

**MOLTEN SALT ASSISTED SELF-ASSEMBLY (MASA):
SYNTHESIS, CHARACTERIZATION and SOLAR CELL
PERFORMANCES OF MESOPOROUS SILICA-CdSe and
TITANIA-CdSe THIN FILMS**

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By

Ahmet Selim Han

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MOLTEN SALT ASSISTED SELF-ASSEMBLY (MASA): SYNTHESIS,
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By Ahmet Selim Han,

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We certify that we have read this thesis and have found that it is fully adequate, in
scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Ömer Dağ(Advisor)

Doç. Dr. Ayşen Yılmaz

Yrd. Doç. Dr. Ferdi Karadaş

Approved for the Graduate School of Engineering and Science:

Prof. Dr. Levent Onural
Director of the Graduate School

ABSTRACT
MOLTEN SALT ASSISTED SELF-ASSEMBLY (MASA):
SYNTHESIS, CHARACTERIZATION and SOLAR CELL
PERFORMANCES OF MESOPOROUS SILICA-CdSe and
TITANIA-CdSe THIN FILMS

Ahmet Selim Han

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A series of solutions of a salt ($[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$), a polymerizing agent ($\text{Si}(\text{OCH}_3)_4$, TMOS or $\text{Ti}(\text{OC}_4\text{H}_9)_4$, TTBO), two surfactants (cetyltrimethylammonium bromide, CTAB and 10-lauryl ether, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{EO}_{10}$) have been prepared and used as the molten salt assisted self-assembly precursors by only changing the Cd(II)/surfactant mole ratios for the preparation of mesoporous films. The thin films were prepared in two steps: in the first step, the titania particles (titania particles are typically 20-25 nm (P25)), dispersed in ethanol, have been spin coated over various substrates and annealed at 450°C and in the second step, the clear solutions given above (salt, CTAB, $\text{C}_{12}\text{E}_{10}$, silica or titania source and ethanol) were drop casted or spin coated over the titania (P25) films and calcined at 450°C.

Slow calcination of the films (with an increment of 1 °C/min), starting from the melting point of the salt (around 65°C) to 450 °C has produced the mesoporous silica/titania-cadmium oxide (CdO) thin films denoted as meso-CdO-SiO₂-P25 and meso-CdTiO₃-P25. The clear solutions were also used to make the thin films without P25 and denoted as meso-CdTiO₃.

The films were then exposed to a H₂Se atmosphere at 100°C for 30 min, and the samples were denoted as meso-CdSe-SiO₂-P25, meso-CdSe-TiO₂-P25 and meso-CdSe-TiO₂. The silica sample was further treated with a dilute HF solution (etching process) that results silica free meso-CdSe-P25. The characterization of the materials produced in this thesis was made by using XRD, FT-IR spectroscopy, UV-VIS, Raman, EDX and Solar Measurement techniques.

Silica samples have greater amount of CdSe than titania samples according to the Raman and EDX data which implies that silica samples are more reactive. Also in both silica and titania, the samples with a Cd/surfactant mole ratio of 6 have the greatest amount of CdSe.

Fluorine doped SnO₂ (FTO) has been used as a transparent conductive substrate for the preparation of the anode electrode for the solar measurements. According to the solar measurements, the silica and titania samples on P25 show greater efficiency than the titania samples without P25 and generally have similar efficiencies (the efficiency is the ratio of the electrical output of a solar cell to the incident energy in the form of sunlight). The most efficient samples are generally the samples prepared using Cd/surfactant mole ratios equal to 6 and 8. In order to increase the efficiency, 3rd row transition metal cations such as Mn(II), Fe(III),

Cu(II) and Co(II) are doped into above samples. The efficiency has been increased by 10 % in the silica and 30 % in the titania samples upon doping with 15% Mn(II). The solar cell characteristics of the electrodes were tested using the following parameters; by changing the Cd(II)/surfactant mole ratio (many samples were prepared and used for this purpose), by changing the aging of the electrolyte ($\text{Na}_2\text{S}/\text{S}_8$), by using multiple coating the MASA solution in the preparation stage of the electrodes, by doping the samples with various transition metal ions, and finally by modifying the surface of the electrode by coating with ZnS or CTAB. Each of these parameters has an effect on the cell performance. The effect of each parameter is monitored by measuring the I-V characteristics of the cells and found out that the best results were obtained from the electrodes made using 6 or 8 Cd/surfactant mole ratio in MASA system, freshly prepared $\text{Na}_2\text{S}/\text{S}_8$ electrolyte, coating of the MASA solution twice on electrode, doping Mn(II) cations with 0.15 Mn(II)/Cd(II) ratio and using CTAB for coating anode electrode.

Keywords: MASA process, mesoporous CdO-SiO_2 , mesoporous CdTiO_3 , mesoporous CdSe-TiO_2 , Quantum dot sensitized solar cells, thin films.

ÖZET

ERİYİK TUZ YARDIMLI KENDİLİĞİNDEN OLUŞMA (EYKO):

MEZOGÖZENEKLİ SiO_2 -CdSe ve TiO_2 -CdSe İNCE FİLMLERİNİN

SENTEZİ, KARAKTERİZASYONU VE GÜNEŞ PİLİ

PERFORMANSLARI

Ahmet Selim Han

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Bu çalışmada $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ tuzu, $\text{Si}(\text{OCH}_3)_4$, TMOS veya $\text{Ti}(\text{OC}_4\text{H}_9)_3$, TTBO polimerleştirici ajanları, iki yüzeyaktif madde (setiltrimetilamonyum bromür, CTAB ve 10-löril eter, $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, $\text{C}_{12}\text{EO}_{10}$); eriyik tuz yapılı kendiliğinden oluşma (EYKO) öncülleri olarak kullanıldı ve Cd(II)/yüzeyaktif mol oranları değiştirilerek ince mezogözenekli filmler hazırlandı. İnce filmler 2 basamakta hazırlandı: ilk adımda TiO_2 parçacıkları (P25) (parçacıklar tipik olarak 20-25 nm civarında), etanol içinde iyice homojenize edilip ardından uygun bir alttaş üzerine spin kaplama yöntemiyle kaplandı ve 450°C 'ye kadar ısıtıldı. İkinci basamakta ise yukarıda bahsedilen berrak çözelti (tuz, CTAB, $\text{C}_{12}\text{EO}_{10}$, SiO_2 veya TiO_2 kaynağı ve etanol) TiO_2 (P25) üzerine

damlatıldı ve tekrar spin kaplama yöntemiyle TiO₂ film üzerine homojen dağılması sağlandı ve tekrar 450 °C'ye ısıtıldı.

Filmin tuzun erime noktasından (65°C civarı) başlayarak 450 °C'ye kadar yavaşça ısıtılmasıyla (1 °C/dakika hızla) mezogözenekli SiO₂/TiO₂-kadmiyum oksit(CdO) ince filmleri oluşturuldu ve mezo-CdO-SiO₂-P25 ve mezo-CdTiO₃-P25 olarak adlandırıldı. Berrak çözelti kullanılarak ayrıca P25 kullanılmadan doğrudan cam üstüne spin kaplama yapılarak mezo-CdTiO₃ ince filmi de elde edildi.

Hazırlanan filmler daha sonra 100 °C'de 30 dakika boyunca H₂Se gazı ile tepkimeye sokuldu ve mezo-CdSe-SiO₂-P25, mezo-CdSe-TiO₂-P25 ve mezo-CdSe-TiO₂ filmleri elde edildi. SiO₂ örneği daha sonra seyreltik HF çözeltisiyle muamele edildi ve SiO₂'den arındırılmış mezo-CdSe-P25 elde edildi. Elde edilen ürünlerin karakterizasyonları XRD, FT-IR, UV-VIS ve Raman spektroskopileri, EDX ve Solar Ölçüm teknikleriyle yapıldı.

Raman ve EDX ölçümlerine göre, SiO₂ örneklerindeki CdSe miktarının TiO₂ örneklerinden daha fazla olduğu belirlendi ve bu sonuç ile SiO₂ örneklerinin daha reaktif olduğu tesbit edildi. Ayrıca hem SiO₂ hem TiO₂ örneklerinde CdSe miktarının en yüksek olduğu Cd/yüzeyaktif mol oranının 6 olduğu tesbit edildi.

Flor doplanmış kalay oksit (FTO) camı, güneş pili ölçümleri için kullanılan anot elektrotunun yapımında şeffaf ve iletken bir alttaş olarak kullanılmıştır. Güneş pili ölçümlerine göre, P25 üzerinde hazırlanan SiO₂ ve TiO₂ örneklerinin P25 kullanılmadan hazırlanan TiO₂ örneğine göre daha yüksek verim

gösterdiği ve P25 üzerinde sentezlenen bu iki örneğin verim değerlerinin birbirlerine yakın olduğu görüldü(güneş pilinde verim, güneş pilinin verdiği elektrik enerjisi çıktısının güneşten gelen enerjiye oranı olarak tanımlanır). En verimli örneklerin genel olarak 6 veya 8 Cd/yüzeyaktif mol oranına sahip örnekler olduğu belirlendi. Pil verimini arttırmak için Mn(II), Fe(III), Cu(II) ve Co(II) bazı 3d grubu geçiş metal katyonları dopant olarak kullanıldı. Pil veriminde Mn(II) eklenmiş SiO₂ örneklerinde 10%, TiO₂ örneklerinde 30% oranında artış gözlemlendi. Cd(II)/yüzeyaktif mol oranları değiştirilerek, elektrolitin (Na₂S/S₈) hazırlandıktan sonraki bekleme süresi değiştirilerek, film hazırlama esnasında EYKO çözeltisi birden fazla defa spin kaplama yapılarak, EYKO çözeltisine değişik metal katyonları farklı mol oranlarında ilave edilerek ve son olarak anot elektrodun üzeri ZnS veya CTAB gibi moleküllerle kaplanıp modifiye edilerek güneş pili ölçüm karakterizasyonları yapıldı. Yukarıda bahsedilen her bir parametrenin güneş pili performansını değiştirdiği görüldü. Her bir parametrenin güneş pili verimine etkisi I-V eğrisi ile tesbit edildi. Sonuç olarak, Na₂S/S₈ elektrolitinin yeni hazırlanmış olmasının, EYKO çözeltisini 2 defa kaplamanın, Mn(II) katyonunu dopant olarak seçmenin ve Mn(II)/Cd(II) mol oranını 0.15 olarak ayarlamanın ve anodu kaplamak için CTAB kullanmanın isabetli olduğu görüldü.

Anahtar sözcükler: EYKO prosesi, mezogözenekli CdO-SiO₂, mezogözenekli CdTiO₃, mezogözenekli CdSe-TiO₂, quantum nokta duyarlı güneş pilleri, ince filmler.

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Chapter 1:

Introduction

1.1. Mesoporous Structures

Mesoporous materials are the materials that have pores with a diameter between 2 and 50 nm. According to IUPAC notation, the diameters of the microporous materials are less than 2 nm and diameters of the macroporous materials are greater than 50 nm[1]. (see Figure 1)

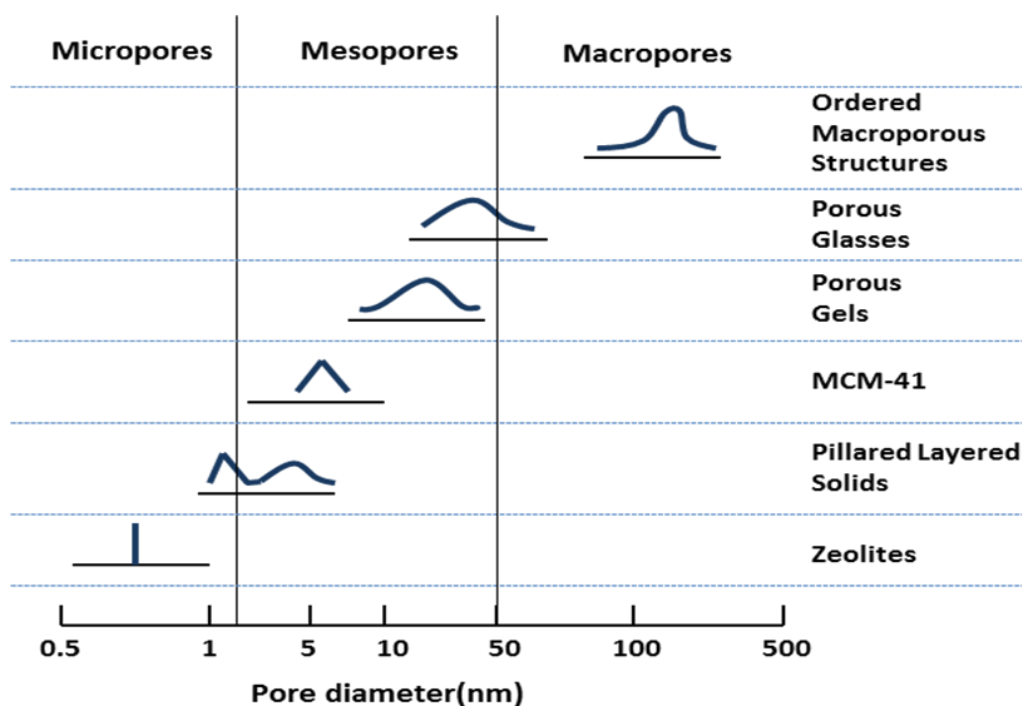


Figure 1. Schematic representation of pore size range of microporous, mesoporous and macroporous materials.

Presence of internal channels and cavities in the mesoporous materials provide high surface areas[2] and even large host molecules can diffuse inside

these cavities in mesoporous materials. Therefore, the mesoporous materials can be used in catalysis, gas sensing, sorption, photovoltaics and optics[3].

In 1992, the first periodic mesoporous material (PMM) was synthesized by Kresge *et. al.* from Mobil Oil Company[4]. Kresge and his co-workers used surfactants as a template and controlled the pore size of PMMs[4]. Until 1992, the main focus was on microporous materials, such as zeolites (the largest pore dimensions are around 10–12 Å[5]), metallophosphates[4][6] and mineral cacoenite (pore dimensions 14 Å)[7]. However, in Kresge's work the pore sizes of synthesized materials (M41S) were in the range between 16 and 100 Å depending on the type of surfactant used[8]. The first investigations of mesoporous materials focus on the synthesis of pure silica. The synthesis pathway is schematically shown in Figure 2.

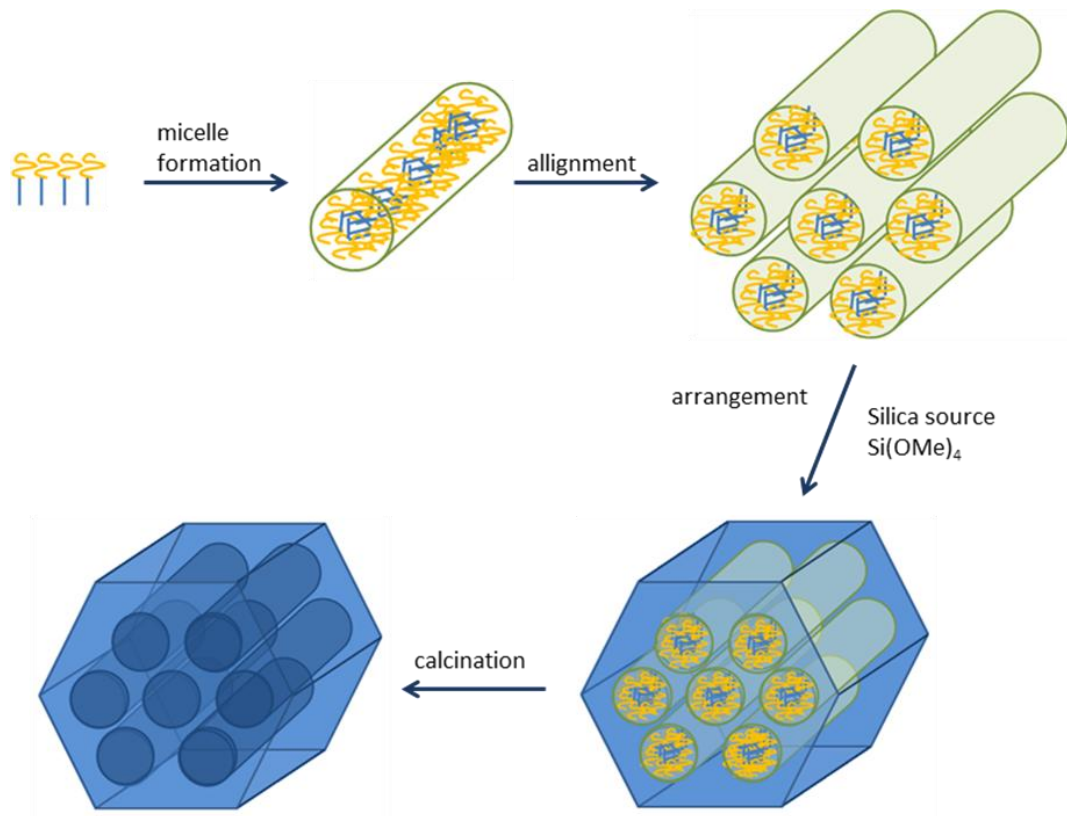


Figure 2. Synthesis pathway of MCM-41.

MCM-41 is the most common and most widely studied mesostructure in M41S family and it has hexagonally packed arrays of pores. Also cubic MCM-48 and lamellar MCM-50 are foremost structures, investigated in the M41S family, see Figure 3[9].

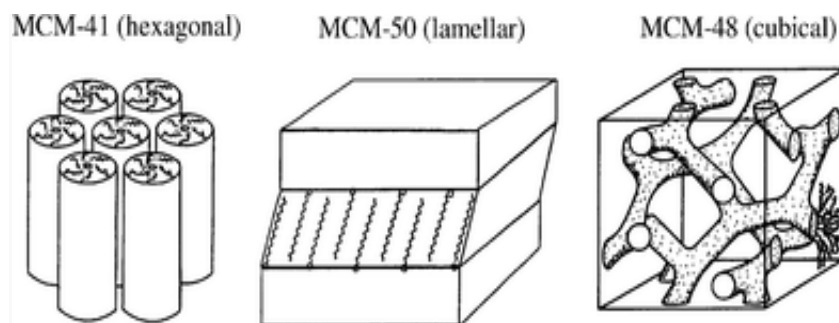


Figure 3. The structure of the mesoporous M41S family.¹

The formation of these mesostructures occurs via a liquid crystal templating mechanism, where the silica precursors polymerize in the hydrophilic domains of the surfactant micelles and/or preformed lyotropic liquid crystalline mesophase[10].

Furthermore, by changing the surfactant type or sizes, different mesoporous structures have been developed. Using cationic or nonionic surfactants in acidic solution SBA-n series were synthesized in 1996[11]. Stucky *et. al.* synthesized the SBA-15(Santa Barbara Amorphous) material, which is also mesoporous hexagonal silica and the pore size of this mesostructure is larger (46 to 300 Å) and the wall thickness is thicker (around 20 nm). In this assembly process, the poly(alkylene oxide) triblock copolymers, such as poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO) have been used as the structure directing agents[11].

¹ Reprinted from New J. Chem., vol. 32, A. Corma, M. Moliner, M. J. Díaz-Cabañas, P. Serna, B. Femenia, J. Primo, and H. García, “Biomimetic synthesis of microporous and mesoporous materials at room temperature and neutral pH, with application in electronics, controlled release of chemicals, and catalysis,” (2008), with permission from RSC.

1.2. Lyotropic Liquid Crystalline (LLC) Mesophases as Reaction Media for the Assembly of Mesoporous Materials

The LLC mesophase has been demonstrated to be a right media for the synthesis of mesoporous oriented thin film and monolith in 1995[12]. Attard, in his pioneering work, showed that the silica species can be polymerized in the hydrophilic domains of the LLC mesophase and named the assembly process, true liquid crystalline templating (TLCT)[12]. In this process, the surfactant is a nonionic oligo ethylene oxide (such as $C_{16}H_{33}(OCH_2CH_2)_8OH$, $C_{16}EO_{10}$) and silica precursor is tetramethylortosilicate ($Si(OCH_3)_4$, TMOS). A small amount of acid helps to polymerize the hydrolyzed TMOS. After polymerizing silica and removing surfactants by calcination, a 2D hexagonal mesoporous silica structure is obtained, see Figure 2.

In the LLC phase, concentration of the components is the most important variable on determining the structure of the mesophase. Changing the concentration and type of surfactants, many mesoporous materials such as meso-metals, meso-metal oxides have been synthesized using the TLCT method. Attard's group synthesized well characterized mesoporous tin[13], platinum[14][15] and their alloys[16]. Stucky's group synthesized different mesoporous metal oxides such as TiO_2 , WO_3 , SnO_2 , Nb_2O_5 , HfO_2 , $ZrTiO_4$ [17] and Stupp's group synthesized mesostructured ZnS, CdS and CdSe which are semiconductors[18][19].

In all these synthesis, the metal ion concentrations were kept very low because the LLC phase of water-surfactant is not stable at high metal salt concentrations. The metal ions are not actually one of the main components of the LLC phase. The solvent water and surfactant forms the LLC phase, where the metal salt is a host in the media; the amount of metal salt that can be incorporated into the water-surfactant LLC mesophase is limited. As a result of this fact, the mesostructured metals and metal oxides have only be formed of very fine, ultra-small powders and small quantities[12][13][17][18].

Dag's group introduced a new type of LLC mesophase that consists of a transition metal aqua complex salt, such as $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ and oligo(ethylene oxide) type surfactant[20][21][22]. The salt species behave like a solvent and form the LLC mesophase in this new LLC system[23].

It has been shown that the surfactant molecules form cubic or hexagonal mesostructures, in which the coordinated water molecules stabilize the mesophase through hydrogen bonding interactions with oxygen atoms of the ethylene oxide groups of the surfactant ($\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH}$, $\text{C}_{12}\text{EO}_{10}$, 10-lauryl ether), see Figure 4[20]. It has been shown that it is possible to prepare stable $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2\text{-C}_{12}\text{EO}_{10}$ LLC phase up to 70 w/w% (weight percent of salt)[20].

