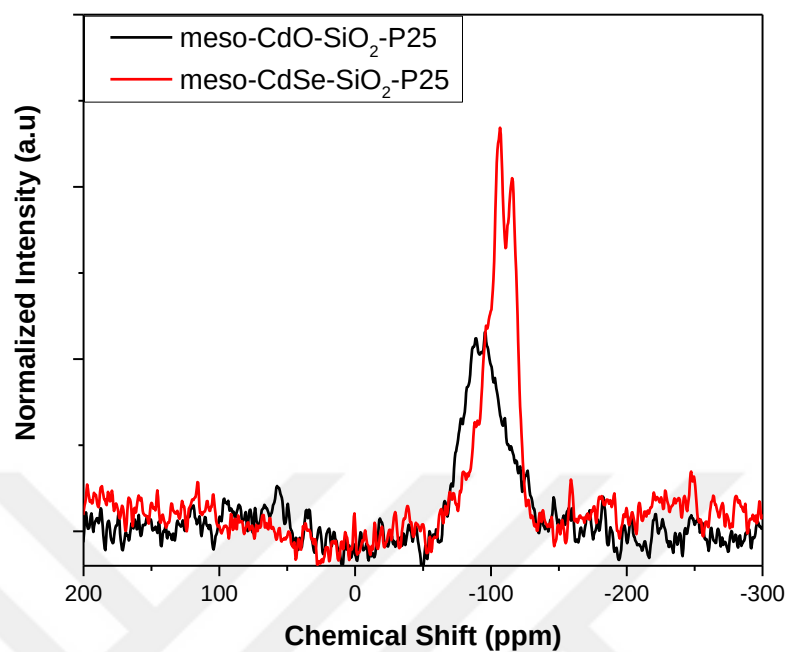


Figure 3.24. ^{29}Si MAS-NMR spectra of (black line) meso- $\text{CdO-SiO}_2\text{-P25}$ and (red line) meso- $\text{CdSe-SiO}_2\text{-P25}$ film, infiltrated using 5ml ethanol MASA solution.

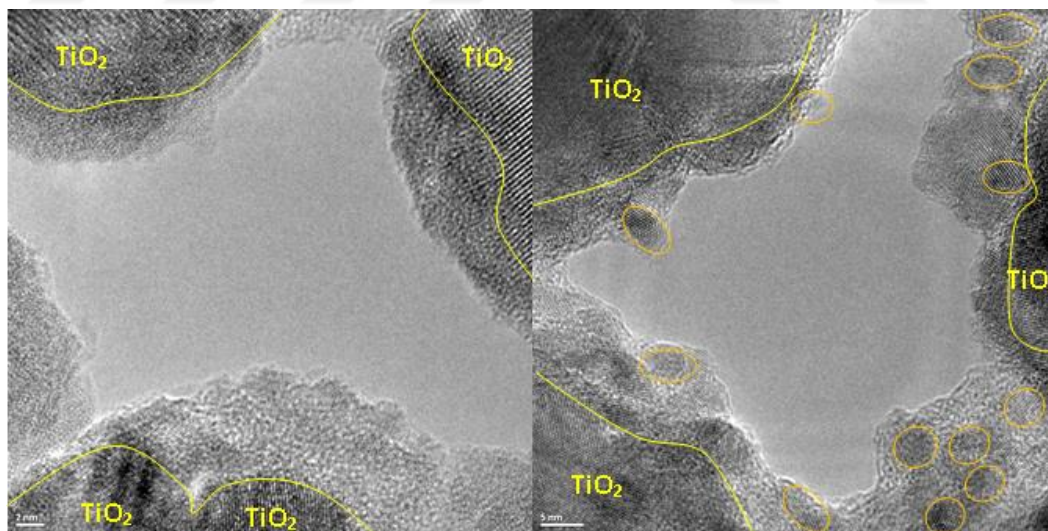


Figure 3.25. TEM images of (left) meso- $\text{CdO-SiO}_2\text{-P25}$ and (right) meso- $\text{CdSe-SiO}_2\text{-P25}$ film, prepared using 5 ml of ethanol MASA solution. Yellow lines show titania nanoparticles and orange circles show CdSe nanoparticles.

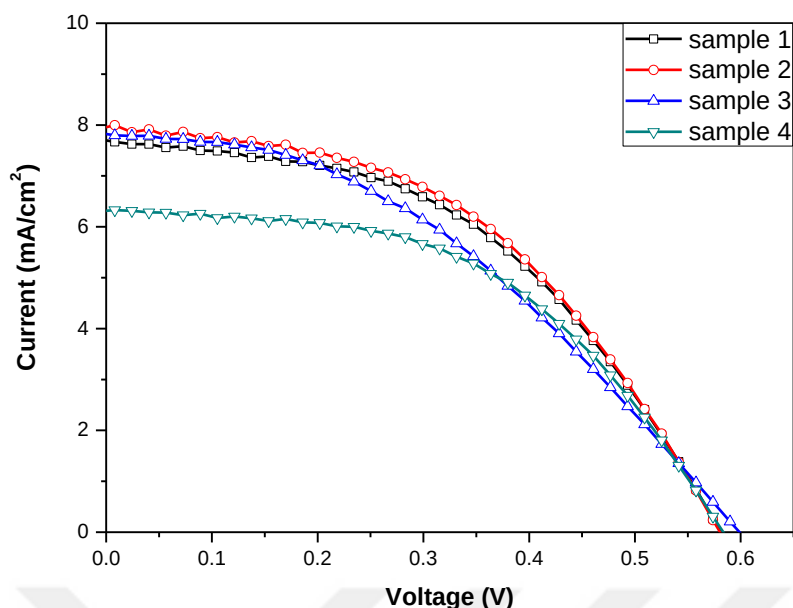


Figure 3.26. *I-V* Curves of the 4 photoanodes, prepared using same MASA solutions (same composition, 5 ml of ethanol).

3.2.2 Multiple Loading of meso-P25 Films

The amount of CdSe on titania nanoparticles increase with increasing the Cd(II) concentration in the MASA solution or multiple loading. Remember that the infiltrated concentrated MASA solution formed an insulating film layer over meso-P25 and decreased the solar cell efficiency. To increase the amount of cadmium selenide on titania nanoparticles without the film formation, diluted MASA solution was infiltrated multiple times (by consecutive infiltration followed by a calcination). The samples, upon multiple loading, were investigated using FT-IR, XRD, SEM and N₂ sorption techniques. In **Figure 3.27** (a), XRD patterns of meso-P25 coated with a single layer and also multiple layers of CdO-SiO₂ are shown. After H₂Se reaction, CdO is converted to CdSe, as detected in the XRD patterns, see **Figure 3.27** (b). The complete H₂Se reaction was also correlated by recording the FT-IR spectra, see **Figure 3.28**. The spectral changes show that the CdO species are converted to CdSe; notice that after H₂Se reaction, there is no peak related to ν Si-O-Cd at around 1000 cm⁻¹.

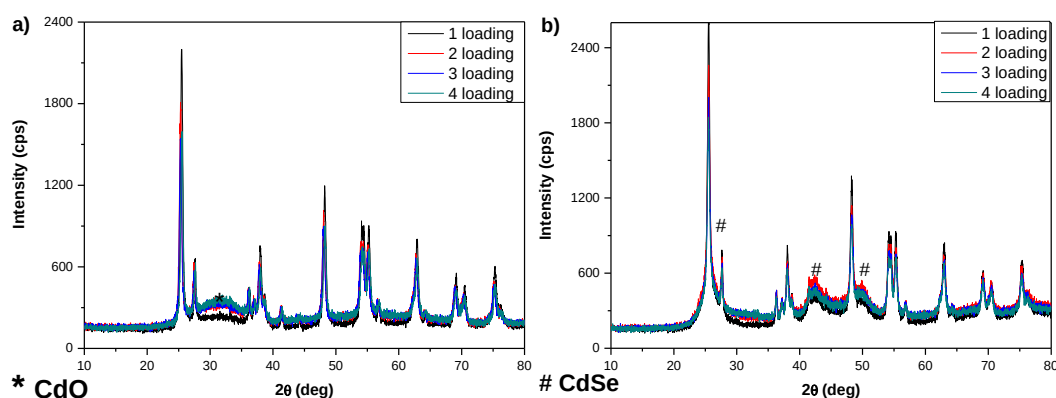


Figure 3.27. XRD pattern of meso-P25 films, multiple times coated with CdO-SiO₂, (a) before and (b) after H₂Se reaction.

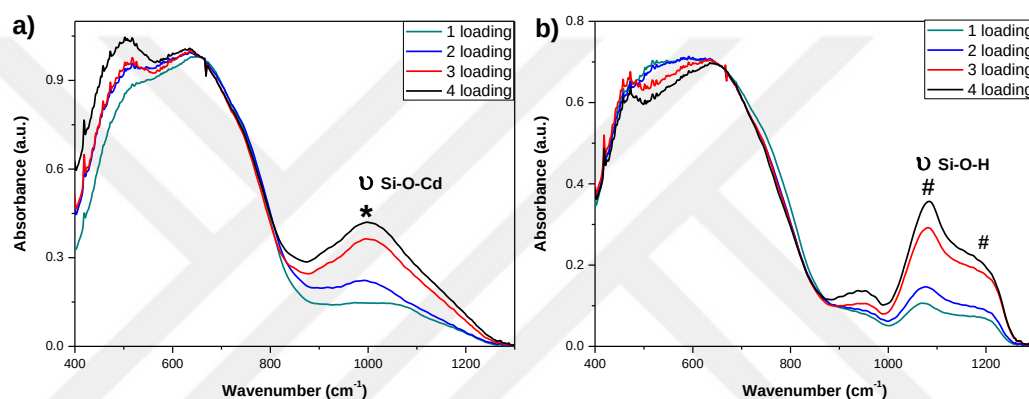


Figure 3.28. FT-IR Spectra of meso-P25 films, multiple times coated with CdO-SiO₂, (a) before and (b) after H₂Se reaction.