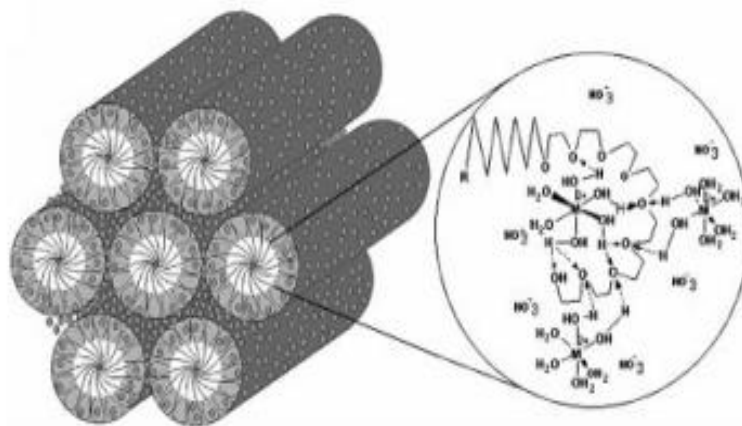


Figure 4. Schematic representation of an hexagonal LLC phase of a salt-surfactant system.²

Adding charged surfactants, such as sodium dodecyl sulphate (SDS) or cetyltrimethylammonium bromide (CTAB) to the salt-surfactant system makes possible to increase the amount of metal salts up to 8/1 metal salt/surfactant mole ratio[24]. The role of charged surfactants is to balance the charge of the metal salts at the surfactant molten salt interface that makes the LLC mesophase stable even at very high concentrations. As a result, Dag group's studies have been shown that the $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ salt is in the molten phase in the hydrophilic domains of the mesophase and assists to form LLC mesophase[23].

1.3. Molten Salt Assisted Self-Assembly (MASA) Process

The MASA process is a new self-assembly process, introduced by Dag's group in 2011[25]. In this assembly process, two surfactants, CTAB and $\text{C}_{12}\text{EO}_{10}$ with a 1:1 mole ratio, are used as structure directing agents. The solvents are

² Reprinted from Angew. Chemie Int. Ed. English, vol. 40, no. 20, pp. 3799–3803, Ö. Çelik and Ö. Dag, "A new lyotropic liquid-crystalline phase is formed from oligo- (ethylene oxide) surfactants and $\text{M}(\text{H}_2\text{O})^n$ ", (2001), with the permission from John Wiley and Sons.

ethanol (volatile) and the salt (non-volatile). There is also a polymerizing reagent that is either $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (titanium butoxide) [26] [27] or $\text{Si}(\text{OCH}_3)_4$ (TMOS)[25]. All these ingredients turn into metal titanates or metal oxide-silica at the end of the MASA process, see Figure 5[25]. The metal salt/surfactant mole ratios have been varied from 4 to 10 that corresponds to 4/7 and 10/7 metal salt/titania or silica (the $\text{Ti}(\text{IV})$ or $\text{Si}(\text{IV})/\text{C}_{12}\text{EO}_{10}$ mole ratio is kept constant as 7) [23][24][25][26][27].

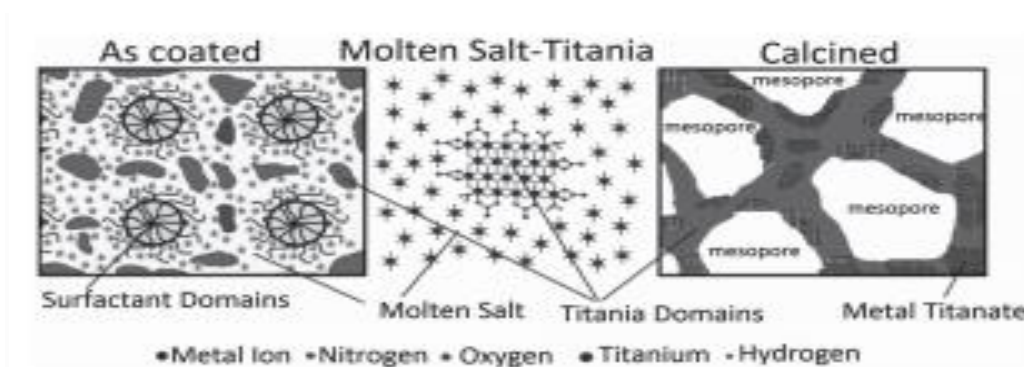


Figure 5. Schematic representation of the MASA process.³

The use of titanium butoxide as a precursor produces the mesoporous metal titanate thin films (such as CdTiO_3 , Zn_2TiO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, CoTiO_3 , MnTiO_3 etc.) [26] [27] and use of TMOS produces the mesoporous metal oxides and silica (such as CdO-SiO_2 or ZnO-SiO_2)[25]. It is also possible to synthesize mesoporous semiconductors such as CdS , CdSe , ZnS and ZnSe by reacting meso metal oxides

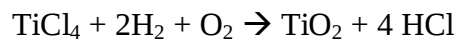
³ Reprinted from Chem. Mater., vol. 23, pp. 3062–3071, C. Karakaya, Y. Türker, C. Albayrak, and Ö. Dag, “Assembly of Molten Transition Metal Salt Å Surfactant in a Confined Space for the Synthesis of Mesoporous Metal Oxide-Rich Metal Oxide Å Silica Thin Films”(2011), with the permission from ACS.

with H₂S or H₂Se gases and these mesostructured semiconductors can be used in solar cells[26][28].

1.4. Sensitizing Mesoporous Materials with Using Titania Nanoparticles (P25)

In solar cells; a mesoporous film, prepared using nanoparticles of anatase phase of titania (TiO₂, the trade name is P25) has been the mostly used material in the literature[29][30][31][32]. P25 comprises of nanoparticles less than 25 nm sized. It has a high surface area (specific surface area is between 45 and 55 m²/g) that enables to bind or load enough sensitizer(dyes or quantum dots)[33][34] [35] [36]. The sensitizers are usually loaded from the solution phase into the calcined mesoporous titania.

P25 can be prepared using pure TiCl₄ liquid that is vaporized and mixed with air and hydrogen gas[35]. These gases react suddenly at temperatures between 1000 and 2400°C to form nanostructured titanium dioxides:



By regulating the process parameters, it is possible to obtain the P25 nanoparticles with different sizes[35][36].

The role of titania in solar cell system is to take electron(s) from excited sensitizer(s) and to transfer them to conducting glass (indium tin oxide, ITO or fluoride doped tin oxide, FTO). Titania is a wide band gap (3.2 eV)[37]

semiconductor and the energy level of conduction band of titania is suitable for accepting electrons from the excited sensitizers, see Figure 6.

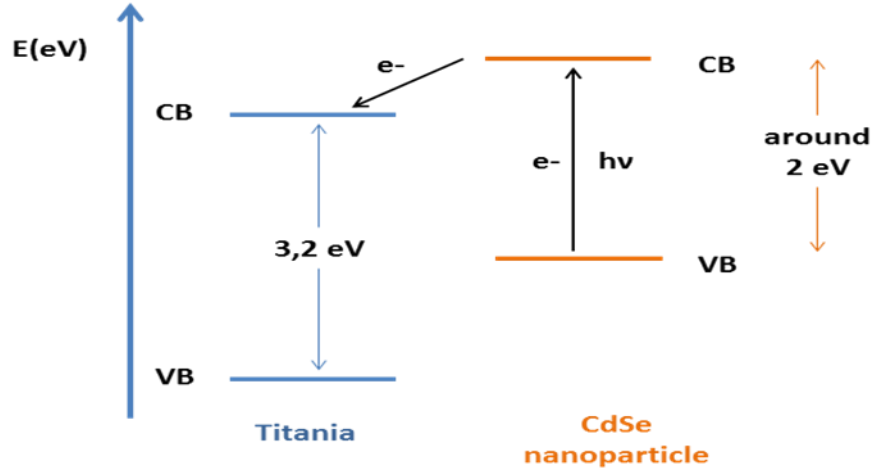


Figure 6. Schematic representation of the energy levels of titania and sensitizer and the photophysical process during solar action.

1.5. Sensitizing Mesoporous Materials

1.5.1. Sensitizing Using Dye Molecules

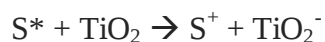
At the beginning of 1970s, it was discovered that organic dye molecules can be used in electrochemical cells[38]. The dye sensitized solar cell (DSSC) concept was introduced by Herman Tributsch in 1972[39]. The DSSCs are members of the thin-film solar cells[40]. In the DSSC system, the dye molecules absorb the sunlight and get excited and the excited molecule undergoes to an oxidation upon transferring its electron to the conduction band of mesoporous titania and then to conducting glass (FTO or ITO) electrode. Then these electrons are transferred to the cathode, Pt electrode, where the electrons are transferred to

the I_3^-/I^- redox couple in the electrolyte between the two electrodes in the photovoltaic cells. Then this redox couple supplies the electron of the oxidized dye to regenerate the dye and completes the circuit for the photo generation of the current in the cell, see the following reactions and Figure 6 and 7.

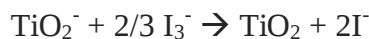
DSSC reactions;[41]



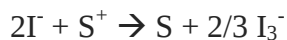
(dye absorbs solar light and electrons move from HOMO to LUMO)



(excited dye molecule transfers electron to titania)



(electron goes to cathode side and reduce I_3^- to I^-)



(I^- is oxidized to I_3^- with giving electron to HOMO orbital of dye)

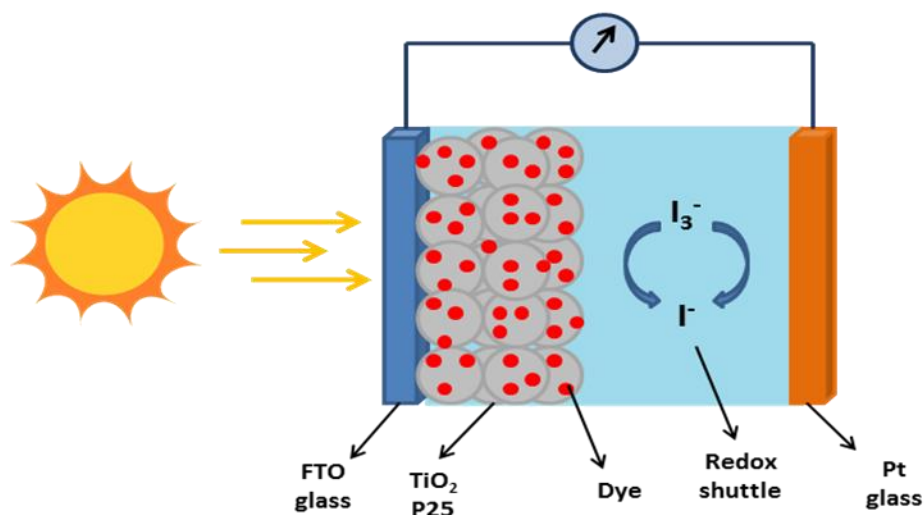


Figure 7. Schematic representation of a DSSC.

The investigations and experiments have shown that the polypyridyl complexes of ruthenium and osmium (see Figure 8)[42] have greater efficiency and long-term stability[43][44][45]. The maximum efficiencies of DSSCs are around 12-13%[43][45]. The goal in efficiency for DSSCs is to increase the efficiency to around 15 % for the commercialization of these cells.

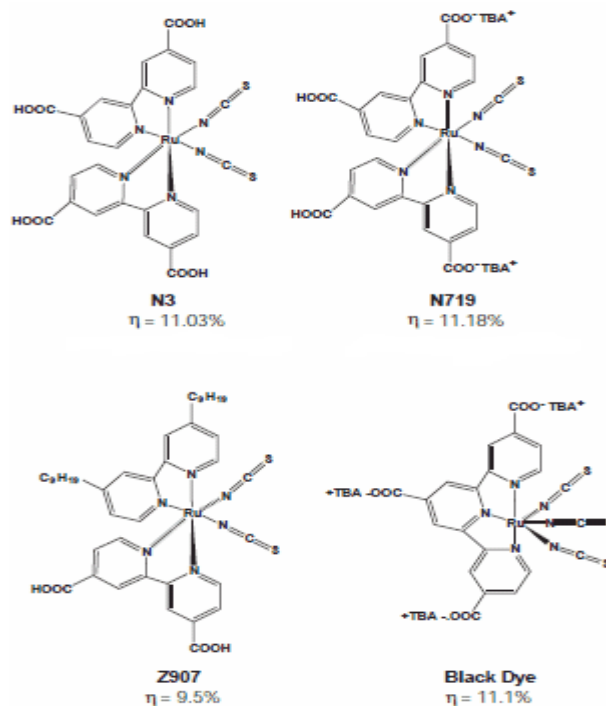


Figure 8. Structures of some of the most efficient dye molecules(cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)(N3), Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)(N719), cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II)(Z907), “black dye” (tris(cyanato)-2,2',2''-terpyridyl-4,4',4''-tricarboxylate)Ru(II)) for dye sensitized solar cells.

1.5.2. Sensitizing Mesoporous Titania Using Quantum Dots

Highly efficient and cheap solar cells were produced using Ru based dyes at the beginning of 90s and many researchers have contributed to the DSSCs until now. Another group of researchers show that quantum dots can be a good alternative to the dyes for the solar cells; because the optical and electrical properties of quantum dots are suitable for solar cells[46][47]. Semiconductor

quantum dots have narrow emission spectrum, broad excitation spectra, very high extinction coefficient. In addition to these, by changing the sizes of the QDs, physical and chemical properties can be changed. For instance, band gap energy is very important for solar process and it is possible to control band gap energy of the quantum dots by controlling their particle size, see Figure 9[48].

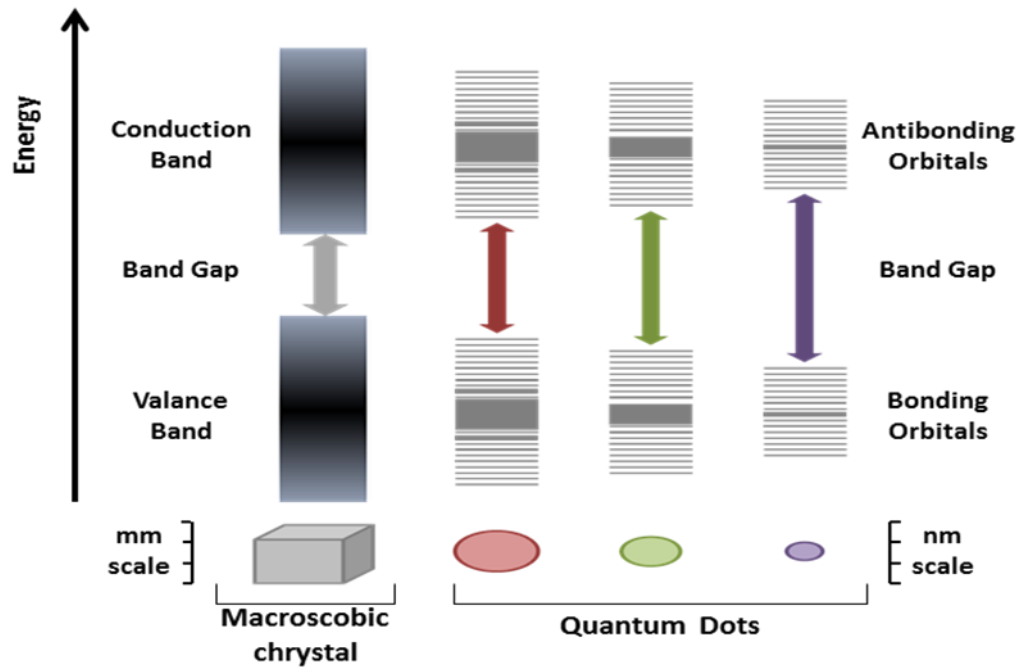
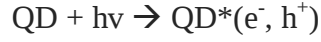


Figure 9. Changing of the band gap of QDs with respect to particle size.

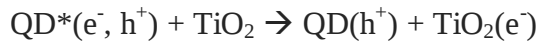
The operation of QDSCs is very similar to DSSCs. Firstly QDs absorb the sunlight and electrons move from the valence band of the QD to the conduction band of the QD. After that these electrons are transferred to conduction band of mesoporous titania and to conducting glass (FTO or ITO). Then electrons move to the cathode side of the electrochemical cell. In the cathode side, brass[48] or graphene and its derivatives especially RGO (reduced graphene oxide)-coated

FTO[49] is used and generally S_n^{2-}/S^{2-} redox couple is preferred as an electrolyte.[50]

QDSC reactions;



(QD absorbs solar light and electrons move from the VB to CB)



(excited QD transfers electron to the CB of titania)

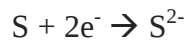


(electron goes to cathode side and reduce S_n^{2-} to S^{2-})

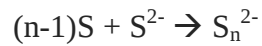


(S^{2-} is oxidized to S_n^{2-} by giving electron to the VB of QD)[51]

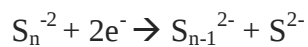
Actually reducing half reaction for sulfur is;



When the concentrated S and S^{2-} solution is prepared in water, sulfurs combine both other sulfurs and one of sulfide to form S_n^{2-} ;[52]



Therefore, the reduction half reaction of sulfur in water can be written as;[52]



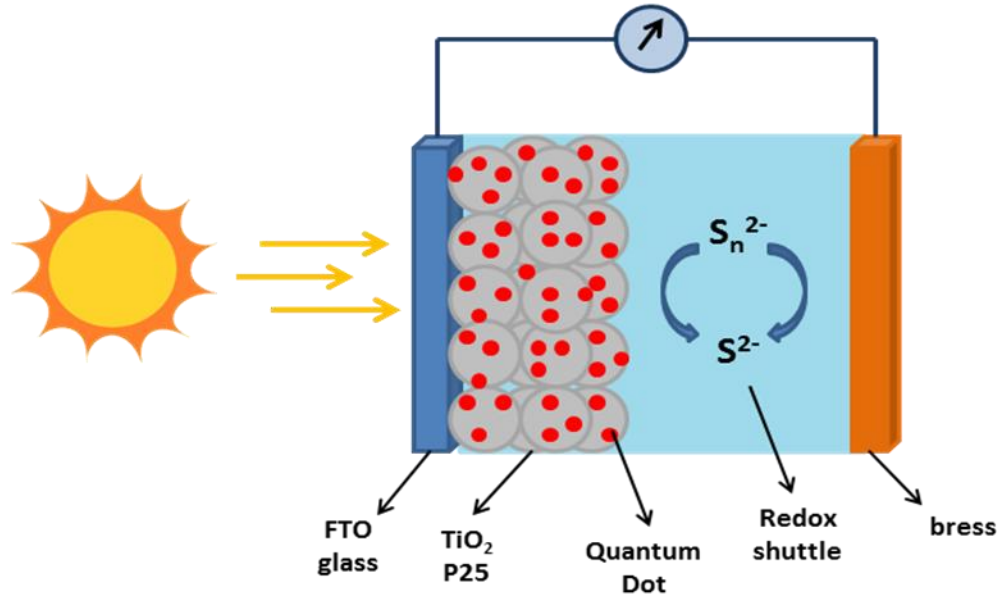


Figure 10. Schematic representation of a QDSC.

In recent years, cadmium chalcogenides QDs (CdS, CdSe, CdTe) have been more popular in QDSC research[53][54][55][56]. The band gaps of bulk CdS, CdSe and CdTe are 2.25, 1.73, 1.49 eV, respectively and these QDs, especially CdSe and CdTe, can absorb nearly all visible spectrum[57]. Most efficient examples of these cadmium chalcogenide QDSCs are around 5-6% [58][59][60]. Nowadays, QDSC efficiencies pass over 7% and the highest value for efficiency is 8.6%[61][62].

1.6. The CdSe-TiO₂ Solar Cells

If the energy of photon is equal to or greater than the band gap energy of the semiconductor; the photon can be absorbed by the semiconductor by exciting

an electron to the CB. The bulk band gap of CdSe is 1.74 eV, which means CdSe can absorb nearly all visible range[63].

A similar electrochemical/photochemical process takes place in the CdSe sensitized TiO_2 solar cells similar to dye sensitized solar cells (Route 2 in Figure 11 and route 4 in Figure 11). However, there are other paths for these electrons to flow in the cell, which reduce the solar efficiency of the cells. The excited electrons can be directly transferred to the electrolyte from the CB of CdSe (Route 5 in Figure 11) and/or from the CB of TiO_2 (P25) (route 6 in Figure 11) due to direct contact of the electrolyte solution and the electrodes in these electrochemical cells. To minimize this problem; a protecting layer is coated over the CdSe- TiO_2 anode electrode[59][64].

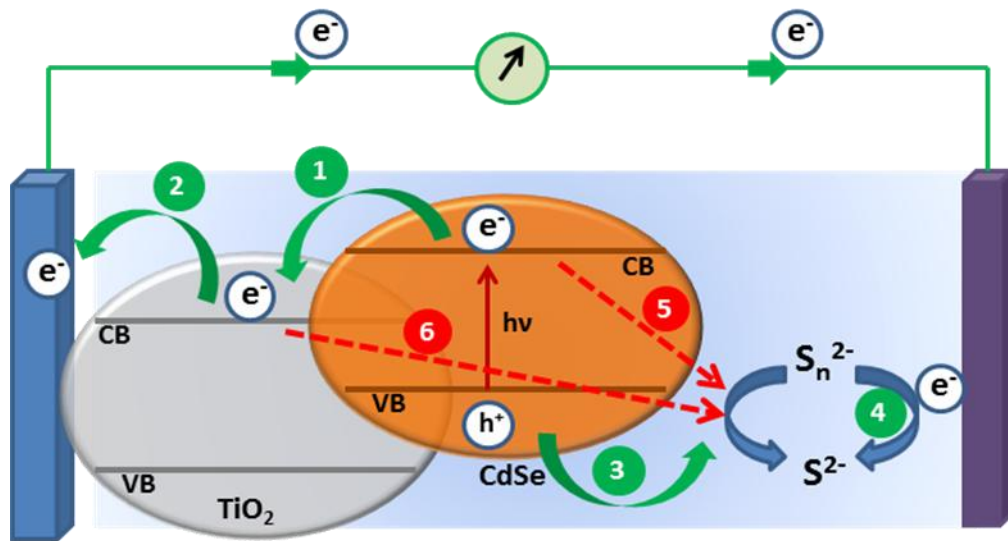


Figure 11. Schematic representation of the operation of the CdSe-TiO₂(P25) solar cell.

In the literature, the highest efficiencies of CdSe based QDSCs are around 5-6%[58][59][60]. Many groups, in the world, are trying to increase the efficiency

of these cells using different methods, such as doping different metal ions, mixing cadmium selenide with cadmium sulfide, and modifying anode side etc.[58]

1.7. Efficiency Measurements and Calculations of the Solar Cells

The efficiency for a solar cell can be described as the ratio of energy output from the cell to input energy, energy of the 1 sun exposed to the cell. Efficiency of a solar cell is the best parameter to compare the performance of one solar cell to another[65].

In order to get a comparable efficiency, some parameters must be kept constant. For instance the temperature and power of the light source have effects on the efficiency. Generally, the temperature is kept constant at 25 °C and the power of the light source, at 1 sun(1000 W/m²)[66][67].

The efficiency of a solar cell is equal to ratio of maximum power ($P_{\max}$) to input power (P_{in}).

$\eta = P_{\max}/P_{\text{in}}$, where $P_{\max}$ is calculated from the following equation,

$$P_{\max} = V_{\text{OC}} * I_{\text{SC}} * \text{FF},$$

$$P_{\text{in}} = 1000 \text{ W/m}^2 (\text{under 1 sun condition})$$

$$\text{FF} = (V_{\text{mp}} * I_{\text{mp}}) / (V_{\text{oc}} * I_{\text{sc}}) = \text{AreaA} / \text{AreaB} \text{ (in Figure 12) [68]}$$

FF(fill factor) is one of the most important parameter for efficiency. If any cell has high fill factor, it has a low equivalent series resistance and a high equivalent of shunt resistance, which means that produced current does not dissipate much inside the cell[69]. Typical commercial solar cell has a fill factor of 0.70 or greater and generally in thin film cells between 0.4 and 0.7[70].

The short circuit current (I_{SC}) is the current, when the solar cell is short circuited, where the voltage is equal to zero. The open circuit voltage (V_{OC}) is the voltage at zero current and it is the maximum voltage available from a solar cell. The V_{mp} and I_{mp} are the voltage and current values at maximum power (maximum $I \cdot V$ value), respectively [69] (see Figure 12).

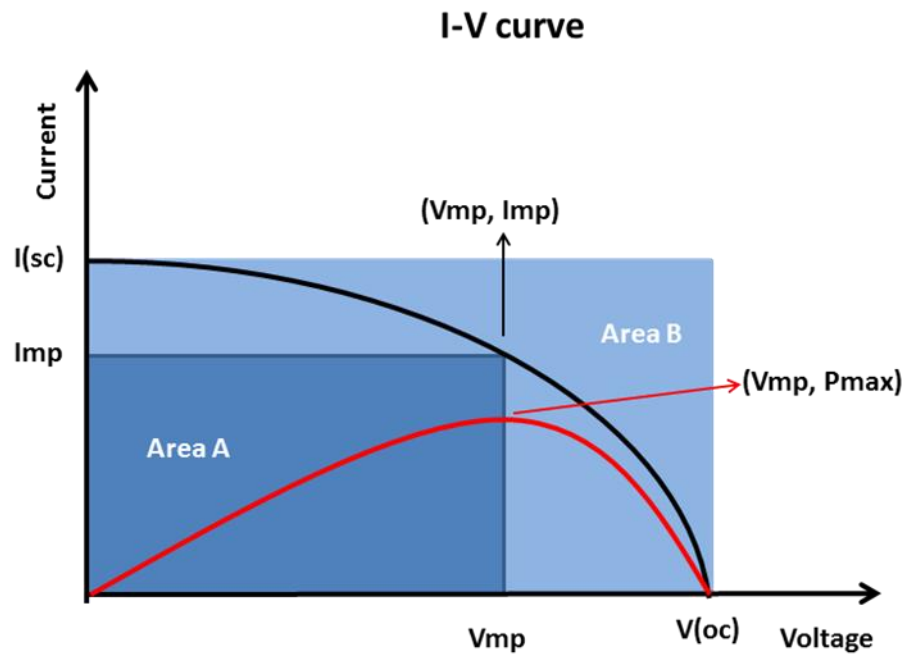


Figure 12. I-V curve of a solar cell.

Chapter 2:

Experimental

2.1. Materials

All chemicals and solvents were reagent grade and used as received without any further treatment.

The surfactants are 10-lauryl ether, $\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{10}\text{OH}$, (designated as $\text{C}_{12}\text{EO}_{10}$, $M_w = 626.9$ g/mol, Aldrich) and cetyltrimethylammonium bromide, $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$, (designated as CTAB, $M_w = 364.45$ g/mol, Aldrich). The used salts are: cadmium(II) nitrate tetrahydrate ($[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ 99%, Fluka), zinc(II) nitrate hexahydrate ($[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ 98%, Aldrich), copper(II) nitrate pentahydrate ($[\text{Cu}(\text{H}_2\text{O})_5](\text{NO}_3)_2$, Aldrich), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%, Aldrich), cobalt(II) nitrate hexahydrate ($[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$, 98%, Aldrich), manganese(II) nitrate tetrahydrate ($[\text{Mn}(\text{H}_2\text{O})_4](\text{NO}_3)_2$, 98%, Aldrich), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98%, Aldrich). The other compounds are: Hydrogen selenide (H_2Se , 99.99%, Air Products), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%, Merck), hydrochloric acid (HCl , %37, Reidel-de Haën), hydrofluoric acid (HF , 40-45%, Aldrich), nitric acid (HNO_3 , %65, Reidel-de Haën), titanium tetrabutoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, %98, Aldrich), tetramethylorthosilicate (TMOS, %99, Aldrich), polyethylenimine, branched (designated as PEI, $MW = 25000$ g/mol) and sulfur (S_8 , 99.5%, Aldrich).

2.2. Coating of FTO with Protecting Layer

Fluorine doped tin dioxide (FTO) coated glass was used for the deposition of anode that was first coated with a thin layer of bulk titania. Firstly, some part of the FTO glass is isolated by a scotch tape. Then, the FTO glass is spin coated with a solution of 5 ml ethanol and 0.25 g of $\text{Ti}(\text{BuO})_4$ and 0.5 g nitric acid at 2000 rpm and heated at 450 °C for 15 min.

2.3. Synthesis of Mesoporous Cadmium Titanate Thin Films (meso- CdTiO_3)

Dissolve 0.500 g $\text{C}_{12}\text{EO}_{10}$ and 0.291 g CTAB in 5 ml ethanol. Then add 1.970 g (for 8:1 salt: surfactant ratio) $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ and stir the solution for 5 min. Add 0.50 g HNO_3 and then 1.970 g $\text{Ti}(\text{OBu})_4$ to the above solution and stir the solution for another 5 min. Locate the glass or FTO coated glass over the spin coater and put an above solution as drops and spin at 1000 rpm for 30 seconds. Immediately after spin coating, place the film into an oven at 65 °C and calcine the sample up to 450°C with a 1°/min increments. The same procedure was employed for the other composition by only changing the cadmium nitrate amounts, see Table 1.

2.4. Preparation of Mesoporous Titania(P25) Films (meso- TiO_2)

1.5 g P25 (titania, Aldrich grade) was dispersed into 5 ml ethanol and stirred and sonicated for 30 min and then 0.25 ml of $\text{Ti}(\text{BuO})_4$ was dropped into

the dispersion and stirred for 5 minutes. The dispersion is spread over glass or FTO coated glass by using either a spin coater or doctor-blade method. Then the films were calcined at 450°C for 1 hour, denoted as meso-TiO₂.

2.5. Synthesis of Mesoporous Cadmium Titanate-Titania Films (meso-CdTiO₃-TiO₂)

Dissolve 0.500 g C₁₂EO₁₀ and 0.291 g CTAB in 5 ml ethanol. Then add 1.970 g (for 8:1 salt: surfactant ratio) [Cd(H₂O)₄](NO₃)₂ and stir the solution for 5 min. Add 0.5 g HNO₃ and 1.90 g Ti(OBu)₄ to the above solution and stir the solution again for another 5 min. Locate the meso-TiO₂ film over the spin coater and put an above solution as drops (make sure the solution really soaks into the film) and spin at 1000 rpm for 30 seconds. Immediately after spin coating, place the film into an oven at 65°C and heat the sample up to 450°C with a 1°/min increments. The same procedure was employed for the other composition by only changing the cadmium nitrate amounts, see Table 1.

2.6. Synthesis of Mesoporous Cadmium Oxide-Silica-Titania Films (meso-CdO-SiO₂-TiO₂)

Dissolve 0.500 g C₁₂EO₁₀ and 0.291 g CTAB in 5 ml ethanol. Then add 1.970 g (for 8:1 salt: surfactant ratio) [Cd(H₂O)₄](NO₃)₂ and stir the solution 5 min. Add 0.85 g TMOS and 0.05 g HNO₃ to the above solution and stir the solution for 5 min again. Locate the meso-TiO₂ film over the spin coater and put an above solution as drops (make sure the solution really soaks into the film) and spin at 1000 rpm for 30 seconds. Immediately after spin coating, place the film

into an oven at 65°C and heat the sample up to 450°C with a 1°/min increments. The same procedure was employed for the other composition by only changing the cadmium nitrate amounts, see Table 1.

2.7. Synthesis of Mesoporous Cadmium Selenide-Titania Thin Films(meso-CdSe-TiO₂), Cadmium Selenide-Silica-Titania Films (meso-CdSe-SiO₂-TiO₂) and Cadmium Selenide-Titania-Titania Films(meso-CdSe-TiO₂-TiO₂)

Insert the calcined meso-CdTiO₃, meso-CdO-SiO₂-TiO₂ or meso-CdTiO₃-TiO₂ into vacuum chamber designed for an H₂Se reaction (see Figure 13) and evacuate the chamber for a few minutes before exposing the sample to an H₂Se atmosphere. Put about 100 torrs of H₂Se and carry the reaction for 30 min at 100°C. Evacuate the chamber by pumping the unreacted H₂Se and water (side product) to the atmosphere through the fume hood and remove the films for analysis and further treatments.

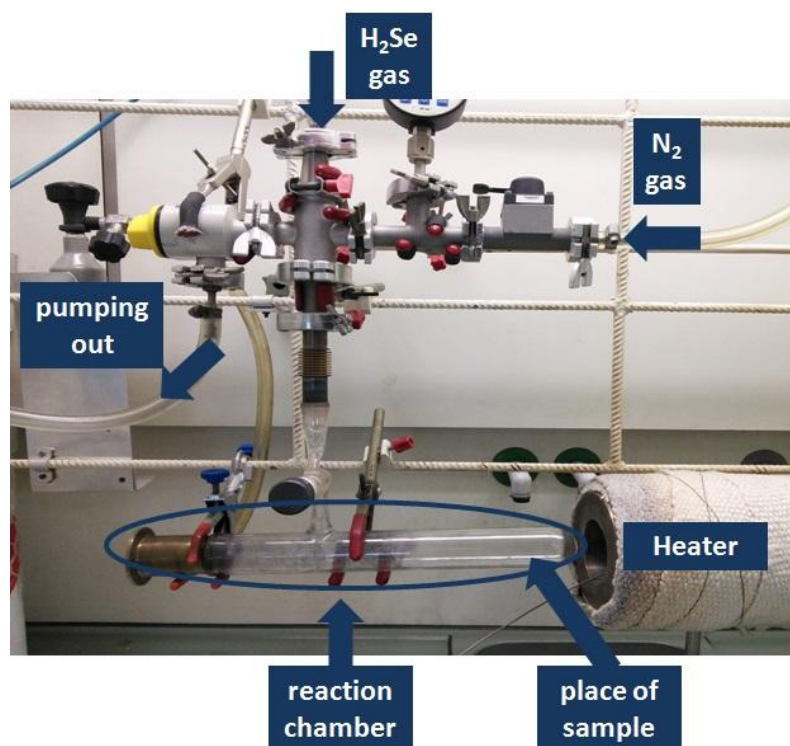


Figure 13. Experimental setup for H₂Se reaction.

2.8. Removing Silica from the meso-CdSe-SiO₂-TiO₂ Films

Gently wash the above films (section 2.7) by using few drops of 4% HF acid over the films (this step is critical to keep the film over the substrate as one piece). Then, immediately wash with a large amount of ethanol and dry using air-dryer.

2.9. Synthesis of Mesoporous Cadmium Metal Titanate Thin Films (meso- $\text{Cd}_x\text{M}_{1-x}\text{TiO}_3$), Cadmium oxide-Metal Oxide-Silica-Titania Films (meso- $\text{CdO-MO-SiO}_2\text{-TiO}_2$) or Cadmium Metal Titanate-Titania Films (meso- $\text{Cd}_x\text{M}_{1-x}\text{TiO}_3\text{-TiO}_2$) and Their H_2Se Reactions

The procedures in section 2.3, 2.5 and 2.6 were employed by adding dopant metal source ($\text{Cu}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ salts) together with the cadmium nitrate salt. The dopant metal content was varied between 0.01 and 0.15 Metal/Cd mole ratio (Table 2). The other synthesis steps for the samples are the same as in the sections 2.3, 2.5 and 2.6 respectively. Then the films were exposed to H_2Se gas as in section 2.7.

2.10. Preparation of the Electrolyte Solution and Counter Electrode.

Prepare the electrolyte solution containing 2 M $\text{Na}_2\text{S}\cdot 10\text{H}_2\text{O}$ and 2 M S_8 in 10 ml water. The counter electrode was prepared by etching brass with 1 M HCl for 5 min at 70°C and reacted with 0.10 M $\text{Na}_2\text{S}\cdot 10\text{H}_2\text{O}$ solution.

2.11. Coating the Anode Electrode with Passivation Layers

2.11.1. Coating with CTAB

40 mL 0.1 M CTAB solution was prepared with ethanol (20 mL) and water (20 mL). The CdSe-TiO_2 films are immersed into the CTAB solution and kept 20 seconds in the solution. After washing the film with ethanol, this dipping process was repeated twice and then dried in an oven at 80°C to remove ethanol.

2.11.2. Coating with Zinc Sulfide

40 mL 0.1 M $\text{Zn}(\text{NO}_3)_2$ solution and 40 mL 0.1 M Na_2S solution were prepared. The solvents were ethanol (20 mL) and water (20 mL). The CdSe-TiO_2 films are immersed into the Zn^{2+} solution at first and kept for 20 seconds in this solution. Then the films are washed with ethanol. Then these films are immersed into the S^{2-} solution and kept for 20 seconds in this solution (ZnS forms). After washing with ethanol, this process is repeated 2 more times to ensure enough coverage of the empty titania and CdSe surfaces, and finally dried in an oven at 80°C to remove ethanol.

2.11.3. Coating with branched-Polyethyleneimine

40 mL 0.1 M branched-polyethyleneimine (PEI) solution was prepared in ethanol. The CdSe-TiO_2 films are immersed into the PEI solution and kept for 5 to 10 minutes in this solution. The waiting time is greater than CTAB and ZnS because PEI's diffusion is slower. After washing with ethanol, this process was not repeated any more -because the waiting time was long enough- and after all the films are dried in oven at 80°C to remove ethanol.

sample code	Cd/silica or titania mole ratio	Cd/surf actant mole ratio	The amounts of chemicals(g)						
			$[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$	$\text{C}_{12}\text{EO}_{10}$	CTAB	TMOS	$\text{Ti}(\text{OBu})_4$	HNO_3	$\text{C}_2\text{H}_5\text{OH}$
si4	0.57	4	0.99	0.50	0.29	0.85	-	0.05	5.00
si6	0.86	6	1.48	0.50	0.29	0.85	-	0.05	5.00
si8	1.14	8	1.97	0.50	0.29	0.85	-	0.05	5.00
si10	1.43	10	2.47	0.50	0.29	0.85	-	0.05	5.00
ti4	0.57	4	0.99	0.50	0.29	-	1.90	0.50	5.00
ti6	0.86	6	1.48	0.50	0.29	-	1.90	0.50	5.00
ti8	1.14	8	1.97	0.50	0.29	-	1.90	0.50	5.00
ti10	1.43	10	2.47	0.50	0.29	-	1.90	0.50	5.00

Table 1. The amounts of chemicals used in the preparation of meso-silica-CdO and meso-CdTiO₃.

Metal/Cd mole ratio	The amounts of chemicals(g)				
	$[\text{Cu}(\text{H}_2\text{O})_5](\text{NO}_3)_2$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	$[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	$[\text{Mn}(\text{H}_2\text{O})_2](\text{NO}_3)_2$
0.01	0.018	0.026	0.019	0.019	0.014
0.05	0.09	0.13	0.09	0.10	0.07
0.10	0.18	0.26	0.19	0.19	0.14
0.15	0.27	0.39	0.28	0.29	0.21

Table 2. The amounts of extra metal sources(metal salts). All of these salts are added to si8 or ti8 systems (see Table 1).

Chapter 3:

Instrumental

3.1. Raman Spectra

The Raman spectra were obtained by using LabRam model confocal Raman microscope with a 300 mm confocal length. The spectrometer is equipped with HeNe laser operated at 20 mW, polarized 500:1 with a wavelength of 632.814 nm and a diode-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 collected signal was transmitted via a fiber optic cable into a spectrometer with 600 or 1800 g/mm gratings. The spectra was collected by manually placing the probe tip on the desired point of the sample over the glass, FTO glass or silicon wafer. Changes in Raman spectra are followed using a timer.

3.2. Solar Simulator and I-V curves

Solar performance measurements were made by using an AM 1.5 solar Simulator equipped with a 300 W xenon lamp (Model no. 81172, Oriel). The light intensity was set to 1000 W/m^2 by using a reference Si photodiode. I-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent using a Keithley model 2400 digital source meter.

3.3. X-Ray Diffraction (XRD) Patterns

The XRD patterns were collected by using Rigaku Miniflex diffractometer. The source was high power Cu-K α operates at 30 kV/15 mA and generates x-rays with a wavelength of 1.54054 Å filtered using a Ni filter. The detector was a Scintillator NaI(Tl) detector with a Be window. The samples were prepared on glass by spin coating. The measurements were made at small angles between 1° and 5° 2 θ range with a 1 °/min scan rate and at high angles, between 20° and 80°, 2 θ , range with a 5 °/min scan rate.

3.4. FTIR Spectra

The FT-IR (Fourier Transform-Infrared) spectra were collected using a Bruker Tensor 27 model FTIR spectrometer. The detector was a Digi Tech TM DLATGS with a resolution of 4.0 cm⁻¹ in the 400-4000 cm⁻¹ range and scan number was 128. For FTIR measurements, samples were prepared on IR transparent silicon wafers or pressed as a KBr pallets.

3.5. UV-Vis Absorption Spectra

The UV-Vis absorption spectra were obtained by using a Varian Carry 5 double beam spectrophotometer with a 600 nm/min speed and 0.2 nm resolution over a wavelength range from 200 nm to 800 nm. Measurements were collected on absorbance mode. Samples were spin coated on quartz for the measurements.

3.6. SEM Imaging and EDX Analysis

The SEM (Scanning Electron Microscopy) images were obtained using Zeiss EVO-40, operated at 20 kV equipped with a Bruker AXS XFlash EDX (Energy Dispersive X-ray Spectroscopy) detector 4010. Samples were prepared on silicon wafers and these wafers were attached to the aluminum sample holders using conducting carbon adhesive tabs.

Chapter 4:

Results and Discussion

The aim of the thesis is to synthesize anode materials for a solar cell using the MASA method. 3 different anode electrodes were prepared and 2 of them were investigated in detail. These are meso-CdSe-SiO₂-TiO₂ and meso-CdSe-TiO₂-TiO₂ films. The following abbreviations, si# and ti#, were used throughout the thesis. For instance, si6 means that the sample is meso-CdSe-SiO₂-TiO₂ and Cd/surfactant mole ratio is 6 and similarly ti8 means the sample is meso-CdSe-TiO₂-TiO₂ and Cd/surfactant mole ratio is 8.

4.1. Preparation of the Anode Electrode

The molten-salt assisted self-assembly (MASA) approach has been used for the preparation of the anode electrodes. The electrode materials have been characterized using FT-IR, UV-Vis absorption, Raman spectroscopy, SEM-EDX and X-ray diffraction (XRD) techniques. The MASA solution includes salt (Cd(NO₃)₂), surfactants (C₁₂EO₁₀ and CTAB), acid (HNO₃), a polymerizing precursor (TMOS or Ti(OBu)₄), and ethanol (solvent). There are two types of MASA solutions. Both solutions contain two surfactants, cadmium salt, acid with different amounts and a solvent; either water or ethanol depending on the polymerizing precursors. The difference arise from polymerizing precursors; solution 1 contains TMOS and water and solution 2 contains Ti(OBu)₄ and

ethanol. Using these two solutions, 3 different main products were obtained (see Schema 4.1.1 and 4.1.2).

The above solutions are spin coated over a glass or P25 coated glass. The volatile solvent of the ingredients evaporate immediately after spin coating and results a gel-phase over the substrate as thin films or embedded into the pores of P25 films. The freshly prepared films diffract at small angles, indicating the formation of a mesophase. The small angle diffraction prove that there are surfactant domains and the distance between these regularly repeating domains are quite large that their diffractions are observed at small angles (1 to 5° , 2θ). After calcination of the films (silica and titania), the surfactant molecules are burned out and random mesopores are obtained, therefore x-ray diffractions at small angles disappear (see Figure 14). Burning of the surfactants has been followed by Karakaya *et. al* using FT-IR spectroscopy and it is found that the C-H bond frequencies at around 2900 cm^{-1} disappeared at around 250°C [26][28].