Pore size distribution in the films with multiple loadings were also investigated by using N₂ sorption measurements and analysis. Note that the lack of the insulating meso-CdO-SiO₂ film is very critical for an efficient solar cell, because it blocks the diffusion of electrolyte into titania film. If the insulating film forms at the top of meso-P25 film at first loading, next loading is not infiltrated into meso-P25, it only increases the thickness of the insulating film. In **Figure 3.29**, the insulating meso-CdO-SiO₂ films was formed at first loading. After multiple loadings of this sample, showed changes on pore size around 3 nm. Remember that the MASA solution forms films with 3 nm pores after spin coated on glass substrate and calcination [41]. The number of small pores about 3 nm increased with no changes in the large pores upon multiple loadings. This trend shows that first loading formed the meso-CdO-SiO₂ films over the top surface of meso-P25 film and the other loadings just increased the thickness of the insulating meso-CdO-SiO₂ film. However, **Figure 3.30** shows gradual changes on the pore size distribution upon multiple loading of

meso-P25 with a diluter ethanol MASA solution. Pore size distribution in the meso-P25 is very broad (average of 30 nm) but after 4 times loading, pores becomes smaller (decreased down to 10 nm) and much more uniform. This shows that 7.5 nm of the pores were coated with meso-CdO-SiO₂ layer ver the internal surface of meso-P25 during multiple coating steps. Also, no film formation was observed on these samples. However, the meso-CdO-SiO₂ film formation appeared after 4 times loading, because around 3 nm a new peak was appeared due to meso-CdO-SiO₂ film.

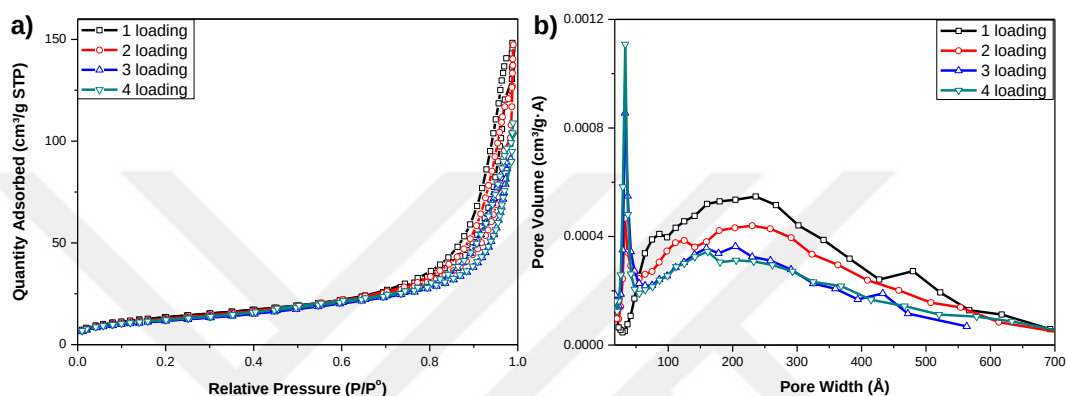


Figure 3.29. Linear N₂ (77K) (a) isotherms and (b) BJH desorption pore size distributions of meso-P25 films and upon loading multiple times of a solution of 1 ml EtOH.

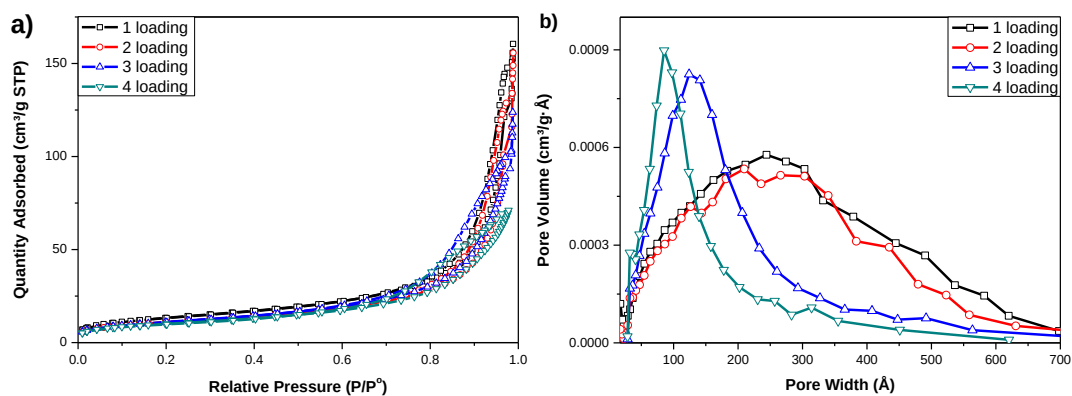


Figure 3.30. N₂ sorption (a) isotherms and (b) BJH desorption pore size distribution of meso-P25 and upon loading multiple times of a solution of 2.5 ml EtOH.

The film formation by multiple loading of MASA solution into and over meso-P25 was further analyzed by using SEM imaging technique. In **Figure 3.31**, the SEM images show that only film formation is observed on the meso-P25 loaded 4 times and is correlated with the other studies. To sum up, it is possible to control the amount of cadmium selenide-silica layer by multiple loading.

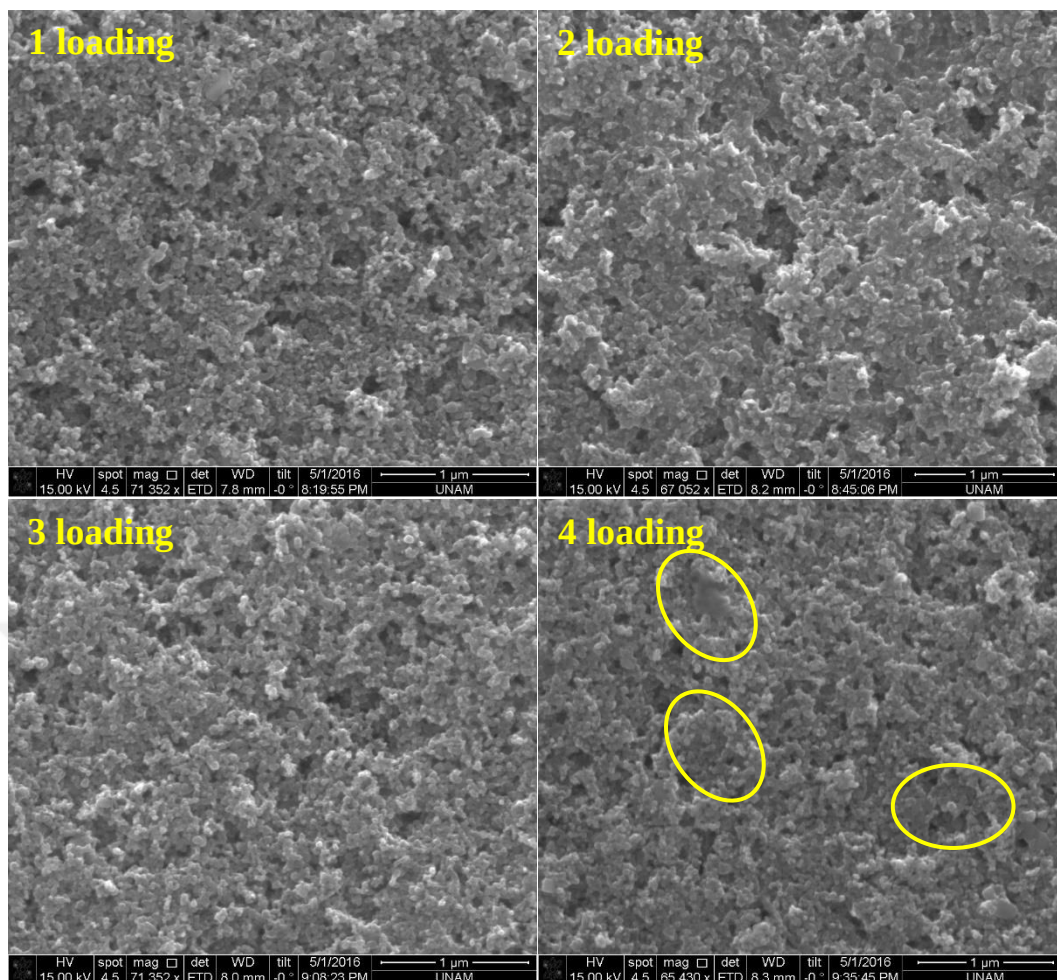


Figure 3.31. SEM images of meso-CdO-SiO₂-P25, upon multiple times loading with a solution prepared using 5 ml EtOH and calcination. The yellow circles show the film morphology.

3.2.3 Reactivity to H₂Se and the Formation of Metallic Selenium

The reactivity of cadmium oxide-silica thin films to H₂Se reaction has been examined previously [43]. However, the reactivity of the coated sample over titania nanoparticles need to be examined. Also, Han in his master thesis showed that cadmium oxide-silica on titania is more reactive to H₂Se gases than cadmium titanate on titania particles [77]. Raman spectra of silica and titania system are shown in **Figure 3.32** and the peaks around 210 cm⁻¹ and around 420 cm⁻¹ (due to its longitudinal optical (LO) mode) are unique and originate from fundamental and 1st overtone vibrational mode of CdSe. These peaks are useful and to understand the formation of cadmium selenide. The other peak around 250 cm⁻¹ is related to metallic

selenium. The amount of CdSe, formed in the silica system, is much higher than the titania system, when the titania peak at around 140 cm^{-1} is normalized.

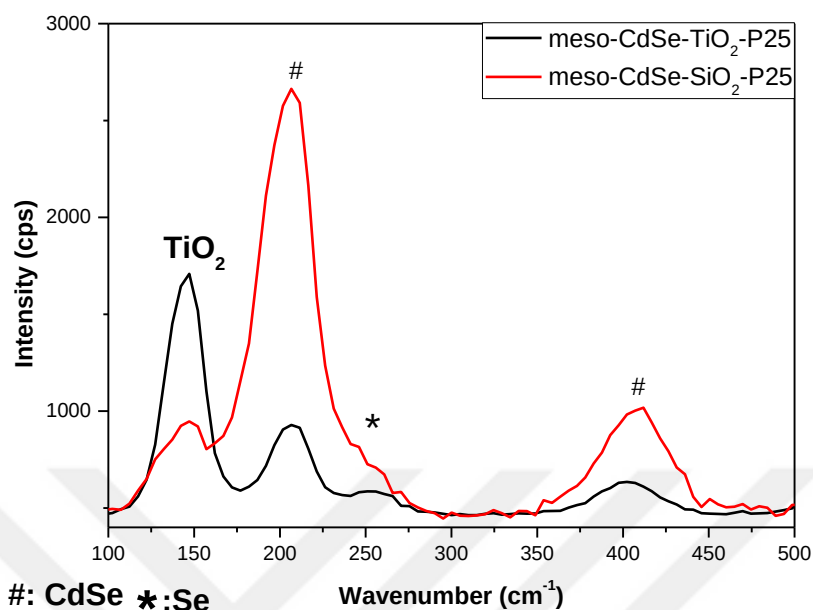


Figure 3.32. Raman spectra of cadmium titanate (black line) and cadmium oxide-silica (red line) in meso-P25 after H_2Se reaction.