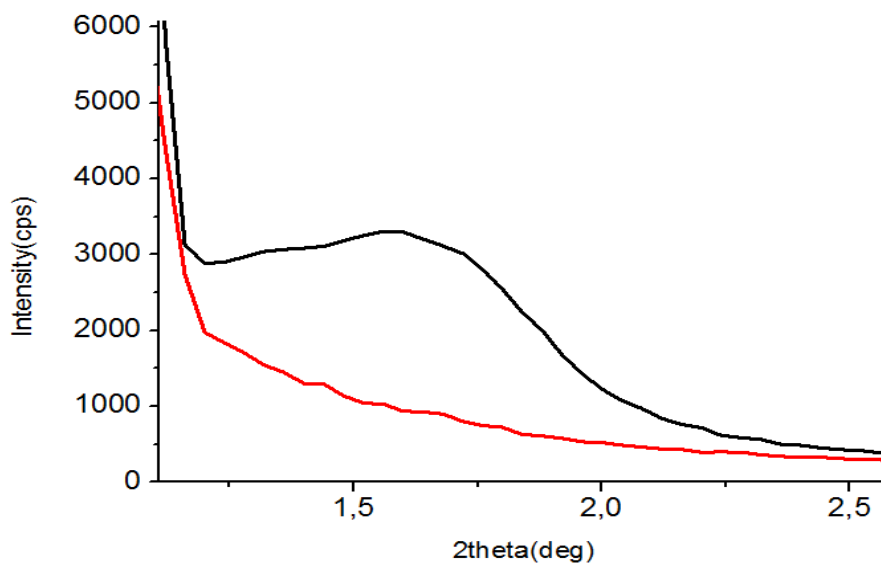


Figure 14. Low angle XRD pattern of the films, obtained using the MASA process, before (black) and after (red) calcination.

Figure 15 summarizes the entire process used in this thesis. The MASA process has been established and the materials have been well characterized in our group, using various microscopy, diffraction and spectroscopy techniques[26][28]. Therefore further characterization has been limited to XRD, Raman, and FT-IR techniques to ensure that the same materials to investigate its solar performance. The MASA process produces mesoporous CdO-SiO₂ in the silica system and CdTiO₃ in the titania systems[28].

Figure 16 shows the coating processes, which are mostly developed in this thesis. The films upon calcination were exposed to H₂Se to convert CdO and CdTiO₃ into CdSe and CdSe-TiO₂, respectively.

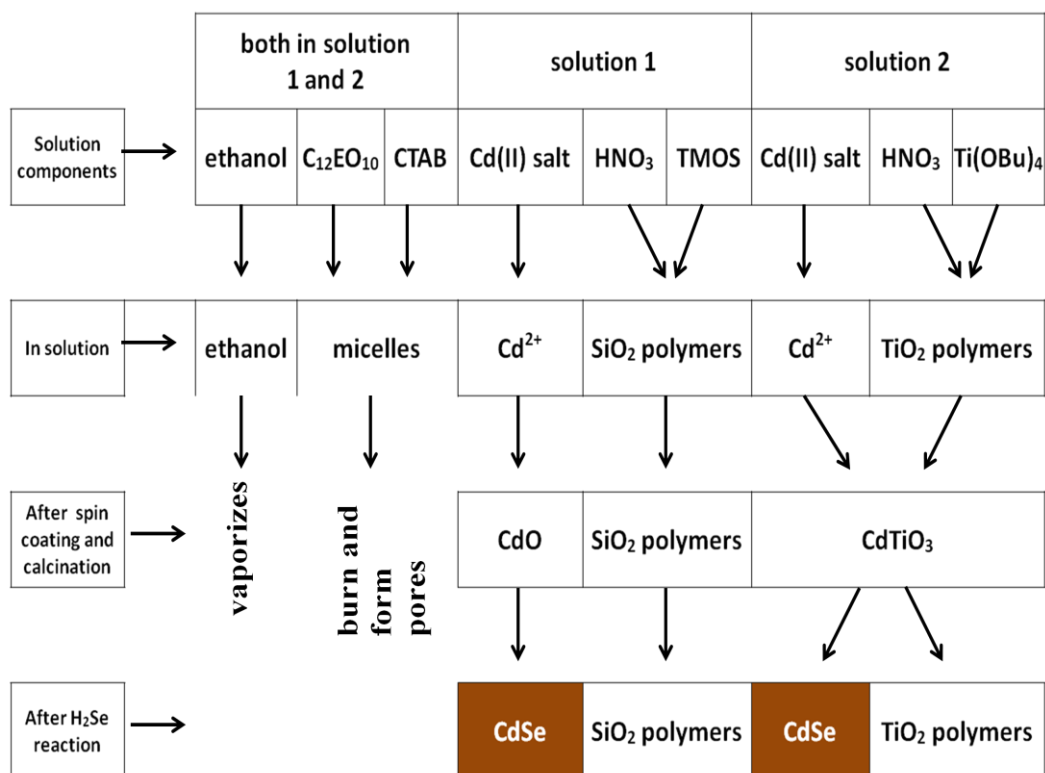


Figure 15. Conversion of the MASA ingredients in entire process.

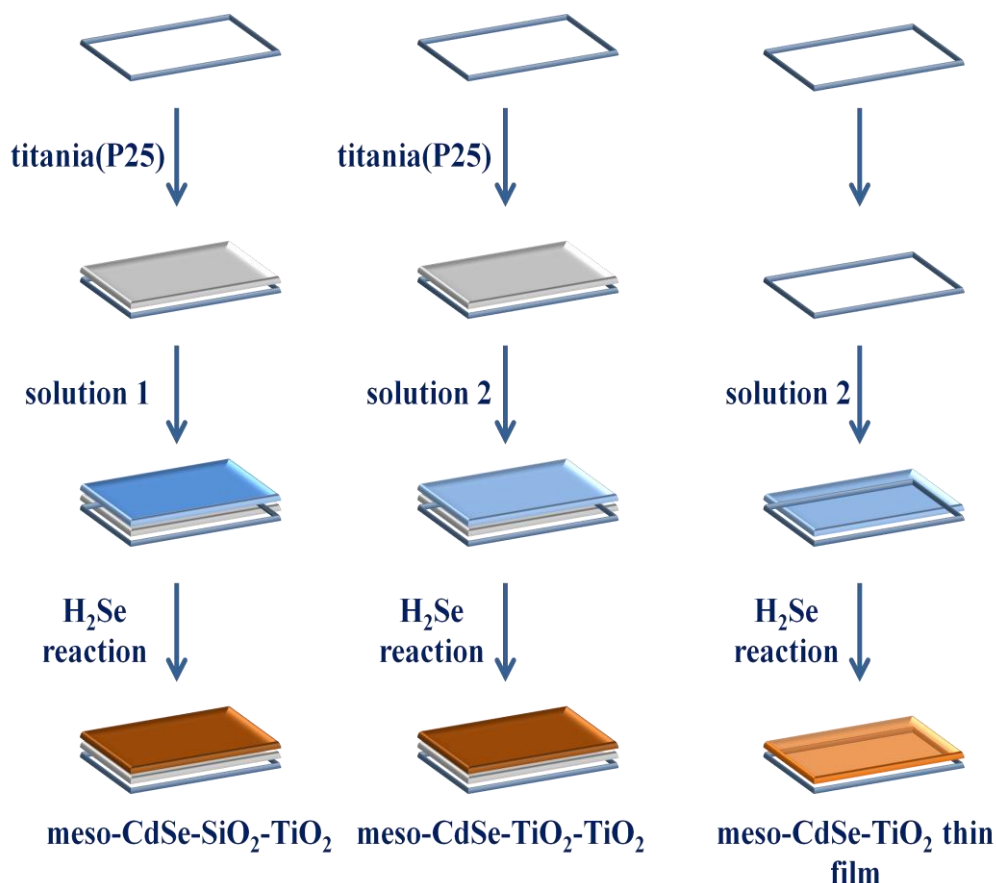


Figure 16. Synthesis pathway of 3 films; meso-CdSe-SiO₂-TiO₂, meso-CdSe-TiO₂-TiO₂ and meso-CdSe-TiO₂ thin films.

After H_2Se reaction, in all systems, the CdSe nanoparticles are formed. The SiO₂ represents the silica pore walls in the mesoporous silica systems and TiO₂ represent either mesoporous titania pore-walls or P25 (degussa) used to form the P25 based films. Upon CdSe formation, Raman, EDX and UV-Vis absorption techniques were used as major characterization techniques. It is clearly seen from the EDX spectra that the films have huge amount of selenium element after H_2Se reaction (see Figure 17). The intense peak at 206 cm⁻¹ in Raman spectrum also

proves the formation of CdSe nanoparticles. The small peak at 245 cm^{-1} is due to elemental selenium (see Figures 18 and 19).

However the Se/Cd ratio is low in the titania samples. The EDX data show that the Cd(II) in the silica react completely but the same reaction in the titania samples are not complete, see Figure 17 and Table 3.

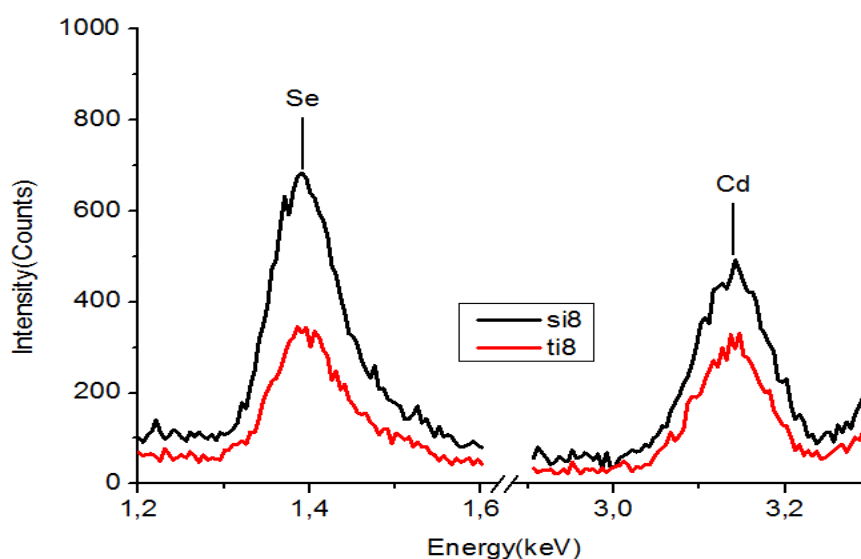


Figure 17. EDX Spectra for si8 and ti8 samples.

The EDX studies of the silica and titania samples, with different Cd concentrations, show that both samples of 8 Cd/surfactant mole ratio have greater amount of Se (See Table 3). Moreover, the EDX and Raman spectra collectively show that the silica samples are more reactive than that of the titania samples. Therefore the amount of CdSe is greater in the silica sample.

cd/surfactant	Si		Ti	
	Se/Cd	Se	Se/Cd	Se
4	1.98	7.92	1.26	5.04
6	1.49	8.94	1.06	6.36
8	1.42	11.36	1.04	8.32
10	0.75	7.50	0.52	5.20

Table 3. Se/Cd ratios and relative Se amounts of si and ti samples at different Cd concentrations.(from 4 to 10 Cd/surfactant ratio).

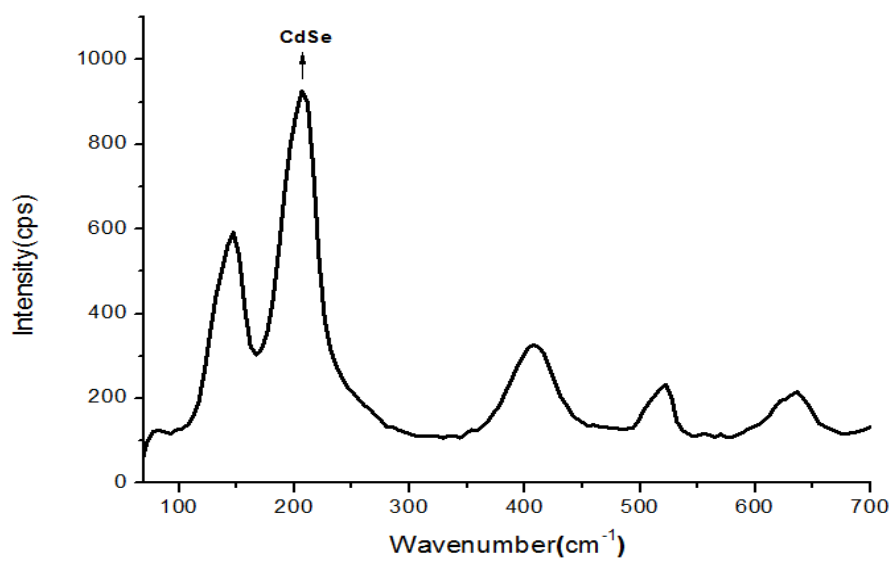


Figure 18. Raman spectrum of si8 sample.

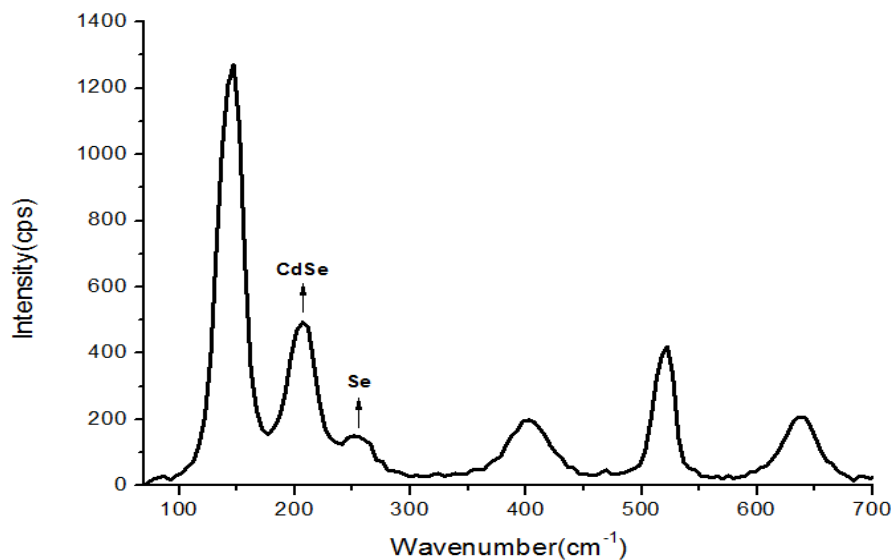


Figure 19. Raman spectrum of ti8 sample.

A huge absorption in the UV-Vis absorption spectrum also shows the formation of the CdSe nanoparticles, because the CdSe nanoparticles can absorb almost the entire visible spectrum. The P25 films have more absorbance than the CdSe thin films (see Figures 20, 21 and 22). According to the UV-Vis data, the samples prepared as thin films, without P25, absorb the visible light weakly, because these films are ultra-thin (typical thickness is around 400 nm). Therefore the solar efficiency measurements were generally made using P25 samples.

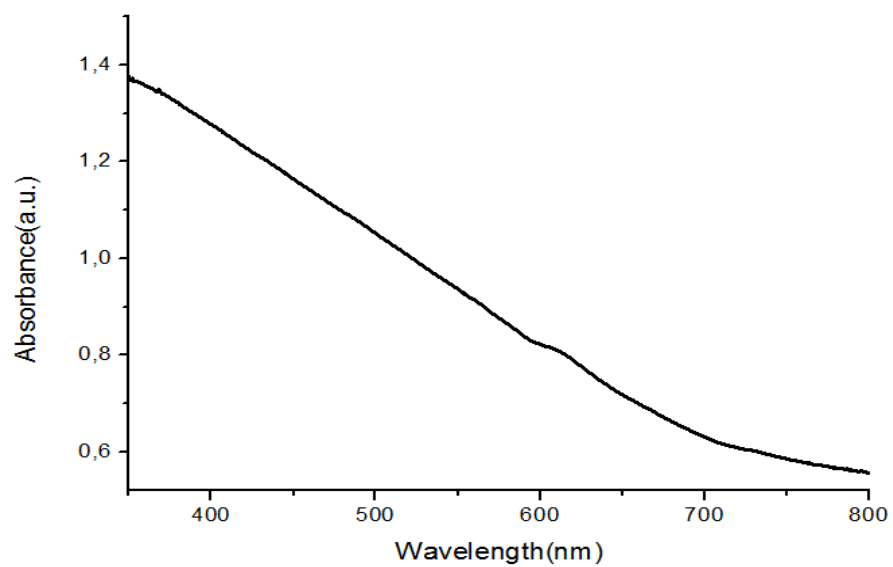


Figure 20. UV-Vis absorption spectrum of the si8 sample.

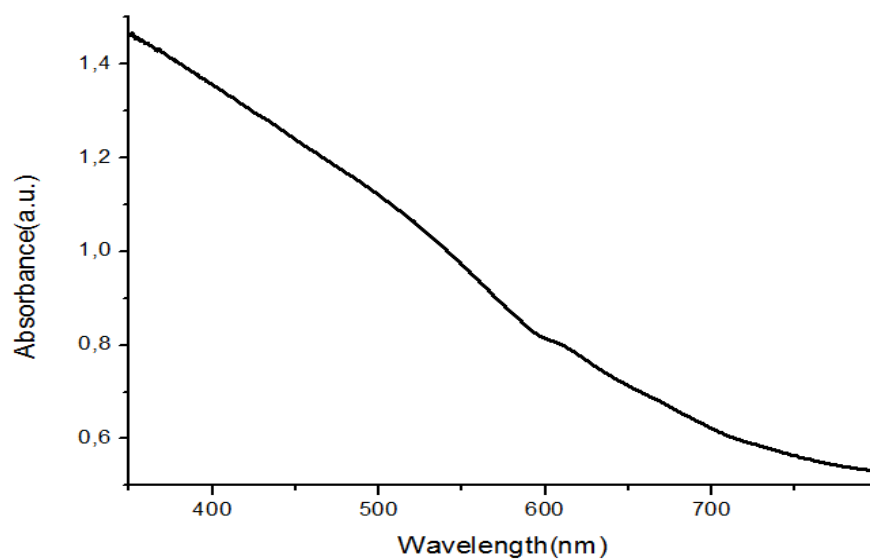


Figure 21. UV-Vis absorption spectrum of the ti8 sample.

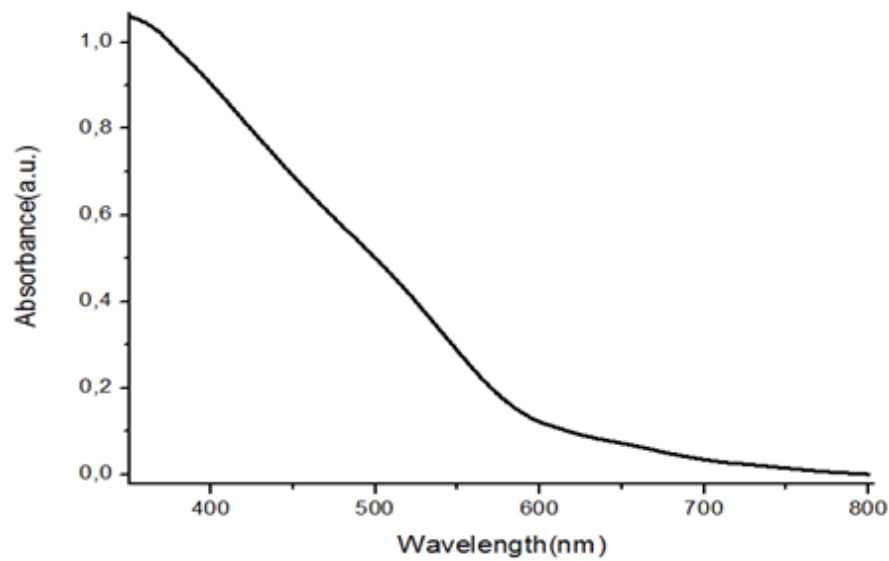


Figure 22. UV-Vis absorption spectrum of the CdSe-TiO₂ thin film.

For the silica samples, one more step may be necessary, the etching step. The silica sample reacts with very dilute HF solution and leach out from the samples as silicon fluorides. This can be monitored using FT-IR spectroscopy. The silica peak located at around 1050-1200 cm^{-1} completely disappears after washing with 4% HF solution. This step is carried out to enhance the efficiency in solar cell however the un-etched silica anodes work as well as etched samples (see chapter 4.3.9).

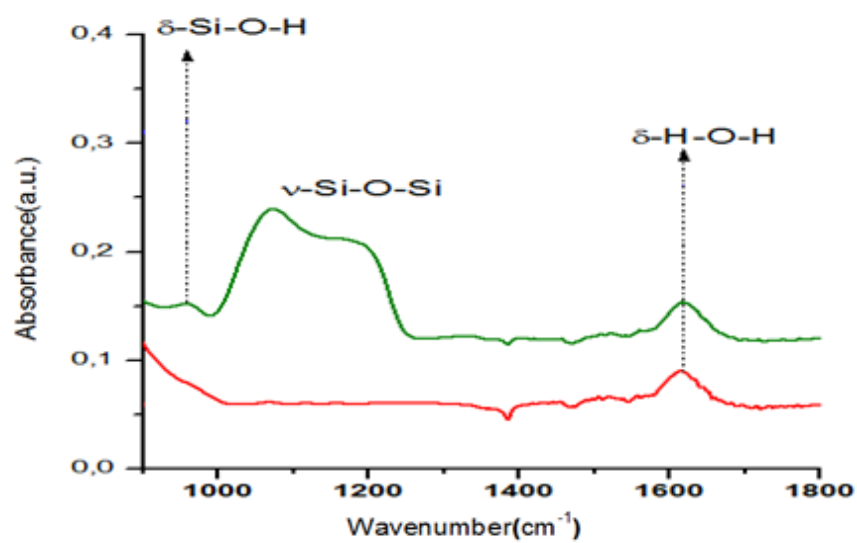


Figure 23. IR spectrum of the CdSe-SiO₂ sample before (top) and after (bottom) etching.

4.2. Raman Studies

Raman is a very useful technique for the characterization of CdSe-TiO₂ films because both anatase and CdSe are very good Raman scatterers. Titania, anatase nanoparticles, has 4 characteristic peaks at around 140, 390, 510 and 630 cm⁻¹. The peak at 135 cm⁻¹ has the greatest intensity (see Figure 24)[71].

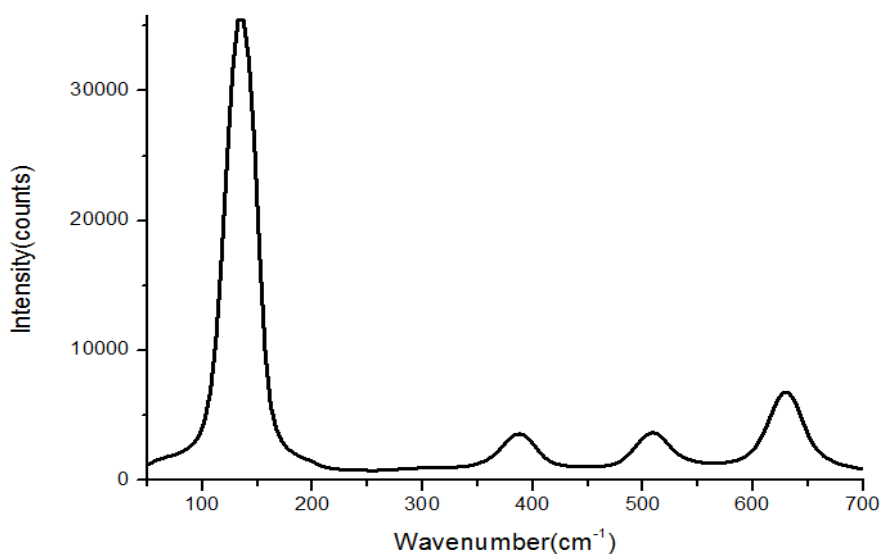


Figure 24. Raman spectrum of titania, anatase phase.

The CdSe nanoparticles also exhibit an intense peak at 206 cm⁻¹ and in some spectra its first overtone can easily be seen at 415 cm⁻¹ (see Figure 25). Both CdSe and TiO₂ peaks are very intense and do not overlap to each other. Therefore it is easy to follow the variation in the CdSe amounts forming on constant amount of TiO₂.

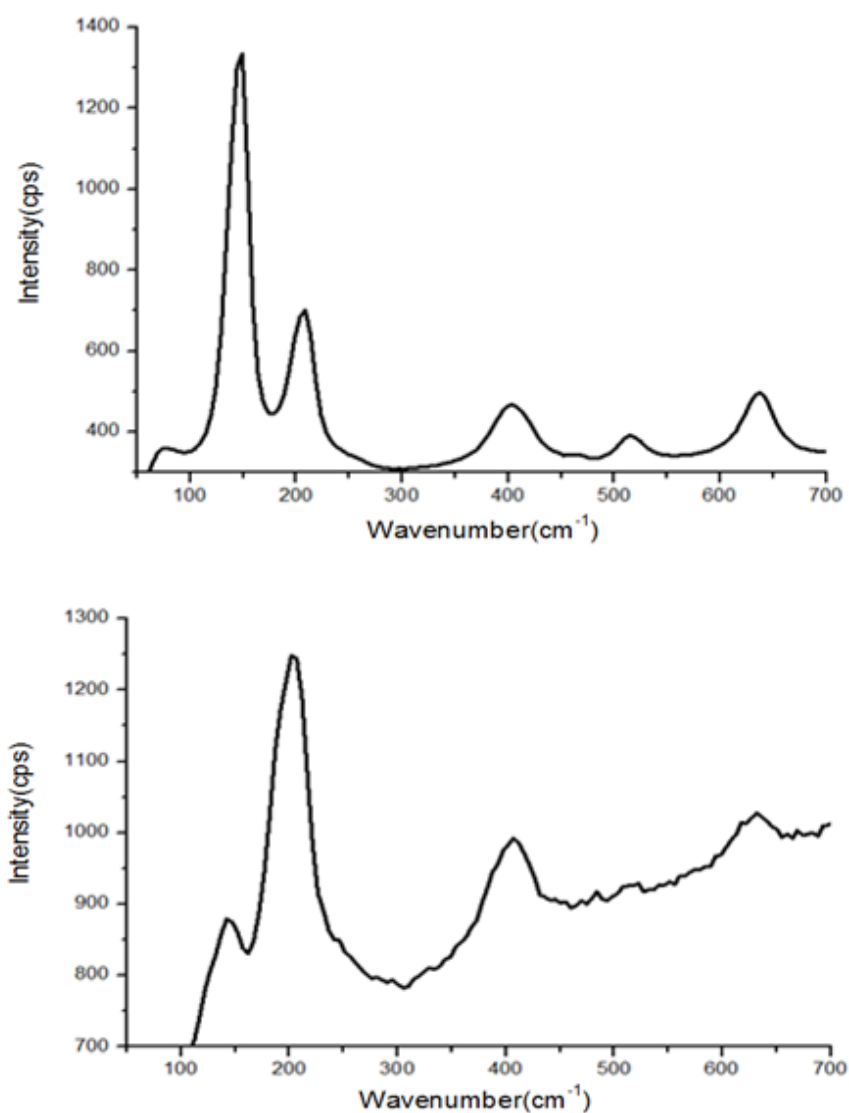


Figure 25. Raman spectra of the CdSe-SiO₂-TiO₂ samples.

During H₂Se reaction of CdO, selenium can also form beside CdSe as aside product. Pure selenium has a Raman peak at 245 cm⁻¹ and doesn't overlap with the anatase or CdSe peaks (see Figure 26). So it is also possible to see the amount of selenium in the films. Selenium is also a good Raman scatterer but the Se amount is generally not as much as CdSe. Therefore Se peak (245 cm⁻¹) cannot

be seen-especially if there is a large amount of CdSe beside the CdSe peak (206 cm^{-1}).

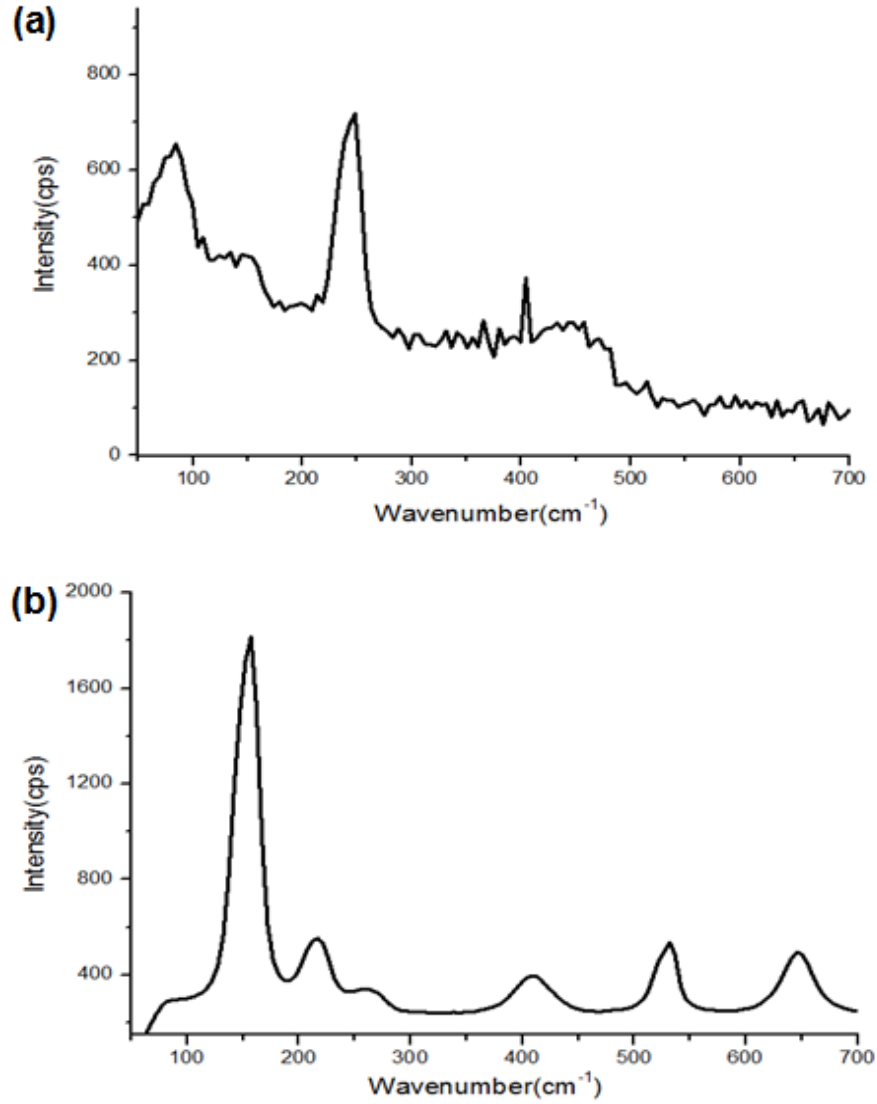


Figure 26. Raman spectra of pure selenium(a) and meso-CdSe-TiO₂-TiO₂(b) film.

The intensity of CdSe peak was also monitored over time during laser exposure. If the substrate used is an insulator, such as microscope slides (glass), the CdSe intensity will be stable but if the substrate material is a conductor, such

as FTO or silicon, the CdSe intensity decreases over time during the Raman measurements and exposure of the laser light.

The Raman intensity of CdSe monotonically decreases if the samples are prepared over FTO or on silicon wafer. In this process, the Raman light pumps electron (from the valance band to the conduction band of CdSe, $\text{CdSe} + h\nu \rightarrow \text{CdSe}^*$). With the help of a conducting substrate, these electrons flow into ground before they recombine with the holes in the CdSe nanoparticles. Thus, the CdSe nanoparticles decompose and its Raman intensity decreases over time. Actually, this process is the half reaction of a solar cell process; in the solar cell, the excited electrons move to cathode side, then to the electrolyte and finally to the VB of CdSe. In Raman process, there is no cathode side and CdSe decomposes. However, it is possible to change this problematic situation to an advantage. The rate of decomposition of CdSe nanoparticles is important and can give important information about the amount of CdSe or activity of CdSe in solar cells.

In the CdSe-TiO₂ films, the amount of titania is constant therefore the spectra, recorded over time, can be normalized to titania peaks and the change of the amount of CdSe can be easily monitored. In all compositions, the CdSe peak intensity decreases over time (see Figures below). Although the CdSe on silicon is unstable for the Raman measurement; it is still possible to make a comment about the amount of CdSe in the samples.

Firstly, even though the cadmium salt concentrations are the same for the silica and titania samples, the CdSe amount is higher in the silica samples than that of the titania samples. Even for the silica sample prepared using 4:1

salt/surfactant concentration, the CdSe peak is very intense, even more intense than the most intense titania peak. However for the ti-4 sample, the CdSe peak is nearly not visible beside the titania peak (see Figure 27).

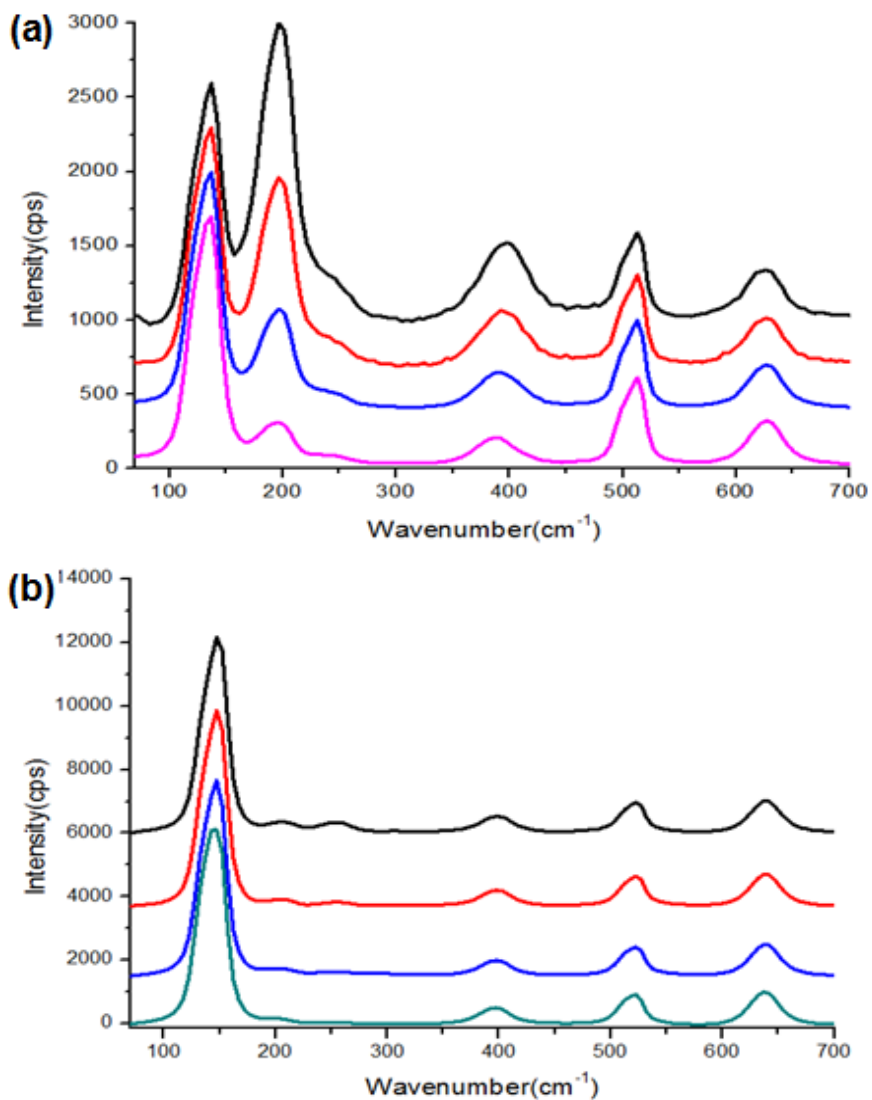


Figure 27. Raman spectral changes over time of the si4(a) and ti4(b) samples.

The CdSe peak intensity increases in both titania and silica samples with increasing Cd(II) in the oxides (CdO in the silica and CdTiO₃ in the titania

samples) and the highest intensity of the CdSe peak is observed from the si8 sample, not from the si10 sample (see Figure 29 and 30). This result is also consistent with the EDX data. According to the EDX spectrum, the si-8 sample has more CdSe than si-10 sample (see Figure 30). Therefore it can be said that at 10 Cd/surfactant mole ratio, larger (bulk) CdO particles are produced and not as reactive with H_2Se as the CdOs in the mesoporous structure to form CdSe.

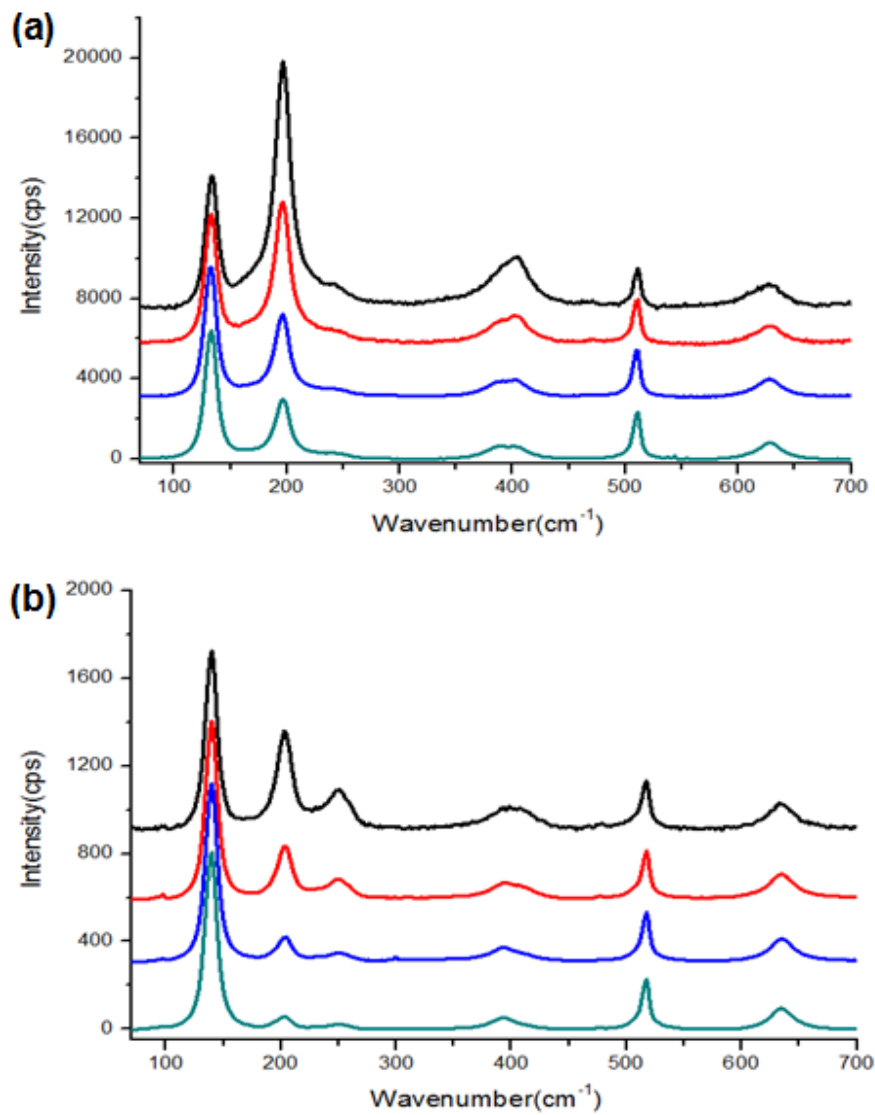


Figure 28. Normalized Raman spectra of CdSe-TiO₂ film for the si6(a) and ti6(b) samples.

It is also possible to observe the first overtone of the CdSe nanoparticles at 415 cm^{-1} from the silica samples. Normally the intensity of this peak is not very intense and overlaps with the characteristic peak of anatase at 388 cm^{-1} . However in the silica systems, because of high intensity of CdSe, its first overtone can also be observed over the anatase peak and decreases in intensity over time under the laser beam, see Figure 29.

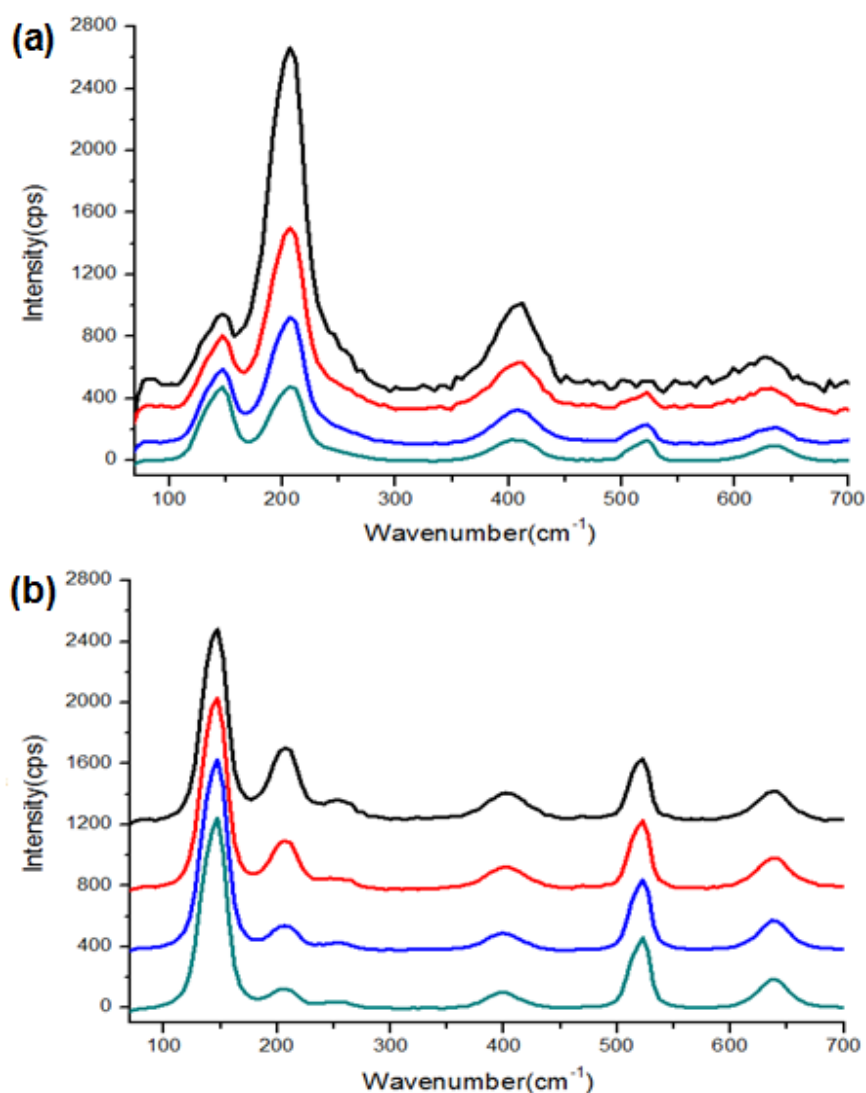


Figure 29. Normalized Raman spectra of the CdSe-TiO₂ film for the si8(a) and ti8(b) samples.