To investigate the effect of various synthesis parameters on the formation of CdSe and Se species and their effect in the quantum dot sensitized solar cells that were fabricated using the molten-salt assisted self-assembly (MASA) process, the Se and Cd K-edge XANES and EXAFS spectra of a series of CdSe sensitized titania solar cells were collected. The CdO-SiO_2 and CdTiO_3 are converted to CdSe-SiO_2 and CdSe-TiO_2 by the H_2Se gas. Also, metallic Se are formed as a side product. The conversion efficiency of the reaction and the amount of Se is unknown. Converting CdO to CdSe causes changes on the K-edge of Cd, and gives information about reaction yield. Second information we seek is the percentage of CdSe and Se upon H_2Se reaction of CdO-SiO_2 and CdTiO_3 . Due to differences on the K-edge of Se in CdSe and pure Se, linear combination analysis (LCA) can be used to determine the percentage of CdSe and Se in the samples.

The reaction conditions directly affect the efficiency of the reaction. To determine the optimum reaction condition, the reaction temperature and the environment in reaction chamber were changed. The reaction was conducted under different conditions (in vacuum, in 300 torr N_2 , in 760 torr N_2 and in air) and temperature (RT, 100°C, 200°C) as discussed before.

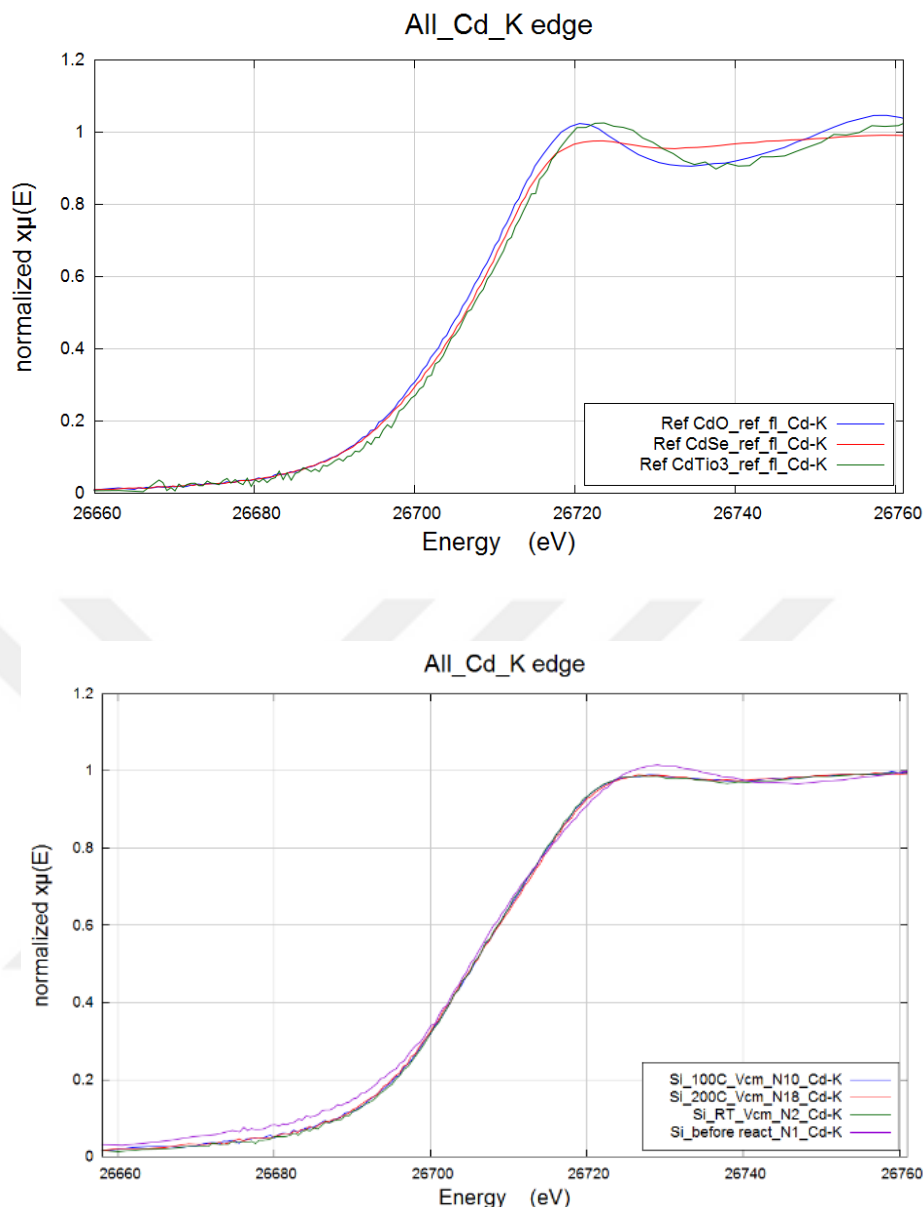


Figure 3.33. Cd K-edge XANES spectra of (up) references (CdO (blue), CdSe (red), CdTiO₃ (green)) and (bottom) the mesoporous materials reacted with H₂Se under different reaction temperature.

Figure 3.33 and **Figure 3.34** show the Cd K-edge XANES spectra upon converting CdO to CdSe. The Cd K-edge XANES spectrum helps to monitor the reaction progress. The absorption edge shifts to higher energy going from CdO to CdSe. **Figure 3.33** (bottom), the purple spectrum is from the starting materials, containing CdO. The maximum shift was observed in the samples reacted at 100 °C and it indicates the conversion from CdO to CdSe is quite high, **Figure 3.33** (bottom). Therefore, 100 °C was taken as the optimum reaction temperature and accordingly the other parameters were optimized. In the silica system, the reactions have been carried at different conditions (vacuum, 300 torr N₂, 760 torr N₂, air). The Se

formation enhanced in the presence of air (the worst condition for the reaction check **Figure 3.8**). However, the CdO to CdSe conversion efficiency is high under vacuum and 300 torr N₂ conditions. (see **Figure 3.34**) In the silica system, we also found that 100 °C and vacuum condition ($\sim 10^{-2}$ torr) is a suitable condition for the reaction because the amount of CdSe product is the highest.

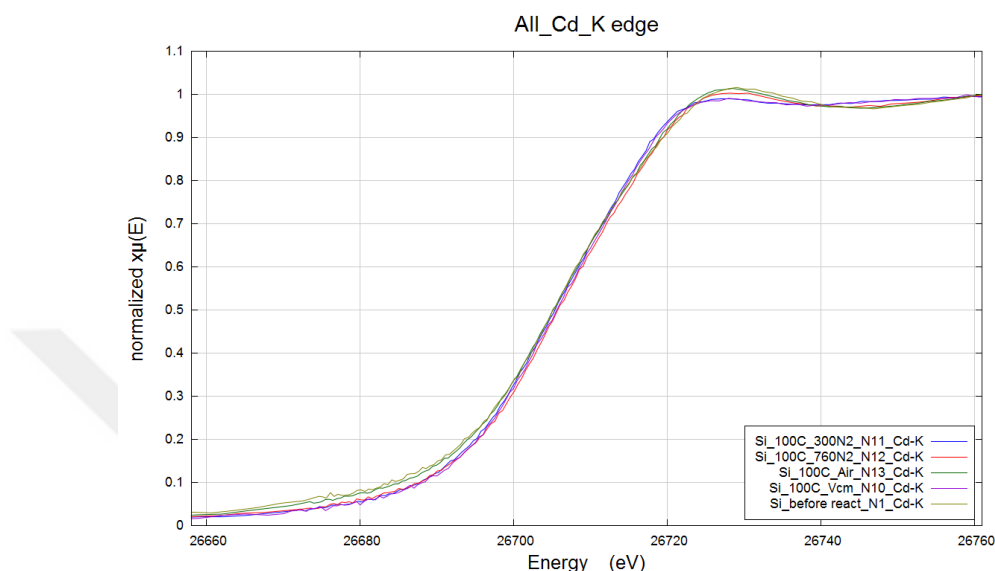


Figure 3.34. Cd K-edge XANES spectra of silica system under different reaction conditions (300 Torr N₂, 760 Torr N₂, 760 Torr air, and 1 torr atmosphere, as shown in the insets, respectively.)

In the titania system, the effect of same reaction condition on the reaction yield was also examined; the H₂Se reaction was conducted at different temperature (RT, 100 °C and 200 °C) like the silica system. At 100 and 200 °C, the conversion from cadmium titanate to cadmium selenide is high. (see **Figure 3.35**). However, compared to the silica system, in terms of blue-shift, the silica system blue-shifts more due to its better reactivity and higher yield.

To determine the optimum reaction conditions in the titania system, the H₂Se reaction has been carried under 4 different conditions (vacuum, 300 torr N₂, 760 torr N₂, air). In Figure 3.35, the blue-shift increased from air (the worst condition for the reaction) to vacuum. We also found out that the conversion efficiency is high under vacuum condition and 300 torr N₂.