Another difference between the silica and titania samples is the amount of selenium. Around 250-260 cm⁻¹, there is a broad peak that originates from the selenium particles. The Se/CdSe peak ratios are greater in the titania samples than that of the silica samples. In the titania system, the selenium formation is more prominent, for instance for the ti-4 sample, Se/CdSe peak ratio is near to 1. Over

the time, the Se peak also decreases, similar to the CdSe peak. So it can be concluded that Se also decomposes like CdSe, however the decomposition also takes place on the glass substrate, therefore the origin of the decomposition can be a chemical reaction (such as reaction with O₂ to form selenium oxides) under the laser beam, instead of an electron transfer that derives the decomposition of CdSe particles. However, elucidation of the decomposition mechanism requires further investigations.

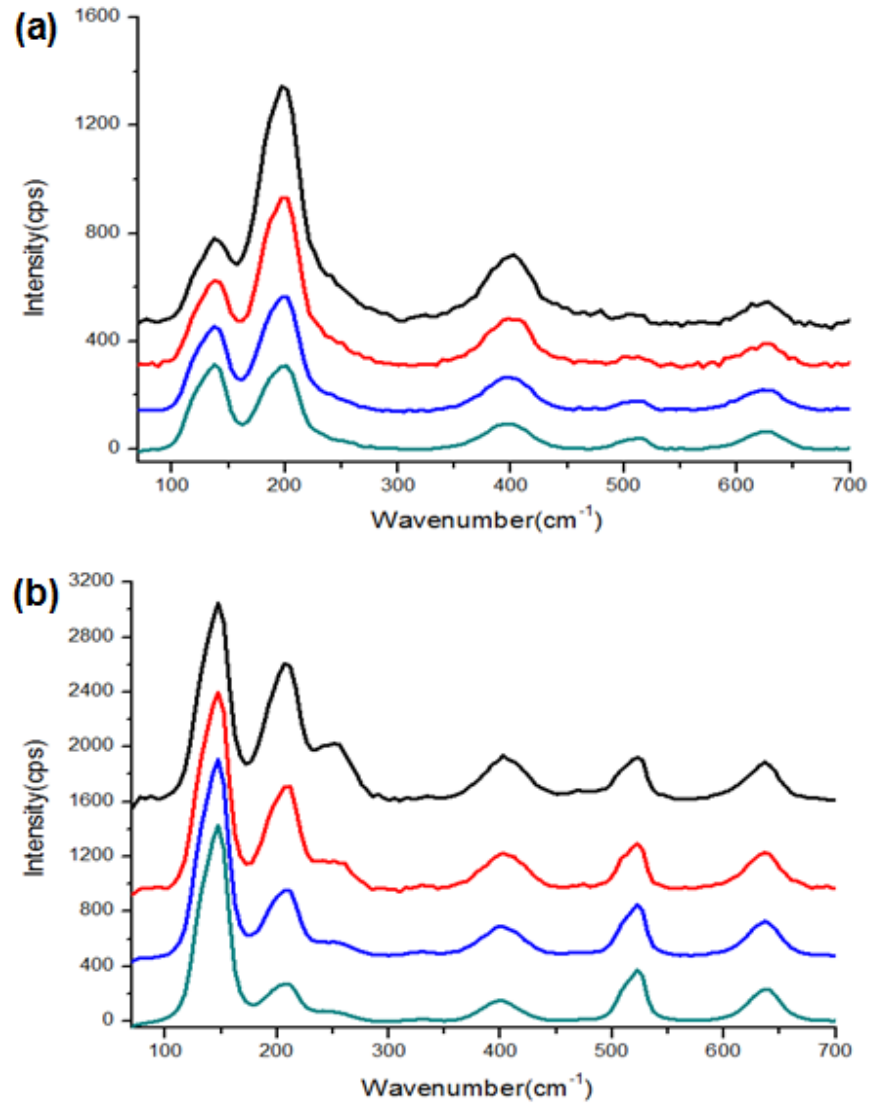


Figure 30. Normalized Raman spectra of the CdSe-TiO₂ films for si10(up) and ti10(down) sample.

Decomposition of the CdSe nanoparticles is normally a disadvantage but following the CdSe peak over time is possible and provides kinetics of the decompositions in various systems. Two different peak ratios are followed and plotted: $[\text{CdSe}]_t/[\text{CdSe}]_0$ and $[\text{CdSe}]_t/[\text{TiO}_2]_t$, where $[\text{CdSe}]_t$ is the CdSe peak intensity at 206 cm^{-1} at any time, $[\text{CdSe}]_0$ is the CdSe peak intensity at first

Raman measurement ($t = 0$), $[\text{TiO}_2]_t$ is the TiO_2 peak intensity at 135 cm^{-1} at any time. The $[\text{CdSe}]_t/[\text{CdSe}]_0$ ratio gives an opinion about the relative amount of CdSe with respect to beginning amount of CdSe, for instance at the beginning; this ratio is equal to 1.

The $[\text{CdSe}]_t/[\text{TiO}_2]_t$ ratio also gives an idea about the amount of CdSe; this ratio is not equal to 1 at the beginning, and can take any value depending on the salt/surfactant ratio in the first stage of the preparation; for instance for every titania samples this value is less than 1 but for silica samples firstly is higher than 1 and then decrease upon exposure of the green laser over the sample.

Compared to a reaction of decomposition of A in an aqueous solution like $\text{A(aq)} \rightarrow \text{P(aq)}$; $[\text{CdSe}]_t/[\text{CdSe}]_0$ ratio represents $[\text{A}]/[\text{A}]_0$ and $[\text{CdSe}]_t/[\text{TiO}_2]_t$ ratio represents $[\text{A}]$.

According to the CdSe peak intensities over time; all the graphs are similar to each other. Peak intensities suddenly decrease at first and then stabilize. The decomposition reaction by the light is not zeroth, first or second order reaction for all samples. After 5 min generally the peak intensities start to stabilize.

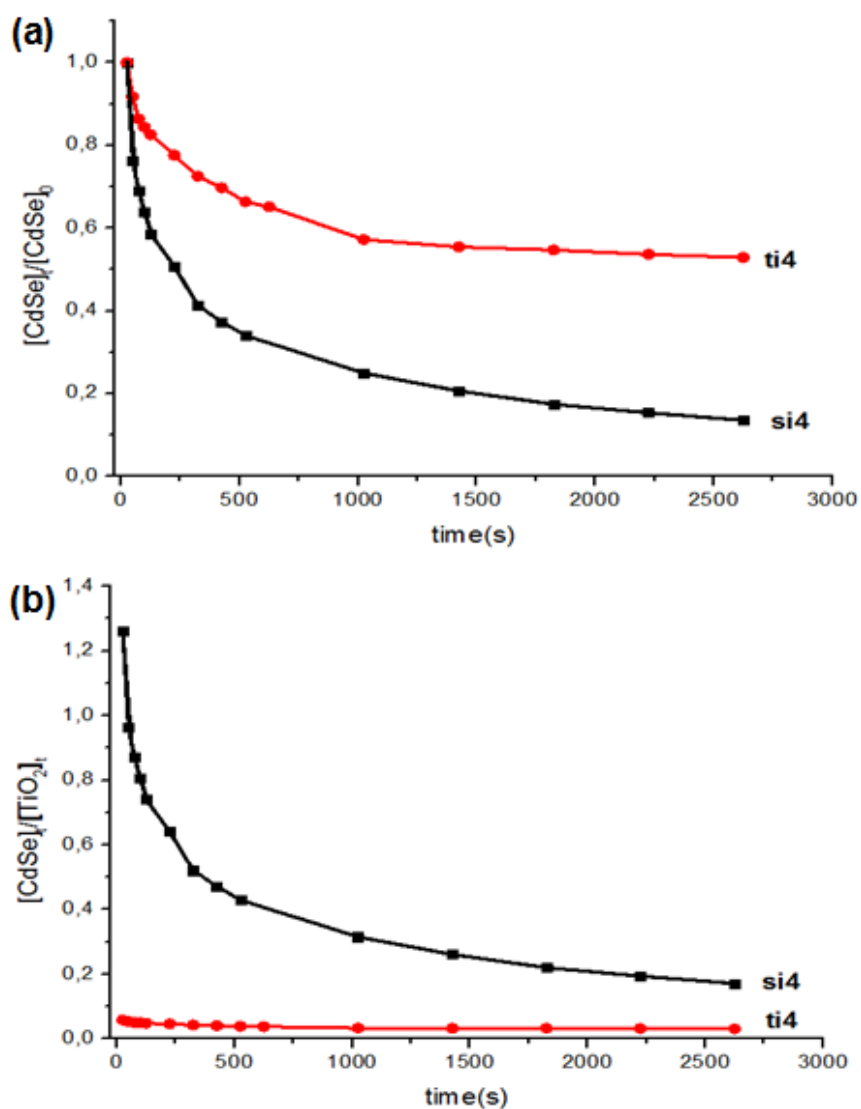


Figure 31. $[CdSe]_t/[CdSe]_o$ (a) and $[CdSe]_t/[TiO_2]_t$ (b) peak ratios change over time for the si4 and ti4 samples.

In the sample si4, 80% of the CdSe decomposes and for samples si6, si8, and si10 this value is around 60%. In the titania samples, nearly 40% of CdSe in ti4 sample decomposes and this value is around 70% in the ti8 and ti10 samples. The highest activity is observed from the ti6. Note that the decomposition ratio after 5 min is around 80% in the ti6 sample. This reality is consistent with solar

performance, because ti6 has highest efficiency and the si6, si8 and si10 solar efficiencies are very close to each other, so as accords by 60% of decomposition under the Raman light (see latter in section 4.3). Therefore it can be concluded that the decomposition of the CdSe nanoparticles under Raman beam provides indirect evidence for the contact of CdSe nanoparticles and the titania particles, where photo generated electrons follow from CdSe to TiO_2 then to FTO during solar tests.

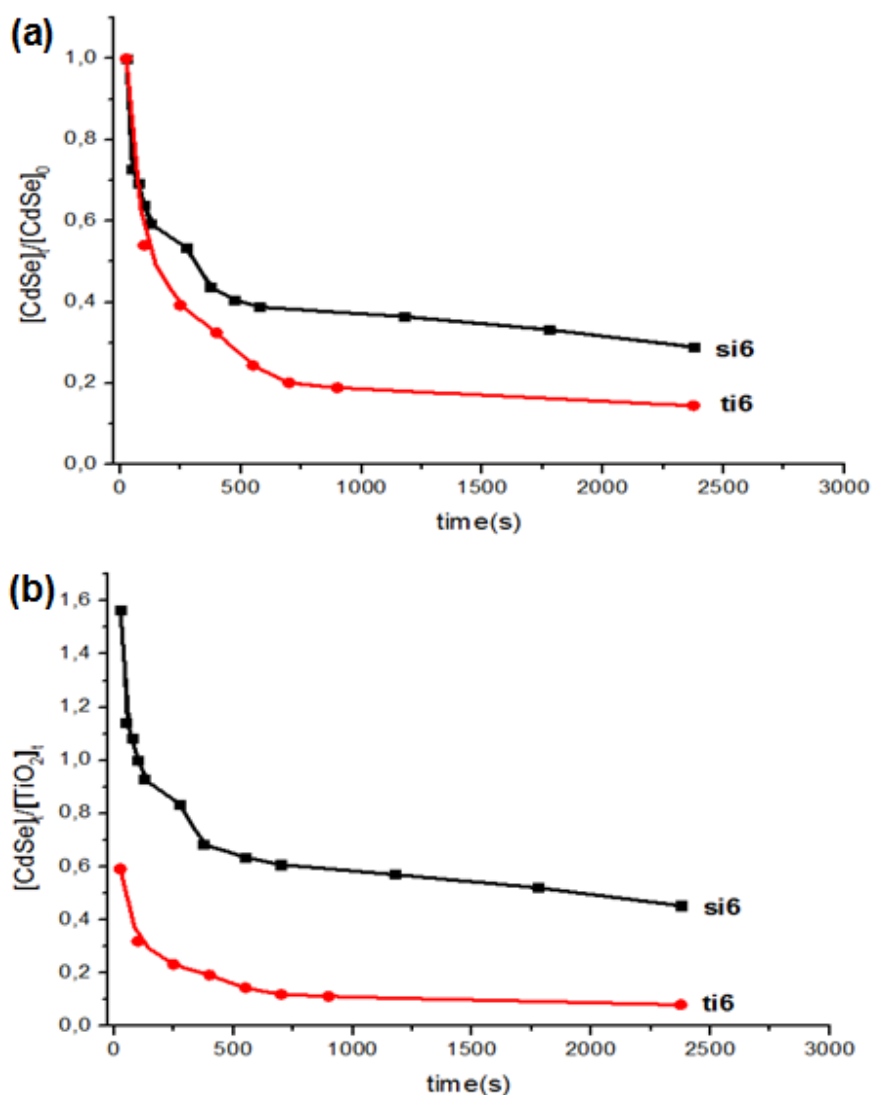


Figure 32. $[CdSe]_t/[CdSe]_o$ (a) and $[CdSe]_t/[TiO_2]_t$ (b) peak ratios change with time from the si6 and ti6 samples.

In all the titania samples, except ti4, the CdSe decomposition is more than the silica samples (for instance the % decomposition in the titania and silica samples are 80 and 60% in the 6 mole ratio, 70 and 60% in the 8, and 70 and 55% in the 10, respectively). The CdSe peak intensity of the ti4 sample is very low, so

it is hard to follow the changes. Therefore ti4 can be excluded from the generalization.

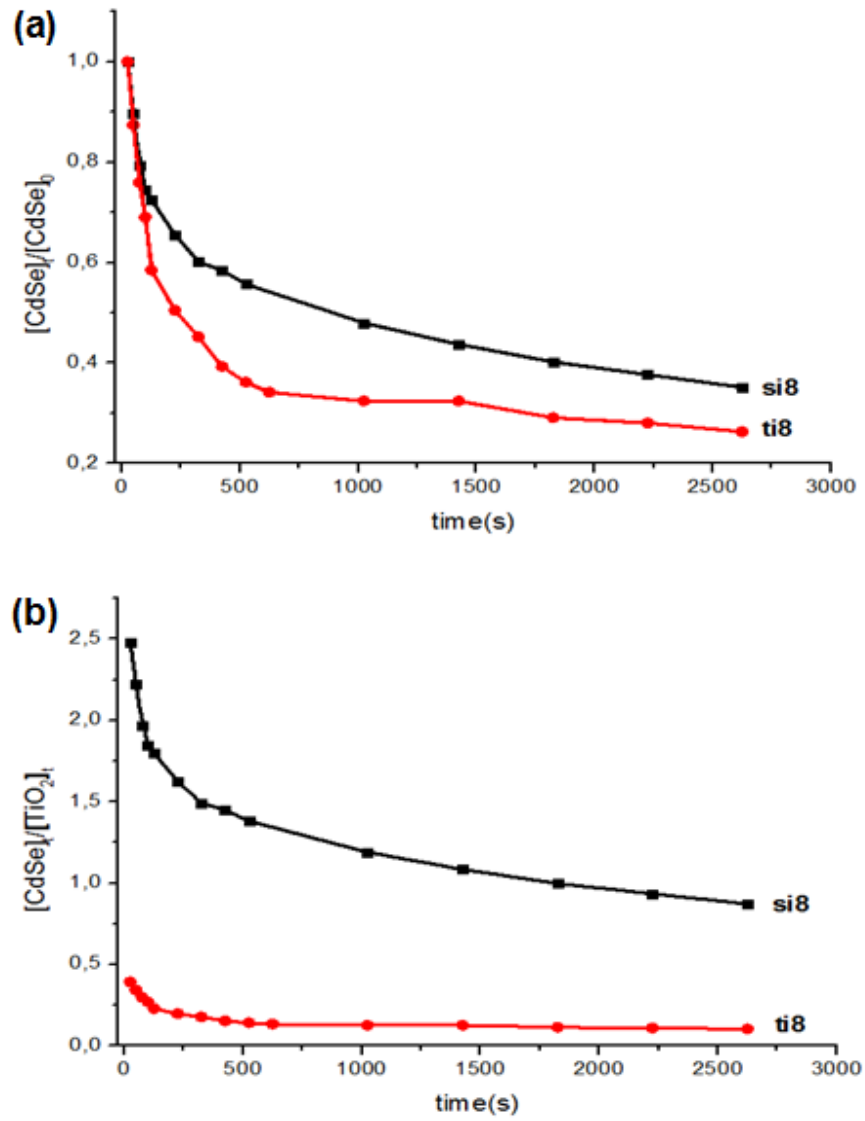


Figure 33. $[CdSe]_t/[CdSe]_o$ (a) and $[CdSe]_t/[TiO_2]_t$ (b) peak ratio changes over time in the si8 and ti8 samples.

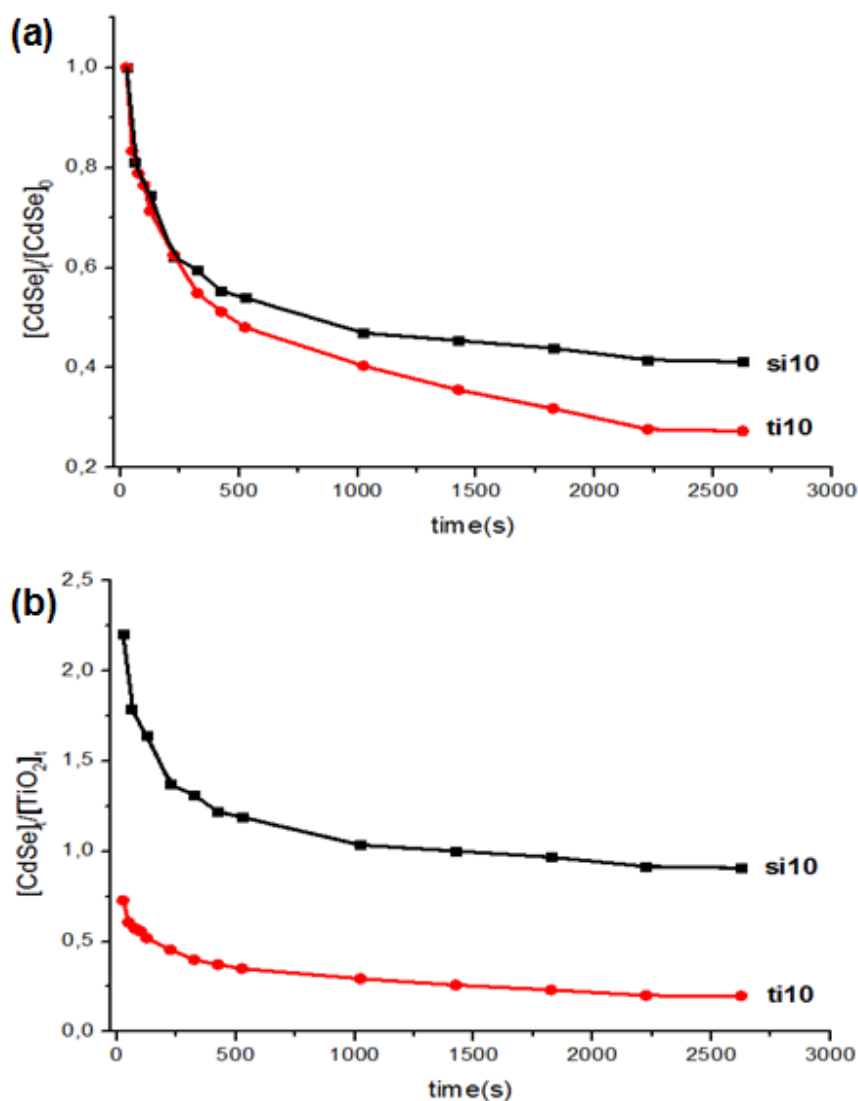


Figure 34. $[CdSe]_t/[CdSe]_0$ (a) and $[CdSe]_t/[TiO_2]_t$ (b) peak ratios changes over time in the si10 and ti10 samples.

The activity of the CdSe nanoparticles is greater in titania samples but the amount of CdSe is more in the silica samples (the $[CdSe]_t/[TiO_2]_t$ ratio in the si4 and ti4 is 1.3 and 0.1, in the si6 and ti6 it is 1.6 and 0.6, in the si8 and ti8, it is 2.5 and 0.5, and in the si10 and ti10 it is 2.2 and 0.7, respectively). As seen in the trend, the CdSe intensity gradually increases with increasing Cd(II) in the silica

samples. However in the titania samples the ratio is almost constant. The EDX data of the same samples also show that the silica samples have more CdSe than titania samples, but this ratio is not as high as in the Raman data. According to EDX data, CdSe amounts are 1.4-1.6 times greater in silica samples than titania samples (see Table 3). According to Raman, this value is between 3 and 5. Therefore, it may be concluded that the same amount of CdSe in silica samples have 2 or 3 times greater intensity than titania samples. This difference is based on the difference of the structure of the CdSe in titania (likely spherical) and silica (likely plates) samples[25][26].

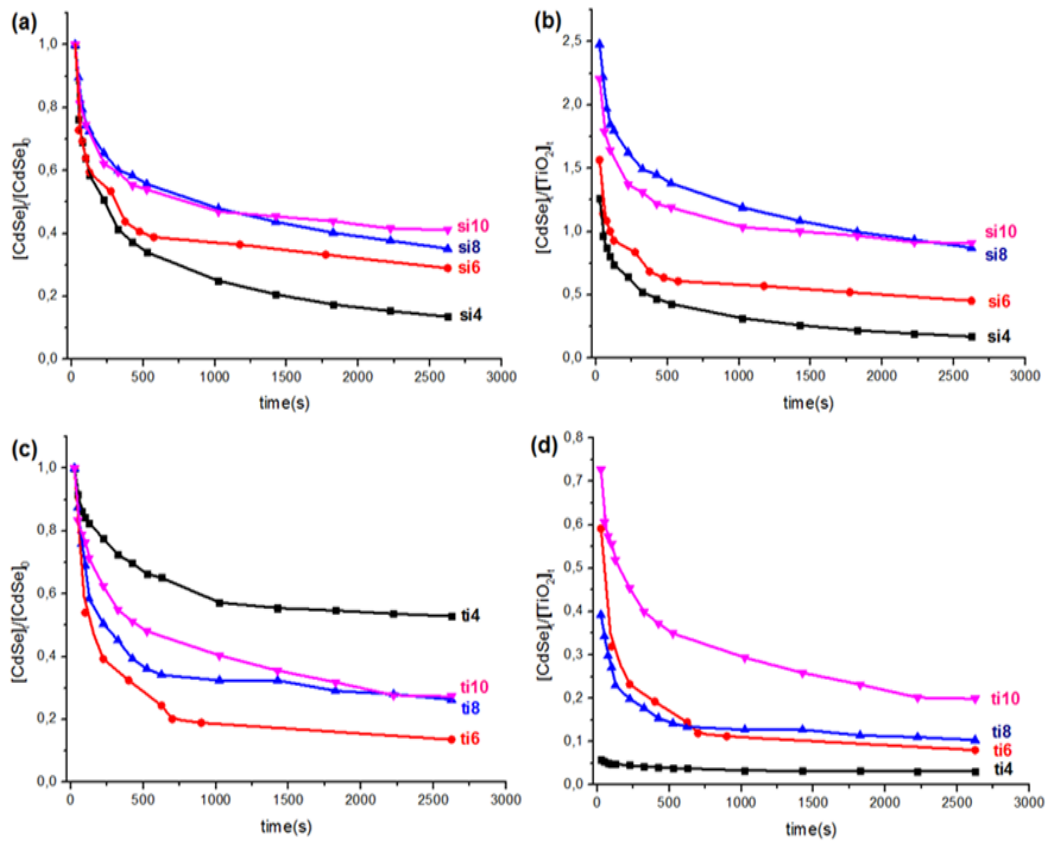


Figure 35. The $[CdSe]_t/[CdSe]_o$ (a,c) and $[CdSe]_t/[TiO_2]_t$ (b,d) peak ratios changes over time for the all si(a,b) and ti(c,d) samples.

4.3. Solar Performances

Solar measurements were made using a solar simulator at 1 sun and the cell in Figure 36. The anode electrode (at left) was CdSe-SiO₂-TiO₂, CdSe-TiO₂-TiO₂ or CdSe-TiO₂ film over FTO glass and the cathode electrode (at right) was brass. The electrolyte was S_n/S²⁻ solution and the volume of the solution is around 2.5 cm³. Solar light came from left side and the applied voltage range during the measurement was between -1.0 V and +0.8 V. I-V curve was obtained in this voltage range and the fill factor and the efficiency of the cell could be estimated from this I-V curve (see section 1.6.4).

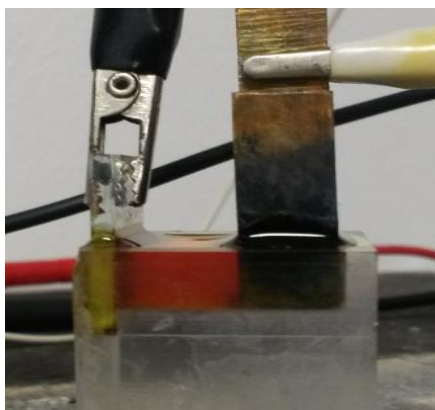


Figure 36. The picture of the cell used in all solar experiments.

4.3.1. Usage of solar light by anode electrodes

In our cell design, until solar light reaches to the CdSe thin films, it passes through the quartz, FTO glass and bulk titania buffer protecting layer. Normally

efficiency of cell is calculated at 1 sun (1000 W/m^2) light intensity. However this light cannot be used totally by the CdSe thin film, see Figure 37.

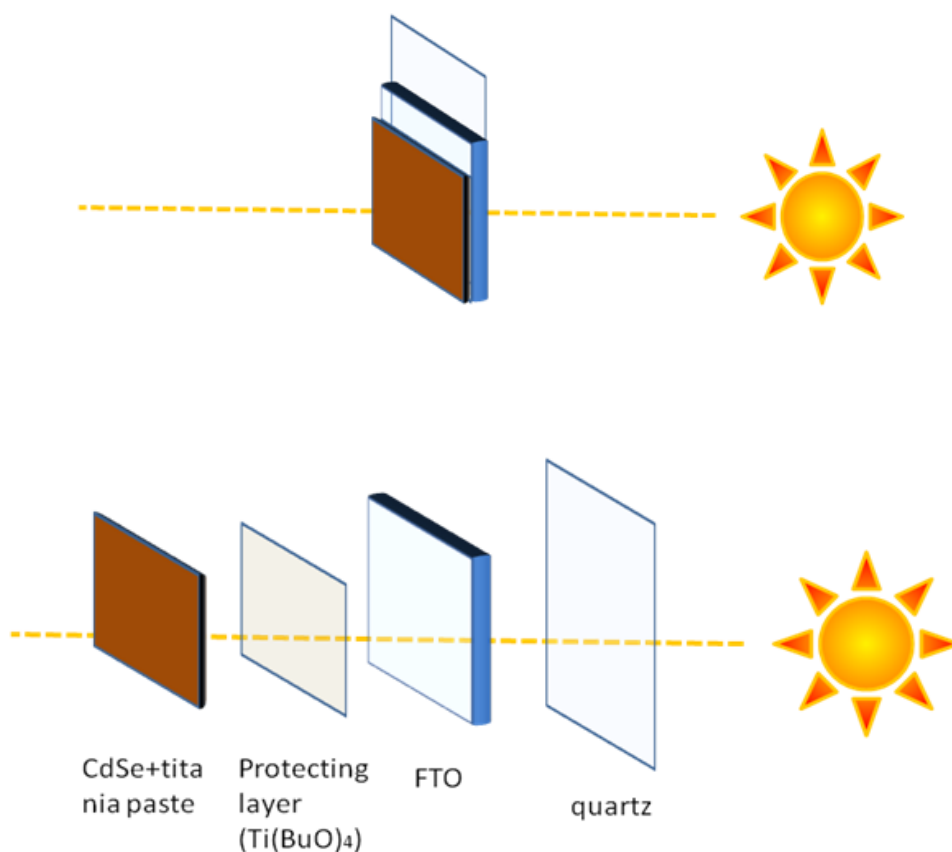


Figure 37. Schematic representation of the sun light through different layers in cell.

A Series of experiments have been performed to determine how much solar light is used by the CdSe films with P25 ($\text{CdSe-SiO}_2\text{-TiO}_2$ and $\text{CdSe-TiO}_2\text{-TiO}_2$) and without P25 (CdSe-TiO_2 thin film). In these experiments, the light intensities measured using a PMA2100 Data logging Parameter.

substances between light source and detector					input light intensity = 697 W/m ²	
Exp no	Quartz	fto + protecting layer	CdSe film with P25	CdSe film without P25	output light intensity (W/m ²)	% transmittance
1	+	-	-	-	646	93%
2	+	+	-	-	419	60%
3	+	+	-	+	254	36%
4	+	+	+	-	40	6%
5	-	+	+	-	50	7%
6	-	+	-	+	267	38%
7	-	+	-	-	445	64%

Table 4. The light intensity and %transmittance values of different experiment sets.

According to these data in Table 4, the transmittance of every material can be calculated.

If x = transmittance coefficient of quartz,

y = transmittance coefficient of FTO and titania protecting layer,

z = transmittance coefficient of the CdSe film with P25,

t = transmittance coefficient of CdSe film without P25,

For any experiment;

% transmittance = $100 \times (\text{multiply the coefficients of substance which exist in the cells})$

Then approximately, $x = 0.93$, $y = 0.64$, $z = 0.10$, $t = 0.60$. The % light that CdSe films used during solar performance can be calculated from two different experiments for two different CdSe films (with P25 without P25).

% light that CdSe film with P25 use = $100 \times 0.93 \times 0.64 \times (1 - 0.10) = 53.5$ (from exp 4)

or

= $100 \times 0.64 \times (1 - 0.10) = 57.5$ (from exp 5)

%light that CdSe film without P25 use = $100 \times 0.93 \times 0.64 \times (1 - 0.60) = 23.7$ (from exp 3)

or

= $100 \times 0.64 \times (1 - 0.60) = 25.4$ (from exp 6)

Overall, % light usage during solar performance for CdSe films with P25 equal **56%** and for CdSe films without P25 is approximately equal to **25%**. It's obvious that P25 increases light usage more than two times and it is necessary for solar work. CdSe-TiO₂ films (without P25) can only use $\frac{1}{4}$ of the solar light and naturally the efficiencies are low for the thin films (see section 4.3.2). Because of this difference, most of the solar cell measurements were made using the samples with P25 (see section 4.3.3-10). It is also obvious that even the samples with P25,

almost half of the light cannot be used. Therefore the real efficiencies can be thought of the two folds of the found efficiencies.

4.3.2. Solar measurements of meso-CdSe-TiO₂ thin films(without P25)

Meso-CdSe-TiO₂ thin films are transparent films and $\frac{3}{4}$ of solar light cannot be used by the film (see section 4.3.1). As a result of that, efficiencies of these thin films are very low. The highest efficiency measured is around 0.69% and this sample contains Mn(II) cation in 0.15 Mn/Cd ratio (see Figure 38). Without manganese, the highest efficiency is 0.58%. Actually the fill factor (0.52) and the open-circuit voltage (0.53 V) values are very close to P25 samples; however the short-circuit current is very low: 2.94 mA, where the efficient P25 films are around 10-12 mA.

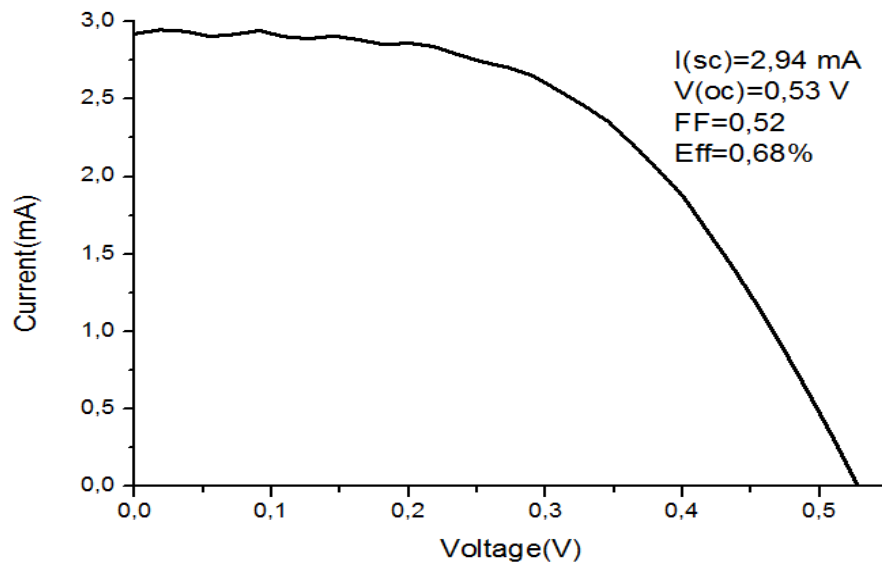


Figure 38. I-V curve of the most efficient sample of the CdSe-TiO₂ thin films.

Not only the transparency but also having smaller pore sizes and instability of the thin films decreases the efficiency. Therefore most of the solar measurements were made using the silica and titanium coated P25 films.

4.3.3. Doctor Blade and Spin Coatings of P25 and Differences

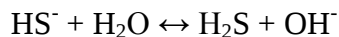
In order to get P25 films generally doctor blade method is used in the literature[31][72][73]. In doctor blade method, the FTO glass is strapped with scotch band at first and after gel-like P25 solution is put on the FTO; with a rigid squeegee this P25 solution is spread quickly on FTO. Thickness is nearly equal to thickness of the band[74].

Another method-mostly used method in this thesis- is spin coating method. This method is very simple: the P25 solution is put on FTO and spin at desired rate and time. It is possible to obtain thinner films with spin coating method and spin coated samples are more comparable than doctor blade method. See section 4.3.6 to see the solar performance differences between two methods.

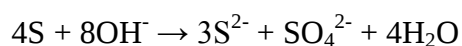
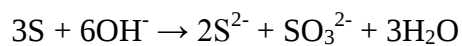
4.3.4. Effect of Fresh Electrolyte

The electrolyte of these measurements is the S^{2-}/S_n couple and the freshness of the electrolyte is very important. Because of solvent of the electrolyte is water, there can be some disproportionation reactions of sulfur. The media is slightly basic because of S^{2-} and in the length of time; sulfur can disproportionate to S^{2-} and oxosulfur (SO_3^{2-} or SO_4^{2-}) species[52].

Reactions that make the solution basic:



Possible disproportionation reactions:



While decreasing the amount of sulfur in electrolyte solution, the efficiency of cell decreases from 1.40% to 0.79%. The change in the efficiency is over 75 %. Therefore it is important to use or keep the electrolyte fresh.

	I(sc) (mA)	V(oc) (V)	FF	eff%
fresh electrolyte	6.60	0.48	0.53	1.40
old electrolyte	3.14	0.54	0.56	0.79

Table 5. Solar measurement variables of the same silica sample with fresh and old electrolyte.

4.3.5. Importance of Surfactant in General

Surfactants in MASA solution ($\text{C}_{12}\text{EO}_{10}$ and CTAB) play important role in solar performances. Without surfactants, mesoporous structure cannot be formed and bulk Cadmium oxides form. During H_2Se reaction, bulk CdOs does not react completely and naturally the amount of CdSe is less than mesoporous CdO

sample. This result lead to decrease in current and efficiency (see Figure 39 and Table 6).

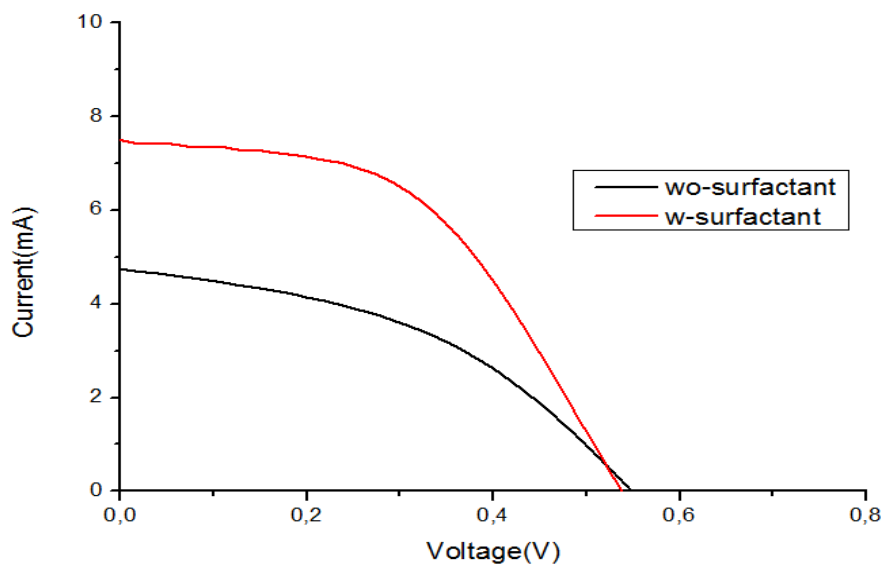


Figure 39. I-V curve of the CdSe-P25 samples with surfactant and without surfactant.

	I(sc) (mA)	V(oc) (V)	FF	eff%
with surfactant	7.48	0.54	0.50	1.68
without surfactant	4.76	0.55	0.43	0.93

Table 6. Solar measurement variables of the CdSe-P25 samples with surfactant and without surfactant.

4.3.6. Solar Cell Response with Time

While measuring the solar performance, time is also an important parameter. The graphs of percent efficiency (%eff) vs time give information about

the stability of the solar cells over time. Two different preparation methods have been used: the doctor blade (DB) method and spin coating (SC) method. Every measurement cycle, which starts at -1.00 V and ends at +0.80 V takes 100 seconds. In both methods, the first measurements give the lowest %eff. The efficiency increases at first then stabilizes and finally decreases over time. The maximum efficiency was recorded at 10th cycle from the DB method and at 4th from the SC method. The reason of increase in efficiency at first is most probably due to the diffusion rate of the electrolyte into the films. If the diffusion process is slow, the increasing trend can be expected. Because, the film designed by DB method is thicker than the ones, designed by SC method, the elapsed time in order to reach maximum efficiency is higher in DB samples and consistent with the above proposal. After some time the efficiencies decrease slightly because the electrolyte also decomposes to many different substances. In basic solution, S_n molecules can disproportionate to S²⁻, SO₃²⁻ and SO₄²⁻ anions and S²⁻ can react with Cu electrode to form Cu₂S or exchange with Se²⁻ anion of the CdSe nanoparticles to form CdS. Another possible reaction is redox reaction between elemental Se and S²⁻ anion to form Se²⁻ and S. In DB samples the amount of elemental Se is greater than SC samples (because of thickness) and the last possible reaction affect DB sample more. These possible reactions are not spontaneous but with time all possible reactions can occur and all of them can decrease the electrolyte activity and the efficiency of the cell.

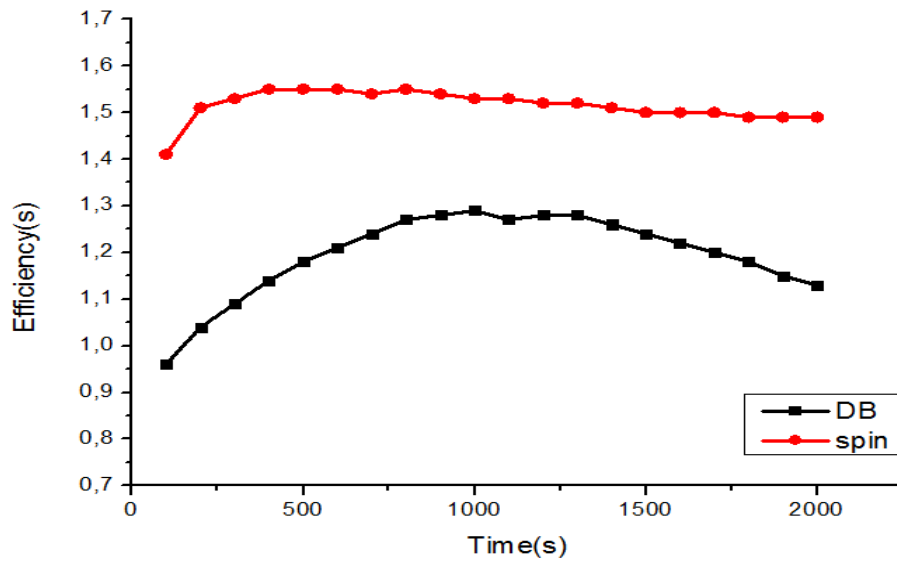


Figure 40. Efficiency changes of DB and SC samples with time.

4.3.7. Effect of Coating Materials

In solar cells; the excited electrons by the solar light must be transferred to the CB of titania (Route 1 in Figure 41) and after that these electrons must be transferred to FTO (Route 2 in Figure 41) and subsequently to the counter electrode through the connection cable. However there are many other paths for these electrons to flow that lowers the solar cell efficiency. Excited electrons can recombine with the hole in the VB of the CdSe particles (Route 5 in Figure 41) or be transferred from the CB of TiO_2 (Route 6 in Figure 41) to the electrolyte. These processes are related to the interactions between the CdSe- TiO_2 anode and the electrolyte. To minimize some of these problems, a protecting layer must be put over these domains in contact with the electrolyte before measurement.

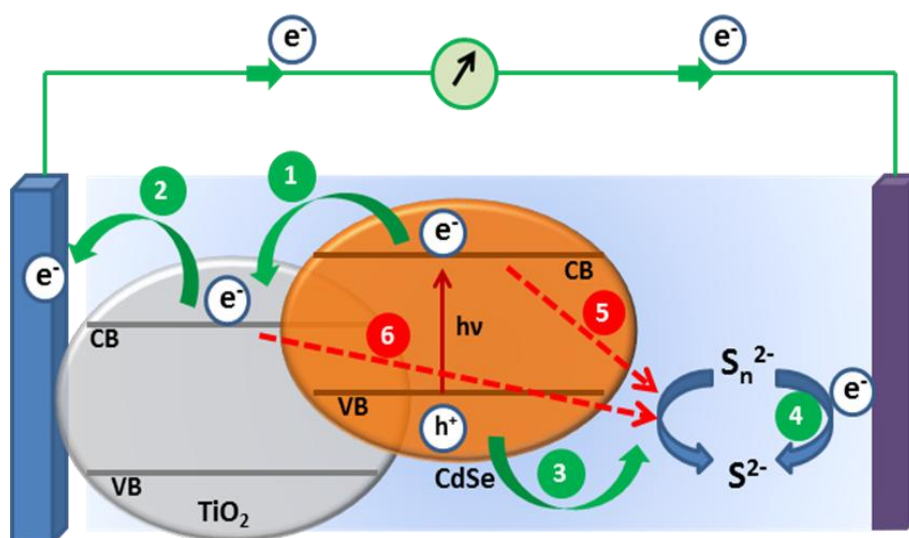


Figure 41. Operation scheme for CdSe-TiO₂(P25) solar cell.

For this purpose, 3 different types of protecting agents were used in this thesis.

4.3.7.1. Cetyltrimethylammonium Bromide (CTAB) as a Protecting Layer

CTAB is a positively charged surfactant (see Figure 42) and interact with negatively charged part of the surface (oxide parts and maybe also cadmium selenide parts) and the organic tale plays an important role for protecting film from the electrolyte solution (see also section 2.11.1). [75]

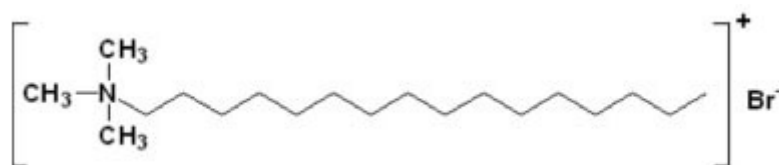


Figure 42. Structure of CTAB.