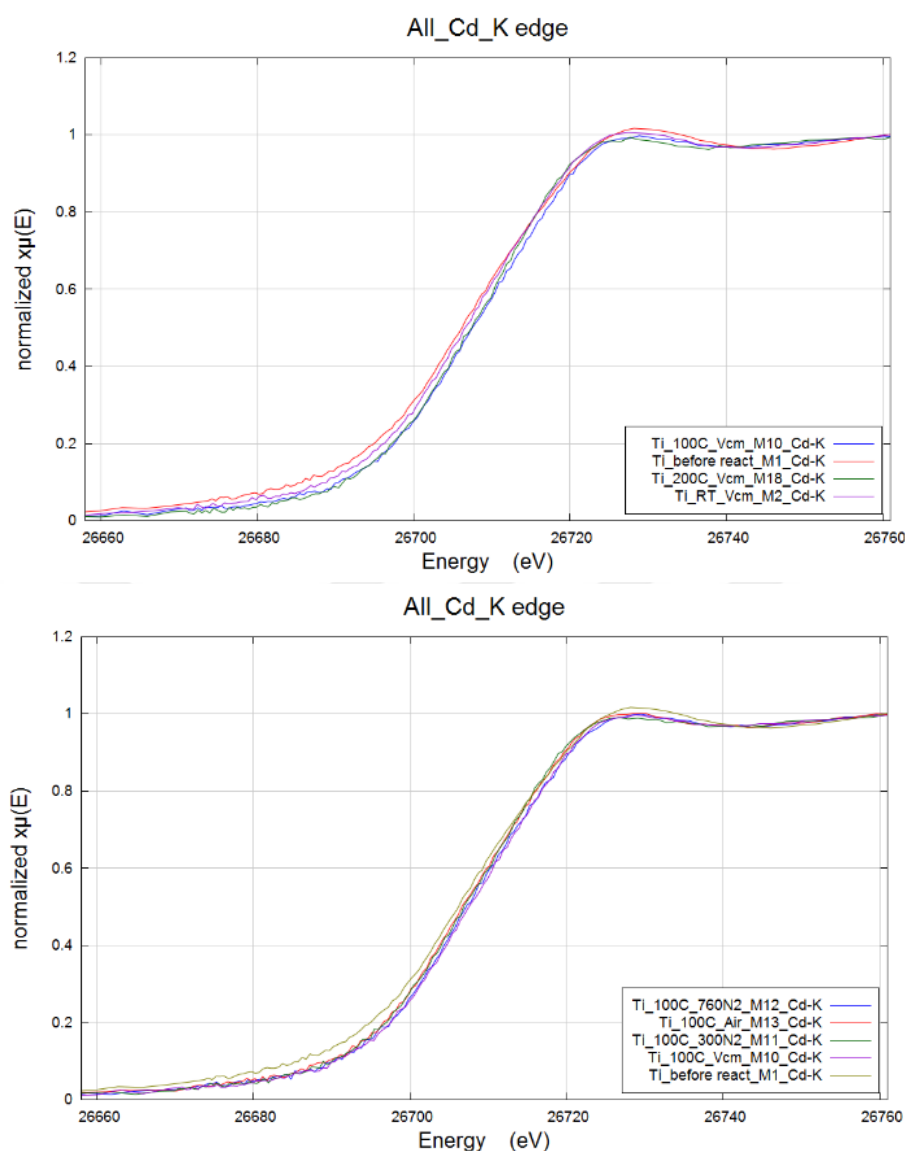


Figure 3.35. Cd K-edge XANES spectra of titania system under different reaction temperature (up) and different reaction conditions(down) (as shown in the insets).

To sum up, after the XANES studies of Cd K-edge at DESY, the optimum H_2Se reaction condition was determined to be 100 °C and under vacuum atmosphere.

Se K-edge of the same samples were also collected to identify the products and side products, CdSe and metallic selenium. **Figure 3.36** and **Figure 3.37** show Se K edge XANES spectra of pure cadmium selenide, selenium and selenium dioxide and our samples. There are appreciable differences on the absorption edge of Se in different samples and useful for the evaluation of the samples. **Figure 3.37** and **Figure 3.38** show the Se K-edge spectra of the reference and the samples upon H_2Se reaction.

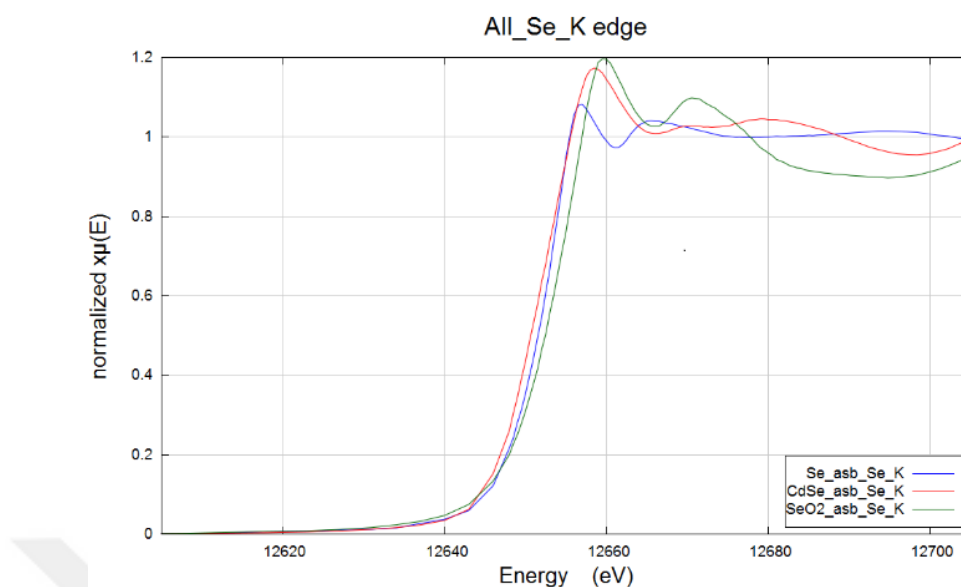


Figure 3.36. Se K-edge XANES spectra of reference samples (Se, CdSe, and SeO₂, red, blue, and green line, respectively).

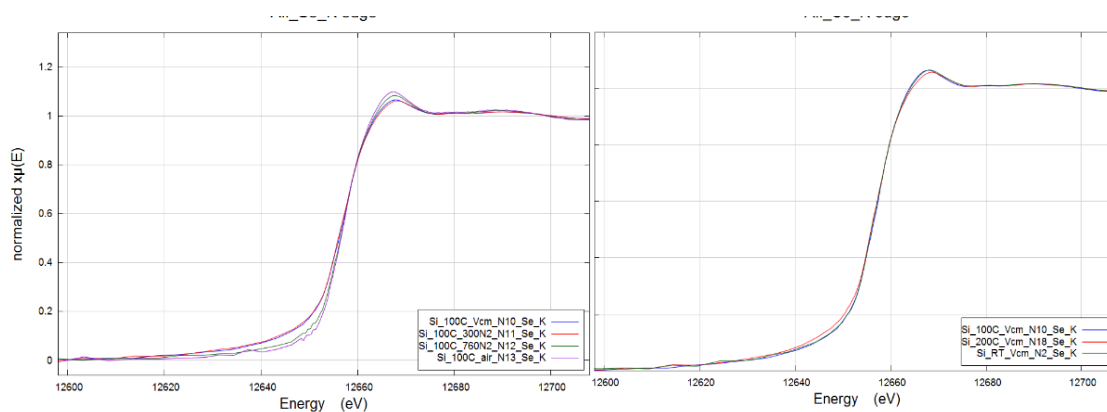


Figure 3.37. Se K-edge XANES spectra of silica systems under different reaction temperature (left) and different reaction conditions (right), as shown in the insets.

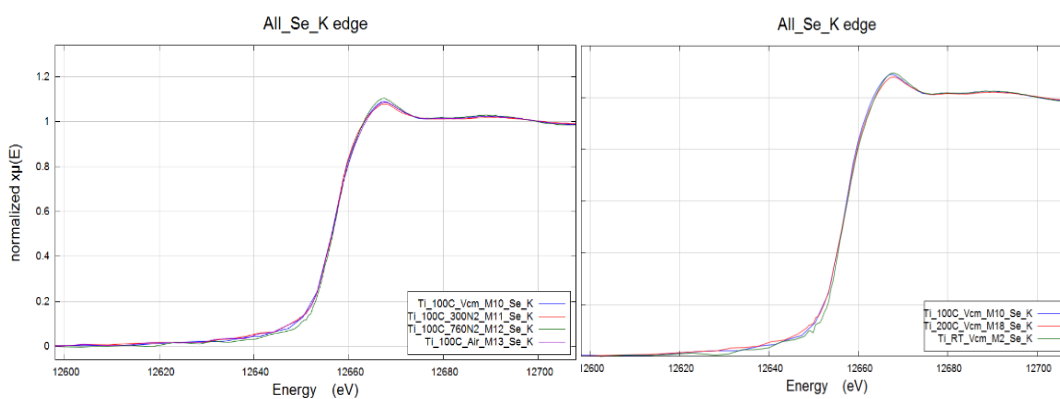


Figure 3.38. Se K-edge XANES spectra of titania system under different reaction temperature (top) and different reaction conditions (bottom), as shown in the insets.

Linear combination fitting (LCF) is helpful if the spectrum was taken in absorption mode. However, all measurement was taken in fluorescent mode because of low intensity in absorption mode. It is difficult to fit the data in fluorescent mode using LCF.

EXAFS data of the Se K-edge also showed presence of Br^- in our samples. Notice that these samples were prepared using two different surfactants; one of these surfactant is CTAB, where the Br^- cannot be removed even at 450 °C calcination. K edge of Br is observed at around 13480 eV. However, some of the Br^- is removed upon H_2Se reaction, likely as HBr from the media, see Figure 3.39. Figure 3.39 displays normalized spectra of both silica and titania systems. Spectra clearly show different Br^- elimination under different reaction conditions. Br K-edge is also useful to indirectly monitor the H_2Se reaction and shows that the H_2Se reactions under N_2 or vacuum are more effective. The Br^- in the titania samples are less than in the silica samples but in both systems highest Br^- remains in the samples that were reacted under air conditions or high N_2 atmosphere.

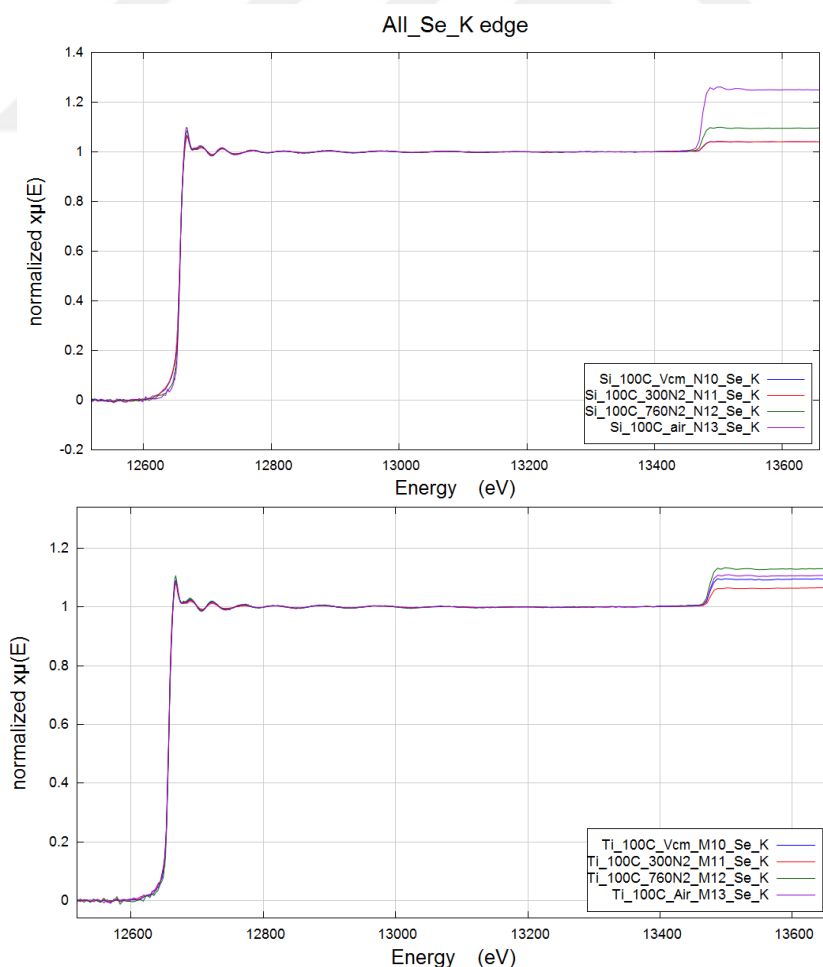


Figure 3.39. Se K-edge EXAFS spectra of silica (top) and titania (bottom) systems under different reaction conditions.

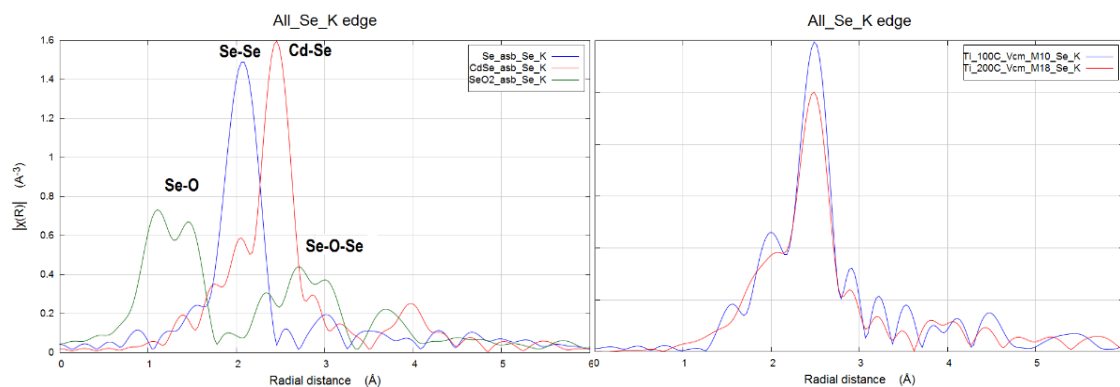


Figure 3.40. Fourier transform of baseline-corrected, normalized and k^3 -weighted EXAFS data of (left) reference samples (SeO_2 , Se and CdSe) and the titania samples (right).

EXAFS analysis also shows the presence of Se in the samples upon H_2Se reaction, but the quality of the data needs some improvements. A set of k^3 -weighted EXAFS data from the reference and our samples are given in Figure 3.40. Clearly the rise on the low r values in the samples is likely due to Se species that have a relatively larger magnitude in the Se rich samples. Both EXAFS and XANES spectra from both silica and titania systems are needed to further analyze to elucidate nature of Se species in these samples.

To sum up, after the XANES studies of Cd K-edge and Se K-edge at DESY, the optimum H_2Se reaction conditions to increase the formation of cadmium selenide and eliminate the formation of byproduct of selenium were determined to be 100°C and under vacuum atmosphere. Although the metallic selenium formation is more at high temperature but easily dissolved in sulfide solution, the amount of cadmium selenide is high which is important to absorb more light and efficient QDSSCs.

3.2.4 Effect of Insulating Silica Amount in the meso-CdO-SiO₂

The cadmium selenide-silica film was formed in the pores of meso-P25 that acts as a photoanode in QDSSCs. However, the meso-CdSe-SiO₂ films at the top of meso-P25 films behaves as an insulator (check **section 3.2.1**). Therefore, the amount of silica in MASA solution are needed to be questioned because silica might be at interface between CdSe nanoparticles and titania and may affect negatively the PCE of QDSCs. The initial amount of silica in MASA solution was reduced systematically from 7 to 0 silica/surfactant mole ratio (7, 5, 3, 1, or 0). The interface

between silica and cadmium oxide layer was investigated by using FTIR. shows FTIR spectra of the samples prepared using different initial amount of silica. Low Si to Cd mole ratio (1/8, 0/8) could not be measured because of the IR absorption of byproducts (like bulk CdO). The ν -Cd-O-Si peak at around 1000 cm^{-1} shifted to a higher energy with increasing the silica amount. (see **Figure 3.41**).

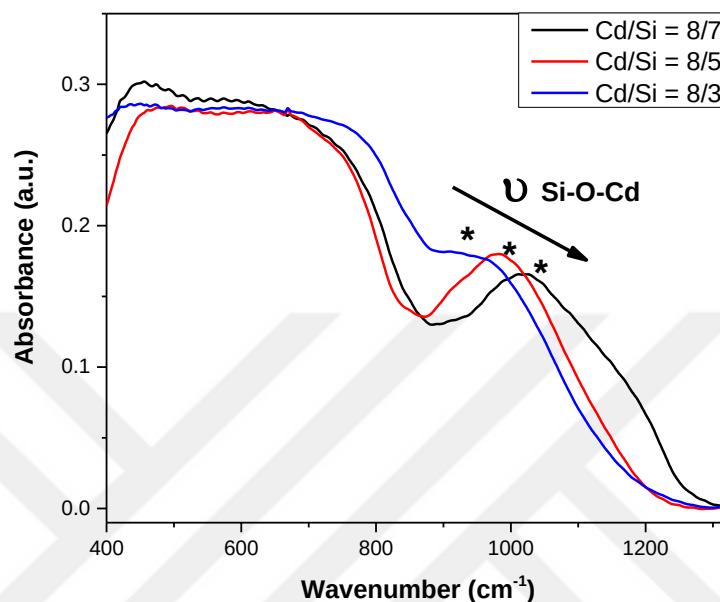


Figure 3.41. FTIR spectra of the samples, prepared using different initial amount of silica.

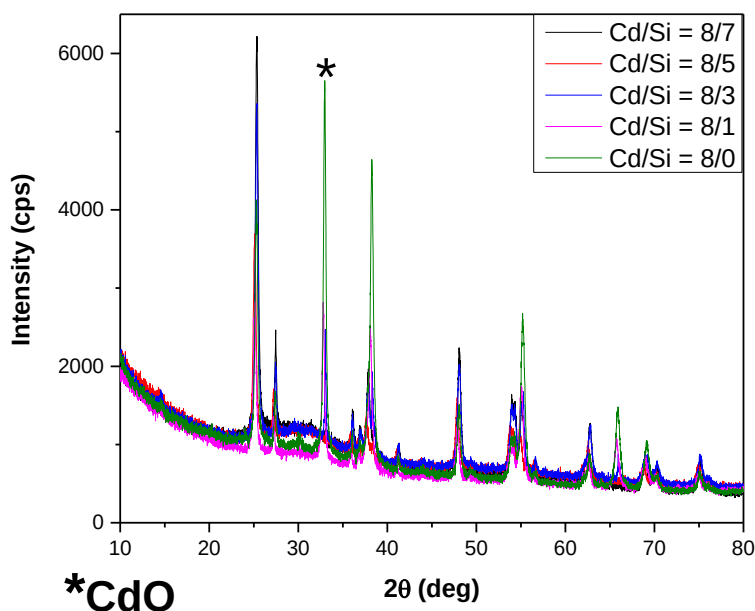


Figure 3.42. The XRD patterns of the samples, prepared using different initial amount of silica.

The XRD patterns of the samples, prepared using different initial amount of silica are shown in **Figure 3.42**. The bulk CdO diffraction line (at 33°) was observed from the samples, prepared using low Si to Cd mole ratio (3/8, 1/8, 0/8), **Figure 3.42**. However, in the high Si to Cd mole ratios (7/8, 5/8), no bulk CdO crystal was observed.

The bulk CdO crystal was also observed in the SEM images, see **Figure 3.43**. The crystalline CdO particles dominate on the images, upon reducing the silica in the media. Reactivity towards H_2Se of those samples are very low and do not display much solar cell activity. Therefore, those samples were not further investigated in this work.

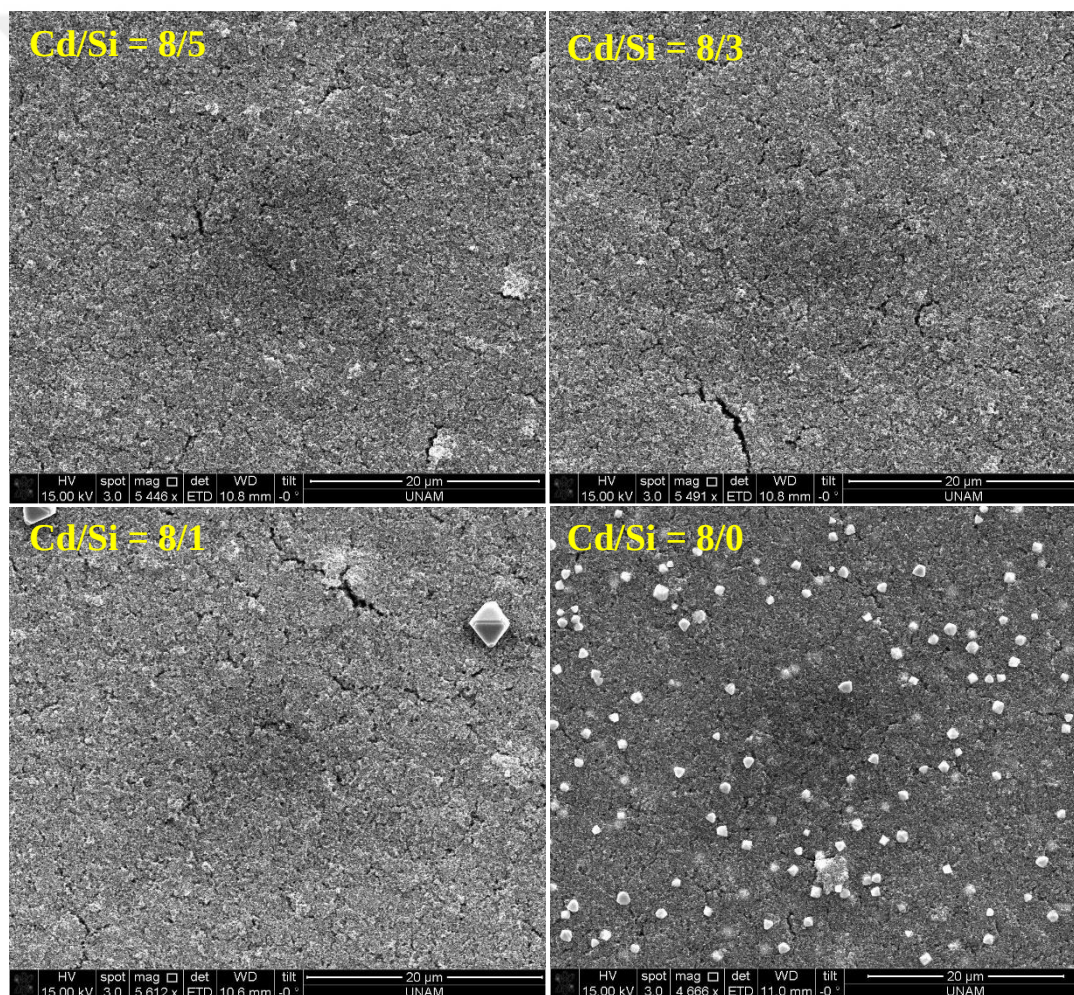


Figure 3.43. SEM images of the samples, prepared using different initial amount of silica, as shown in the images.

To sum up, more amount of silica is needed to infiltrate all solution into meso-P25 without any bulk CdO formation.

3.3 Synthesis of Mesoporous Transition Metal Oxide Thin Films

3.3.1 Synthesis of Mesoporous Iron Oxide Thin Films

Formation of lyotropic liquid crystalline mesophase is an important step for the synthesis of advanced functional materials. In Dag group's, the mesophase have been investigated using many different metal nitrate salts ($[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Cd}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$) [21] and non-ionic surfactants [22]. Here, the formation and stability of the mesophase using iron nitrate $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_3$ salts and $\text{C}_{12}\text{EO}_{10}$ have been investigated. Iron nitrate salt was dissolved in a solution containing CTAB, $\text{C}_{12}\text{EO}_{10}$ and EtOH or H_2O . The mesophase formation after spin coating, is observed that it is stable up to 90 °C. **Figure 3.44** shows a set of XRD patterns of a spin coated film, prepared using above MASA solution and upon ageing the films at different temperature and duration. The diffraction line at 2°, 2θ, shifts to higher angles with aging, that means a shrinkage of the mesophase. A leaching of CTAB from the mesophase (see **Figure 3.44** (b)) have been observed during aging: the line at around 3.5°, 2θ, corresponds to CTAB crystals.

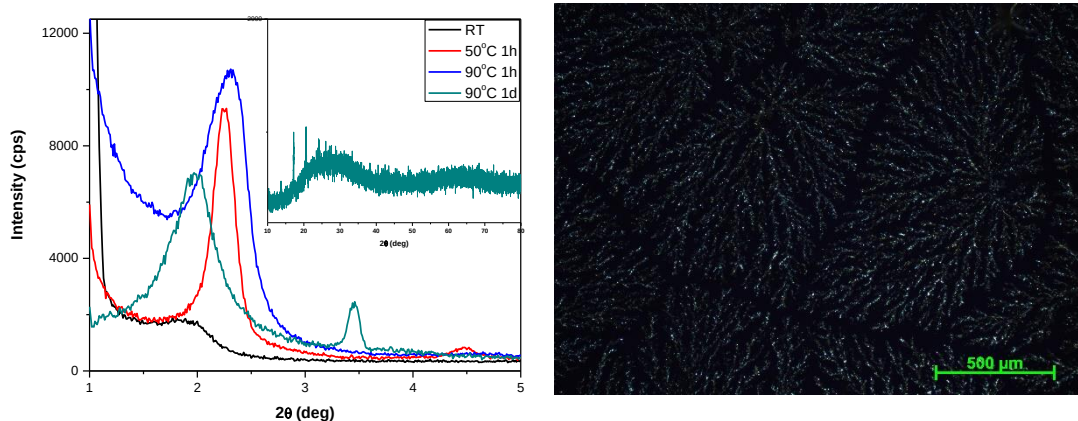


Figure 3.44. XRD pattern of a spin coated film, prepared using a MASA solution containing Fe(III), aged at different temperature and duration (as indicated in graphs, insets are wide angles after 2 days). POM image of the spin coated film, aged 3 weeks.

The mesophase containing Fe(III) salts, which undergoes slow hydrolysis and condensation reaction, was calcined at different temperatures (300, 400, and 500 °C) The XRD patterns of the samples, calcined at high temperatures, are shown in

Figure 3.45. At 300 °C, the broad diffraction lines were observed because of small and amorphous iron oxyhydroxy particles. The diffraction lines get sharper upon crystallization of Fe₂O₃. The XRD pattern overlap with JCP 01-089-0599 pattern of the crystalline Fe₂O₃ in the **Figure 3.45**.

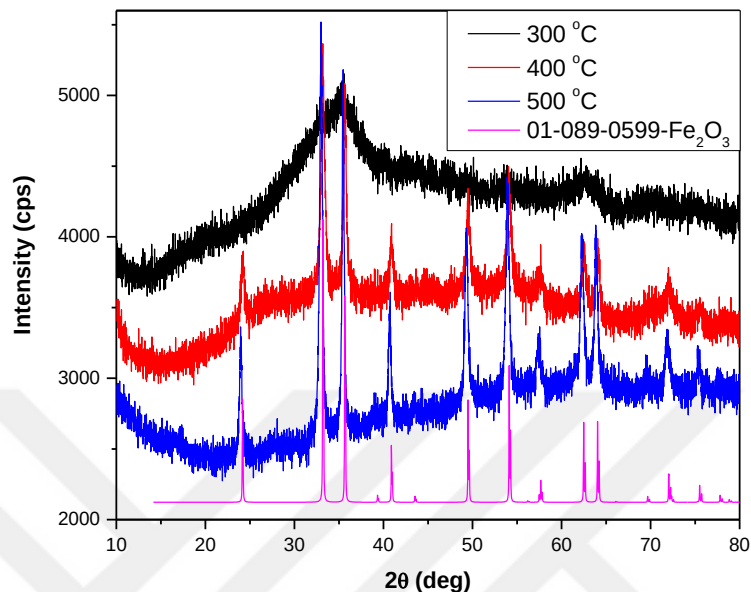


Figure 3.45. XRD patterns of a mesoporous Fe₂O₃, calcined at high temperature, as indicated in the inset.

The crystallinity of iron oxide nanoparticles was further investigated using TEM. **Figure 3.46** shows TEM images of iron oxides calcined at 300 and 400 °C. At 300 °C, the pores of iron oxides are visible and the pore walls are around 4 nm. At 400 °C, the pores get larger, due to growth of the iron oxides pore-walls. The trend in XRD patterns accord well with the TEM images.

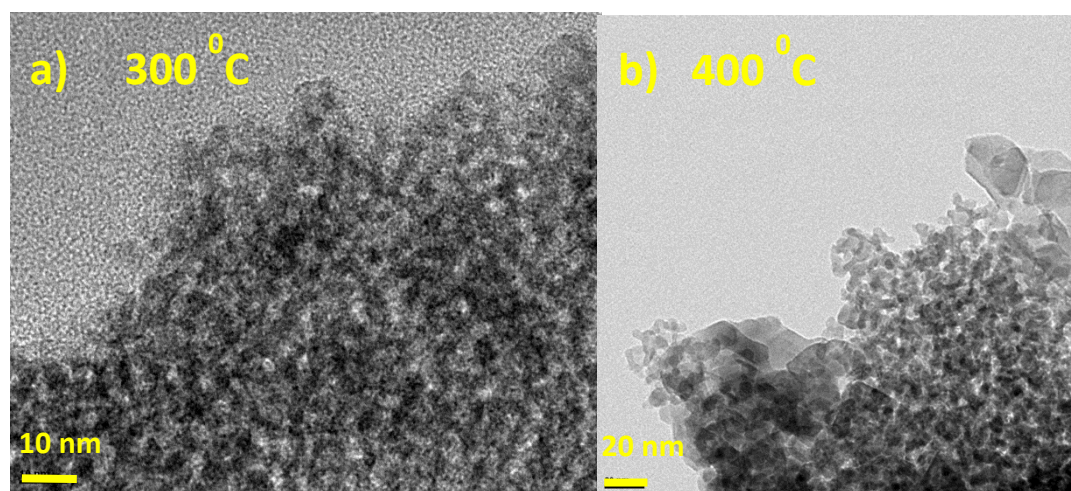


Figure 3.46. TEM images of iron oxides calcined at (a) 300 and (b) 400 °C.

The porosity of mesoporous iron oxide was investigated using N₂ sorption measurement. **Figure 3.47** shows that N₂ sorption isotherms and pore size distribution plots of mesoporous iron oxide at different calcination temperatures. The isotherms are type IV that is characteristic for mesoporous materials. The BET surface area of mesoporous iron oxides, calcined at 300 °C, is 142 m²/g and decrease down to 82 m²/g at 400 °C, to 34 m²/g at 500°C and the pore size of iron oxides, calcined at 300 °C, was around 3 nm. While the surface area decreases, the pore size increase (see **Figure 3.47**) with the heat treatment above 300 °C.

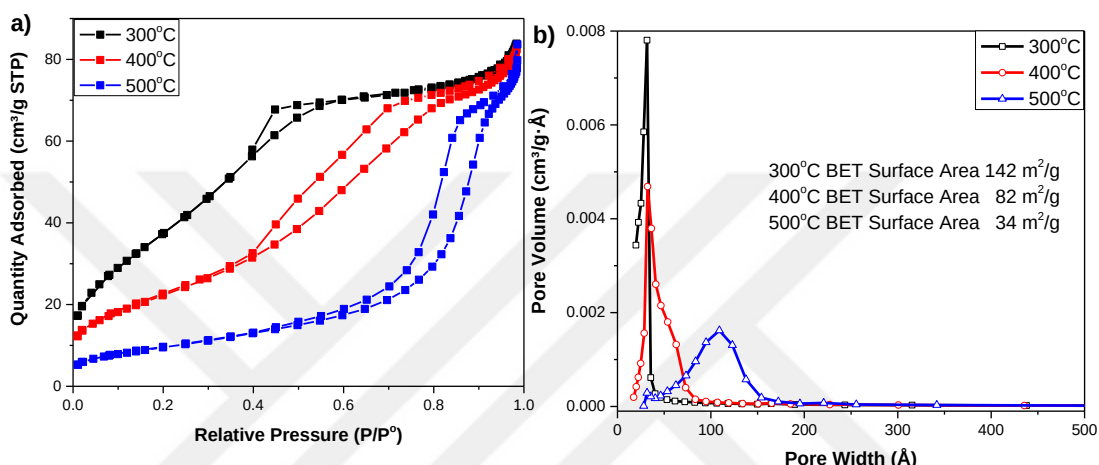


Figure 3.47. (a) Linear N₂ (77K) isotherms and (b) BJH pore size distribution plots of mesoporous iron oxide, calcined at different temperatures (as indicated in the insets).

The surface morphology of iron oxide films was investigated using SEM imaging technique, in **Figure 3.48**. It is found that the different calcination temperature only affects the size of iron oxide nanoparticles and the quality of thin films that decrease at higher temperature.

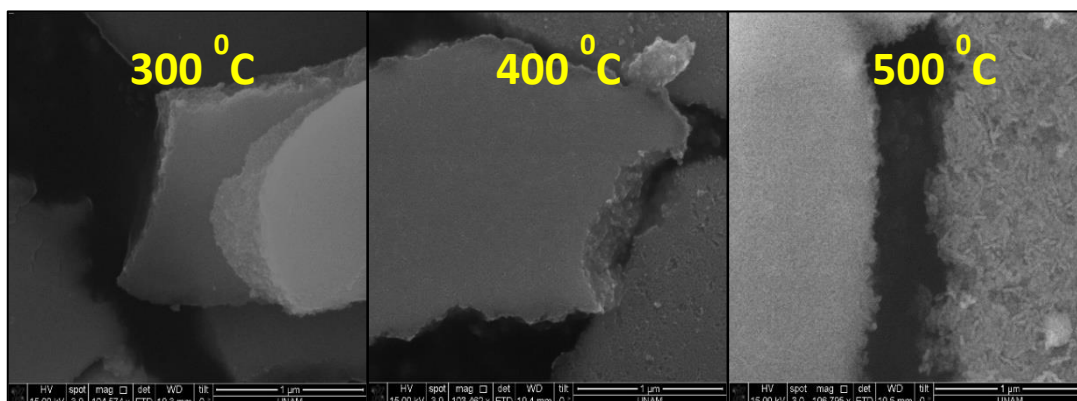


Figure 3.48. SEM images of iron oxide thin films, calcined at different temperatures, as shown in the images.

To sum up, transparent mesoporous iron oxide thin film has been successfully synthesized and the sample could be used in water splitting because of its suitable band gap for water oxidation.

3.3.2 Synthesis of Other Mesoporous Transition Metal Oxides Thin Films

Mesoporous iron oxides thin film has been synthesized starting from $[\text{Fe}(\text{H}_2\text{O})_6](\text{NO}_3)_3$ salts using MASA approach. Note also that Fe(III) ions are not stable in the MASA solution and undergo hydrolysis and condensation reactions to form iron oxyhydroxide nanoparticles in the solution phase. Also note that the mesophase behaviors of $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ with non-ionic surfactant systems have been previously studied [21]. The MASA method allows us to synthesize other transition metal oxides by changing starting transition metal precursors. Transition metal nitrate salts were chosen for each precursor because the mesophase of these salts are well-known and the nitrates can be easily decomposed in the calcination process. For each transition metal, a MASA solution was prepared using their metal nitrate precursors, two surfactants ($\text{C}_{12}\text{EO}_{10}$, CTAB) and a solvent (EtOH). The coating of these solutions results in thin films of LLC mesophase of the corresponding metal precursors and non-volatile species, and then the calcination process produces the corresponding mesoporous metal oxide thin films. **Figure 3.49** show starting clear MASA solutions and calcination products of Mn(II) (brownish powder), Co(II) (dark black powder), Ni(II) (black powder), Cu(II) (dark brownish powder), Zn(II) (white powder), from left to right, respectively. Each product has been investigated step by step.



Figure 3.49. Photograph of starting MASA solutions (top) and calcination products of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), from left to right, respectively.

XRD patterns of calcination products of (a) Zn(II), (b) Cu(II), (c) Ni (II), and (d) Co(II) at 400 °C are shown in **Figure 3.50** with a reference pattern of ZnO, CuO, NiO, and Co₃O₄, respectively. **Figure 3.51** shows Raman spectra of calcination products of Cu(II), Ni (II), and Co(II). Both XRD pattern and Raman spectrum display finger prints of hexagonal ZnO, CuO [78], NiO [79], Co₃O₄ [80] nanocrystals.

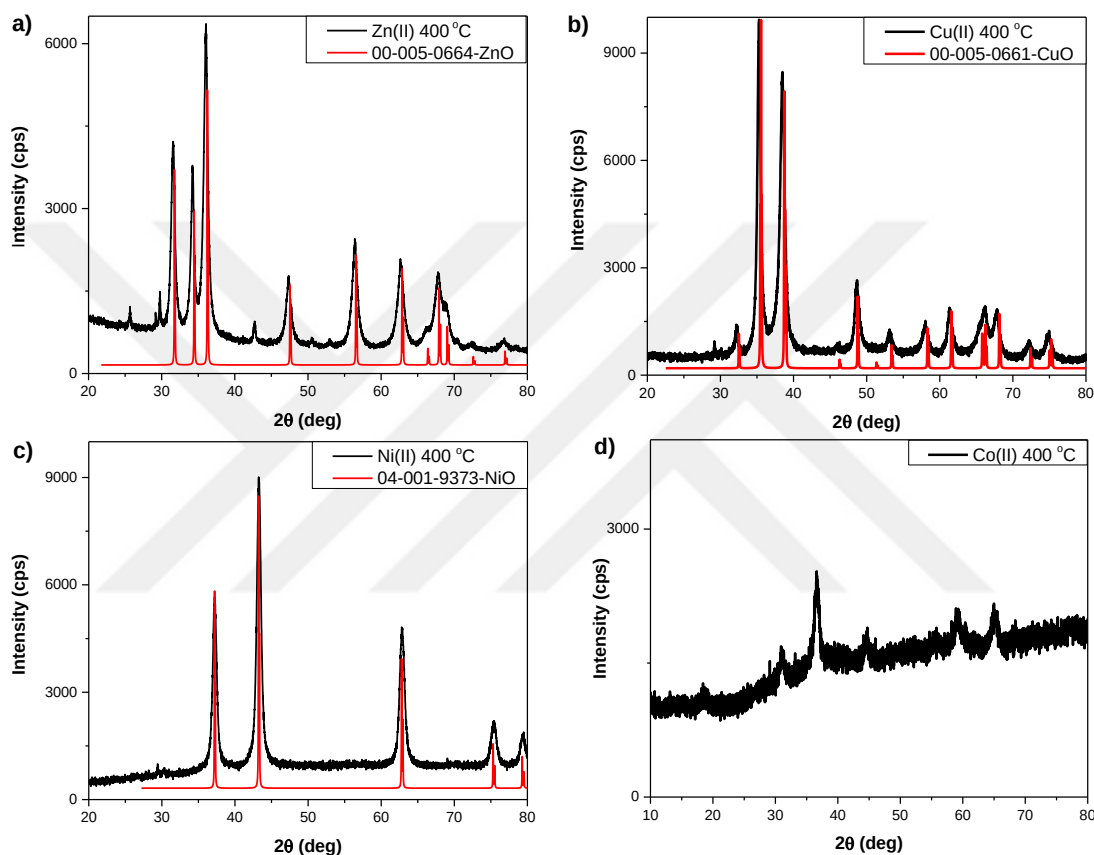


Figure 3.50. XRD patterns of calcination products at 400 °C of (a) Zn(II), (b) Cu(II), (c) Ni (II), and (d) Co(II) with their references.

The porosity and surface morphology of zinc oxide films were investigated using SEM imaging technique. Two different morphologies of zinc oxide nanoparticles are observed in **Figure 3.52** and other transition metal oxide thin films has a uniform morphology. High-resolution SEM image (see **Figure 3.52**) shows the mesoporous nature of the thin films.

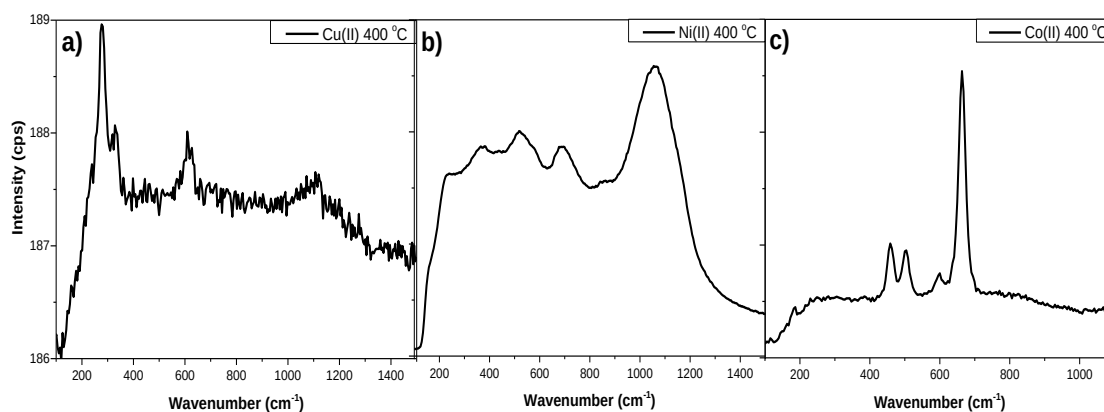


Figure 3.51. Raman spectra of calcination products at 400 °C of (a) CuO, (b) NiO, and (c) Co₃O₄.

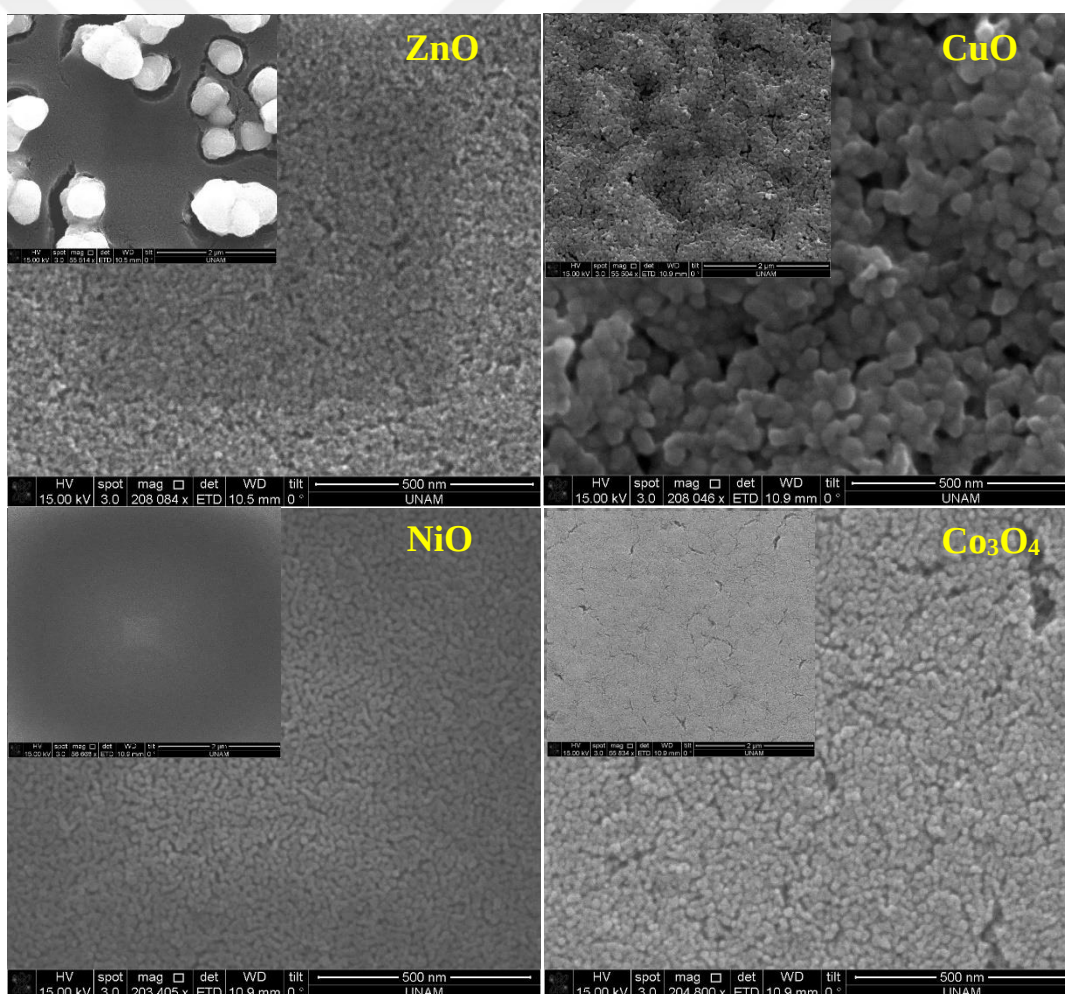


Figure 3.52. High resolution SEM images of mesoporous ZnO, CuO, NiO, and Co₃O₄ thin films, prepared using MASA method. The insets show large area SEM images.

The crystallinity of zinc oxide nanoparticles was further investigated using TEM. **Figure 3.53** shows a high resolution TEM images of ZnO nanoparticles. The ZnO is crystalline and its particle size is around 10 nm. To sum up, mesoporous zinc oxide nanoparticles has been synthesized but further analysis is needed to identify the two morphologies (film, nanoparticles).

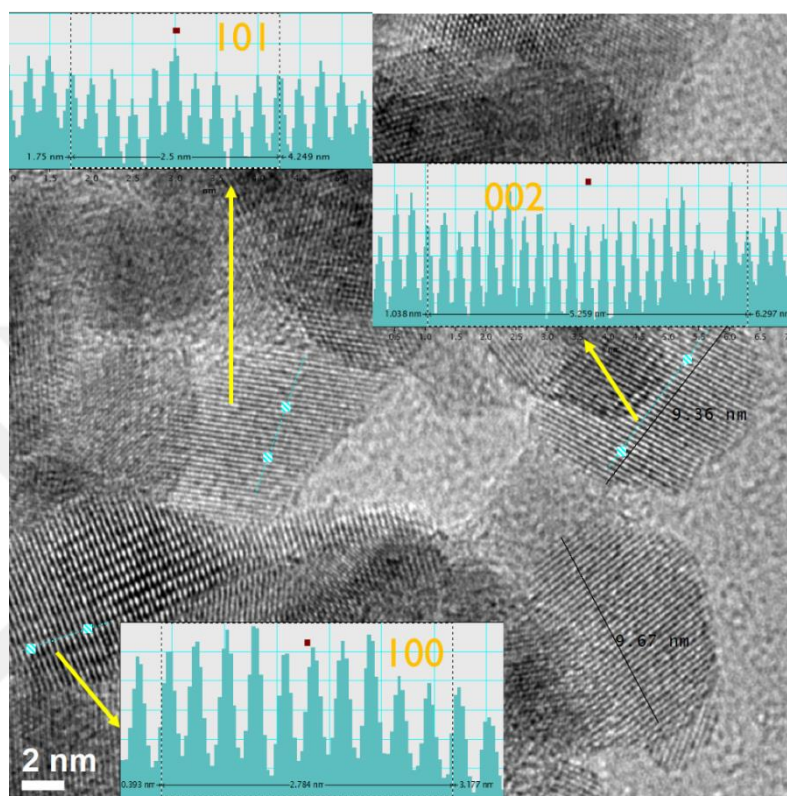


Figure 3.53. TEM images of mesoporous zinc oxide, calcined at 400 °C.

To sum up, our preliminary experiments show that the mesoporous thin films (Fe_2O_3 , Co_3O_4 , NiO , CuO , and ZnO) are nanocrystalline and high quality. Development of nanocrystalline mesoporous metal oxides could be beneficial for the developments of photoanodes and photocathodes for various applications and needs to be explored in the near future.

Chapter 4

Conclusion

In this thesis, CdSe sensitized TiO₂ photoanode thin films has been fabricated using molten salt assisted self-assembly (MASA) approach. In the first part of the thesis, effects of each synthesis parameters of mesoporous CdTiO₃ thin films on solar performance has been investigated. The thickness of the CdSe/TiO₂ thin film, coated at 1000 rpm, is found to be around 400 nm with power conversion efficiency of 0.5 % when the initially coated mesostructured films were calcined at 500 °C. If the thickness of the thin film could be increased 20 times, it might reach to a commercial limit of PCE (10%) and could be commercialized. However, in this synthesis (and also in many of the other literature methods) Se formation has been observed as a side product. The Se formation is found to be related to the amount of titania (especially surface hydroxides), oxygen and reaction temperature that could be controlled by changing the condition in the reaction chamber.

The infiltration and mesophase formation of the MASA ingredients in meso-P25 films have been investigated. The MASA solution, prepared using less EtOH amount, can be infiltrated homogenously throughout the meso-P25 films but it formed an insulating meso-CdO-SiO₂ layer upon calcination. This film layer is insulating, has no power conversion ability, also blocks the diffusion of the electrolyte into the pores of titania nanoparticles, and results a bad solar cell performance. Multiple coatings were tried to coat more without blocking layer formation. 4 times loading is possible with diluted MASA solution. The PCE of the efficient cell is about 2.2%, I_{sc} of 8 mA/cm², V_{oc} of 0.58 V and FF of 0.47. Reducing silica amount in the CdO-SiO₂ film caused formation of bulk cadmium oxide

crystals that are less reactive and the cells constructed from these anodes displayed the worst solar performances.

To demonstrate the applicability of the MASA process, mesoporous Fe_2O_3 thin films have also been synthesized using MASA approach. The pore walls of iron oxide are around 4-5 nm with a pore size of around 3 nm, if the films were calcined at 300 °C. After heat treatment, up to 500 °C, they become larger due to growth of the walls and the surface area of mesoporous iron oxides decreased from 142 to 34 m^2/g .

In addition to Fe_2O_3 , mesoporous Mn_2O_3 , Co_3O_4 , NiO , CuO , and ZnO have been synthesized successfully using MASA approach. However, further characterization is needed to understand the structural properties and thermal behavior of each products.

MASA approach is an effective and alternative method for synthesis of transition metal oxide thin films and can be easily modified for the synthesis of many transition metal oxides. The method is simple and cheap to fabricate porous thin films and is easy to scale up. Therefore, further studies are needed to explore the MASA approach for synthesis of the advanced functional materials.

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