4.3.7.2. Zinc Sulfide (ZnS) as a Protecting Layer

Zn(II) cation also interacts with the negatively charged part of the surface (oxide parts and maybe selenide parts) and washing with ethanol leaves only monolayer coverage of Zn(II) over the pore surface of the electrode. Then Zn(II) ions can be reacted by S^{2-} anions upon dipping into the sulfide solution to form ZnS layer. The ZnS forms as a layer between CdSe-TiO₂ parts of the film and the electrolyte (see also section 2.11.2).

4.3.7.3. Polyethyleneimine (PEI)-branched as a Protecting Layer

PEI is an uncharged polymer but it has so many $-NH_2$ groups (see Figure 43) and can bind to metal sides over the surface. Therefore the polymer can interact with positively charged part of the surface (hydrogens of $-OH$ groups and maybe Ti(IV) and Cd(II) cations) and thus anchors on the surface. This huge polymer structure can protect electrons to move to electrolyte by forming layer between the film and the electrolyte (see also section 2.11.3).

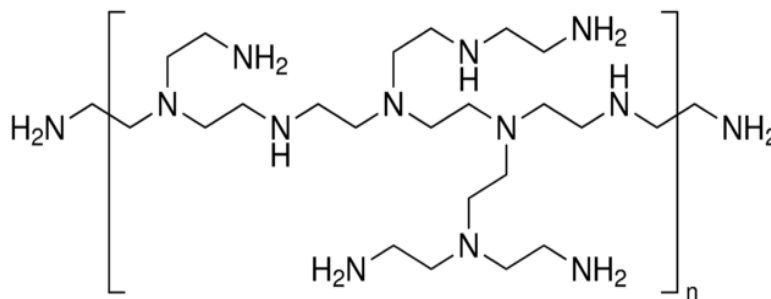


Figure 43. Structure of PEI.

According to solar measurements on these substances, it has been shown that all of the protecting layers improved the efficiency of the cells, constructed using these electrodes; thus all of them partially prevent the electrons to flow into the electrolyte solution. CTAB and ZnS increase the efficiency around 40% and they have greater effect than that of PEI. The increase in the PEI case is around 25%, compare the values in Table 7.

Protecting layer does not increase the fill factor, but increases the current and show different effect on open circuit voltage. CTAB increases, PEI decreases and ZnS doesn't change the V_{oc} . (See Table 8)

	I_{sc} (mA)	V_{oc} (V)	FF	eff%
None	5.32	0.49	0.49	1.05
Ctab	7.40	0.54	0.45	1.49
ZnS	8.53	0.50	0.41	1.45
polyethylene	7.05	0.46	0.48	1.32

Table 7. Solar measurement variables of the silica samples with different protecting layers.

	eff%	increase in eff%
None	1.05	-
CTAB	1.49	40%
ZnS	1.45	38%
PEI	1.32	26%

Table 8. Efficiencies and percentage increases in efficiency of silica samples with different protecting layers.

4.3.8. Comparing the Solar Efficiencies of the Titania and Silica Samples

In MASA synthesis, there are two different polymerizing precursor: TMOS and $\text{Ti}(\text{OBu})_4$ and the oxides form in this process are silica (SiO_2) and titania (TiO_2), respectively. Both materials have advantages and disadvantages; for instance silica samples are more reactive than titania samples (see section 4.1 and 4.2), nevertheless titania is a semiconductor but silica is an insulator. Solar experiments show that efficiencies of silica samples are greater than efficiencies of titania samples.

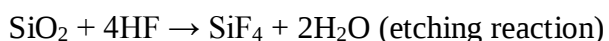
Under the same conditions; the silica sample has 1.40% efficiency but the titania sample has 1.30% efficiency. Many experiments were made using silica and titania samples and efficiency difference ratio is around 10%, like the data in Table 9.

	I(sc) (mA)	V(oc) (V)	FF	eff%
Silica	6.60	0.48	0.53	1.40
titania	6.02	0.52	0.52	1.30

Table 9. Solar measurement data for silica and titania samples.

4.3.9. Effect of Etching Silica and Heat Treatment after Etching

When TMOS was used as a polymerizing precursor; the etching process becomes important. After TMOS polymerizes and the sample is reacted by H₂Se pure silica forms that may cause decrease in the efficiency; because silica is an insulator. However, the sample with silica has 1.40 % efficiency and the sample without silica (etched by HF) has 1.46 %. It implies that it is not necessary to remove silica in order to increase the efficiency. Somehow electrons can pass through the silica layer from CdSe to TiO₂.



Another effect that can change the efficiency is heating of etched film. If heating can increase the interaction area between CdSe and TiO₂; the efficiency of film will be higher. However, the heated etched sample has 1.31 % efficiency, which means the heating of the etched sample is not an effective process to increase the efficiency of the cells (see Table 10, the silica samples, made by doctor blade method and loaded once).

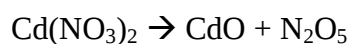
	I(sc) (mA)	V(oc) (V)	FF	eff%
not etched	6.60	0.48	0.53	1.40
Etched	7.10	0.50	0.49	1.46
etched and heated	7.33	0.50	0.43	1.31

Table 10. Solar measurement variables for etched, not-etched and both etched and heated samples.

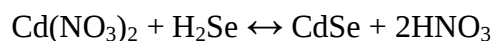
4.3.10. Effect of Calcination Temperature on the Solar Cell Performance of the Silica and Titania Samples

Calcination temperature is also an important factor on efficiency of the cells, because the temperature directly affects the structure of metal oxides and silica or metal titanate. And burning process of surfactants is directly relevant to calcination step.

At around 150 °C, the $\text{Cd}(\text{NO}_3)_2$ salt species are converted to CdO:



If there is any $\text{Cd}(\text{NO}_3)_2$ remains, HNO_3 forms upon reaction with H_2Se :



This reaction is an equilibrium reaction, because HNO_3 acid reacts with CdSe to produce H_2Se gas.

Another important reaction that occurs with temperature is burning of the surfactants. Around 250°C is enough for burning surfactants. Existence of surfactants may cause efficiency problems, because they are insulator and can generate resistance and limits the diffusion of the electrolyte during the operation of the cells. Figure 44 shows the performance of the silica and titania samples, calcined at different temperature and reacted with H₂Se under similar conditions.

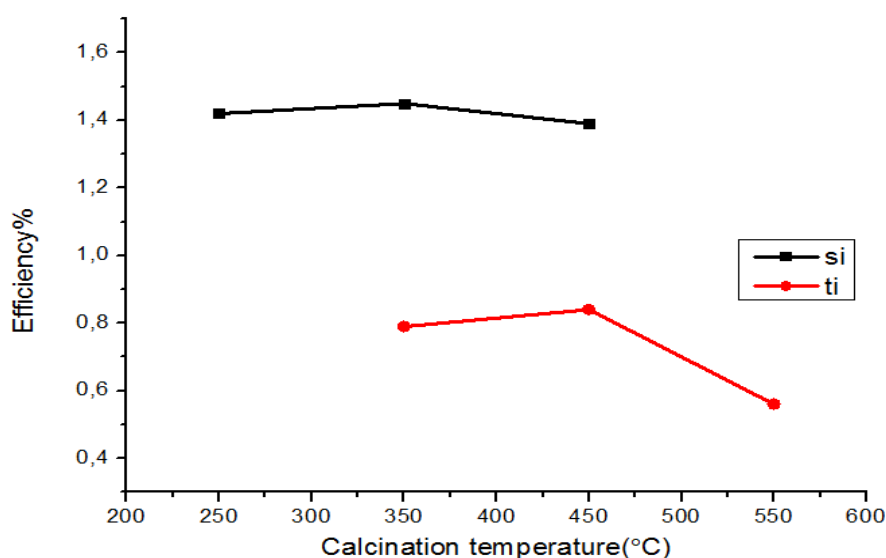


Figure 44. Solar efficiencies of silica and titania samples at different calcination temperature.

At 250°C, the titania sample could not be measured, because the films are not stable and fall apart while treating with the electrolyte solution. The titania samples at low calcination temperatures have rigidity problems but the silica samples are fine. At 250°C, 350°C and 450°C, the silica samples give almost the same efficiencies. The silica network is more rigid than titania network, where even 250°C is enough for the silica samples to rigidify and remain on the FTO

surface during solar cell measurements. The titania samples have maximum efficiency at 450°C but 350°C is also enough for stable and efficient cells. However, at 550°C the mesoporous titania collapse and bulk titanates forms as a result their reactivity with H₂Se gas drops drastically. Notice that the titania samples, calcined at 550°C, have lighter color and naturally lower efficiency.

4.3.11. Silica and Titania Systems with Different Cd(II) Ratios

One of the most important effects on efficiency is naturally concentrations of cadmium salt. The solar light and CdSe interaction and promotes electron(s) from the CdSe's valance band to its CB. Therefore, there is a direct proportion between the CdSe quantity on the films and the efficiency of the films. However, adding more Cd(NO₃)₂ salt does not produce more CdSe particles. According to EDX data of different concentrations of CdSe films; surprisingly; 8 Cd/surfactants mole ratio sample has the greatest amount of CdSe. Nevertheless, amount of the CdSe and efficiency are not directly proportional. Because one of the important effect on efficiency is to transfer the photo-generated-electron(s) from the VB of the CdSe particles to the CB of titania. In this step, maybe the amount of CdSe is important but interaction area between CdSe nanoparticles and titania sphere is more important. In higher amounts of CdSe; there can be passive CdSe nanoparticles. According to solar measurements of the silica and titania systems, there are some similarities and differences.

The si4 sample has the lowest efficiency, because its concentration is also the lowest. Its color also lighter and more transparent that the 4-mole ratio is

seems low for an efficient solar cell. The efficiencies of si6, si8, and si10 are very similar to each other (the efficiency difference is below 5% between two samples, this may not be a significant difference). One can also increase the amount of CdSe nanoparticles in the anode by multiple loadings. But one loading, in the 6-mole ratio samples seems to be enough; there is no need to go to 8 or 10 mole ratios. It has already been established that above 8-mole ratio bulk CdO formation starts. [25] The extra CdO particles, as a result the CdSe particles are over the electrode surface and not effective, they are passive.

Similarly, the ti4 sample has the lowest efficiency of all samples investigated in this thesis; its color is very light. In titania system, ideal concentration is also 6. While going to 8 and 10 mole ratios, the efficiency of the cells decreases. The color of the ti10 sample is very dark but it shows nearly the same efficiency with the lightest ti4 sample. The problem of the ti4 is scarcity of CdSe, it's likely that the CdTiO₃ is coated by the excess TiO₂ that makes the samples less reactive towards H₂Se reaction and the problem of ti10 is the same as in the silica samples, excess CdO formation over the surface of the electrode and no use of these CdSe nanoparticles in the conversion (light to electricity) process, see Figure 45.

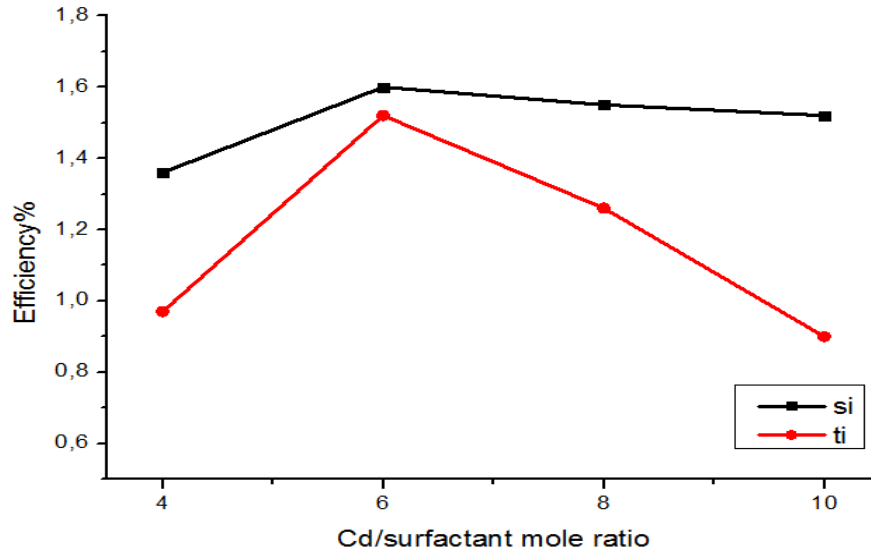


Figure 45. Efficiencies of silica and titania systems with different Cd/surfactant mole ratios.

4.3.12. Loading Dependence of the Silica and Titania Samples

Number of loading is another important parameter that directly affects the efficiency. Increasing the number of loading naturally increases the Cd(II) amount in the samples. At first loading; the solution-contains Cd(II) cations, surfactants and silica or titania source, and ethanol- fills the porous of the anatase template. After calcination step, ethanol vaporizes; surfactant burns and their places create new mesopores. Second and third loadings partially fill the new pores and the remaining pores of the anatase film. By many loadings, one can increase the amount of Cd(II) in the pores with an expense of losing pores among the titania particles in original anatase film; this may cause diffusion problems, diffusion of the electrolytes, during operation of the solar cell. In the silica system, many loading means incorporation of lots of insulating silica and that much of silica

may cause efficiency problems in the solar cells. Solar measurement on the 4, 6, and 8 Cd(II)/surfactants mole ratio samples, loaded 1, 2, and 3 times show that, in all compositions, 2nd loading increases the efficiency around 40-50%, but the 3rd loading does not increase the efficiency much. In all compositions, some of the samples, loaded 3 times have larger efficiency some have lower efficiency. As a result, 3rd loading for all compositions, it can be concluded that 3rd loading does not change the efficiency significantly.



Figure 46. Photographs of the 4, 6, and 8-Cd(II)/surfactants mole ratio samples loaded once and reacted with H_2Se (left to right).

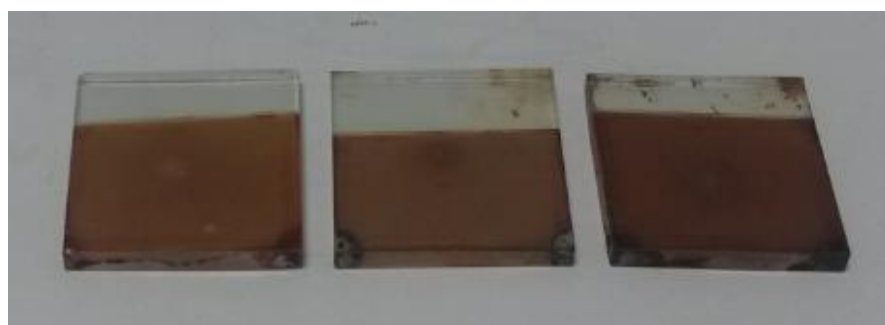


Figure 47. Photographs of the 4-Cd(II)/surfactants mole ratio samples loaded 1, 2 and 3 times and reacted with H_2Se (left to right).



Figure 48. Photographs of the 6-Cd(II)/surfactants mole ratio samples loaded , 2 and 3 times reacted under H_2Se (left to right).

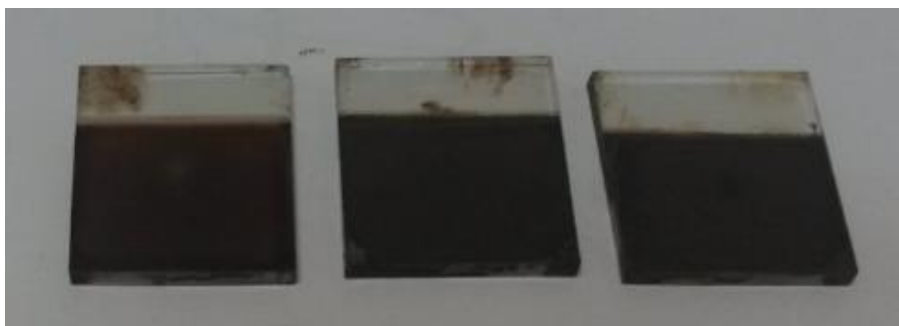


Figure 49. Photographs of the 4-Cd(II)/surfactants mole ratio samples loaded 1, 2 and 3 times and reacted with H_2Se (left to right).

	1st loading	2nd loading	3rd loading
si4	0.75	1.10	1.12
si6	0.88	1.35	1.25
si8	1.01	1.41	1.49

Table 11. Efficiencies of the si4, si6 and si8 samples with different loadings.

4.3.13. Effect of Adding Different Transition Metal Cations into the above Anode Materials and Their Effects on the Solar Cell Efficiency

Incorporating some metal cations into the CdSe quantum dot sensitizers is a widely-used method to increase the efficiency of CdSe sensitized solar cells.[76] [77] [78] Even a small amount of different metal cation can play a very important role in the electron transfer process in the cell. Mn(II), Co(II), Fe(III), Cu(II) and Zn(II) cations were used for this purpose and their impact on efficiency was clearly observed.

4.3.13.1. Mn(II) Incorporation into Silica and Titania Samples

Mn(II) is one of the cation that increases the cell efficiency in both silica and titania systems. The increase on the efficiency of the cell is not detectable at very low Mn(II) samples, upon reaching to 0.15 Mn(II)/Cd(II) mole ratio, the efficiency of the cell increases in significant amounts (ca.12% for the silica, 40 % for the titania system), see Figure 50. In the silica system, after calcination SiO_2 , CdO and MnO are likely forming separately in close vicinity but in the titania system, it is likely to form a solid solution of $\text{Cd}_{1-x}\text{Mn}_x\text{TiO}_3$, because both MnTiO_3 and CdTiO_3 have the same structure with similar unit cell parameters. However the CdO and MnO, in the silica system, form different structure and it is likely that they do not mix with each other as good as in the titania samples. Therefore the differences in structure of the oxides, as a result affects the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ formation may result the difference in increasing the efficiency of these two cells.

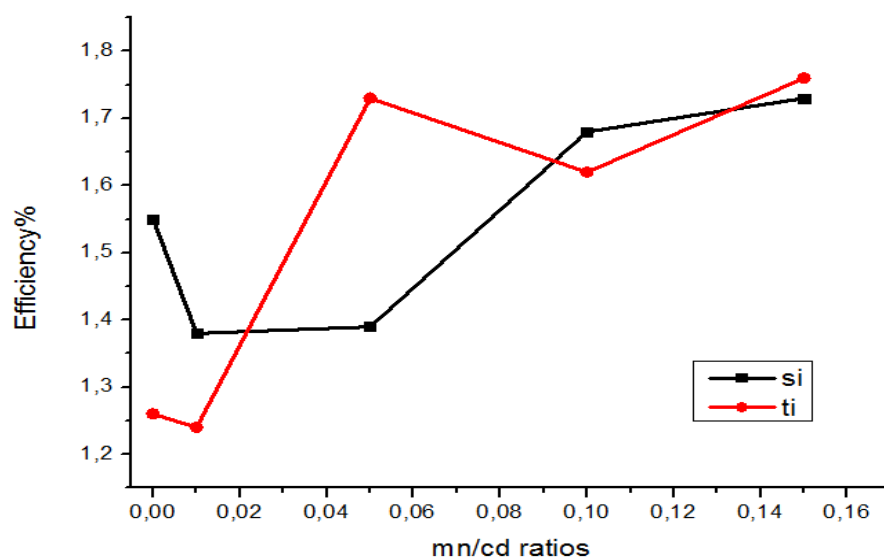


Figure 50. Efficiencies of the si8 and ti8 samples with different Mn(II)/Cd(II) ratios.

4.3.13.2. Co(II) Incorporation into Silica and Titania Samples

Co(II) incorporation in both silica and titania systems has no effect on the cell performance at very low concentrations but it has a negative effect at higher concentrations. The efficiency of the cell decreases with increasing Co(II) concentration in both silica and titania down to zero at 0.15 Co(II)/Cd(II) mole ratio, see Figure 51.

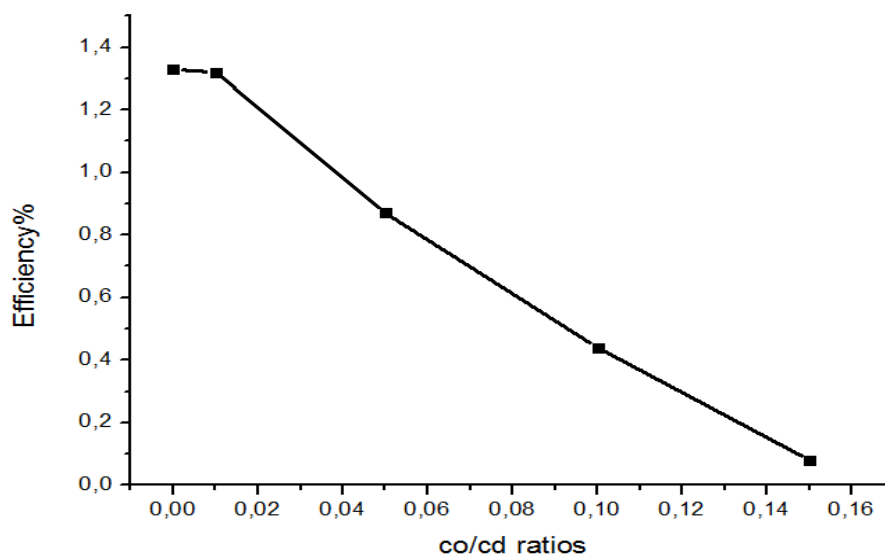


Figure 51. Efficiencies of the ti8 samples with different Co(II)/Cd(II) ratios.

4.3.13.3. Cu(II) and Fe(III) Incorporations to Silica and Titania Samples

Cu(II) and Fe(III) cations also decrease the efficiency of the cells. Fe(III) is the worst cation that even a small amount of Fe(III) cation makes the efficiency to go to zero. However, Cu(II) is not as bad as Fe(III), even shows better performance than Co(II) samples. At 0.15 Cu(II)/Cd(II) ratio, the cell has 0.57% efficiency. There is about 40% efficiency lost in the Cu(II) incorporated samples compared to the Cu(II) free sample, this value is 94 % for the Co(II) and 100% for the Fe(III) incorporated samples, see Figure 52.

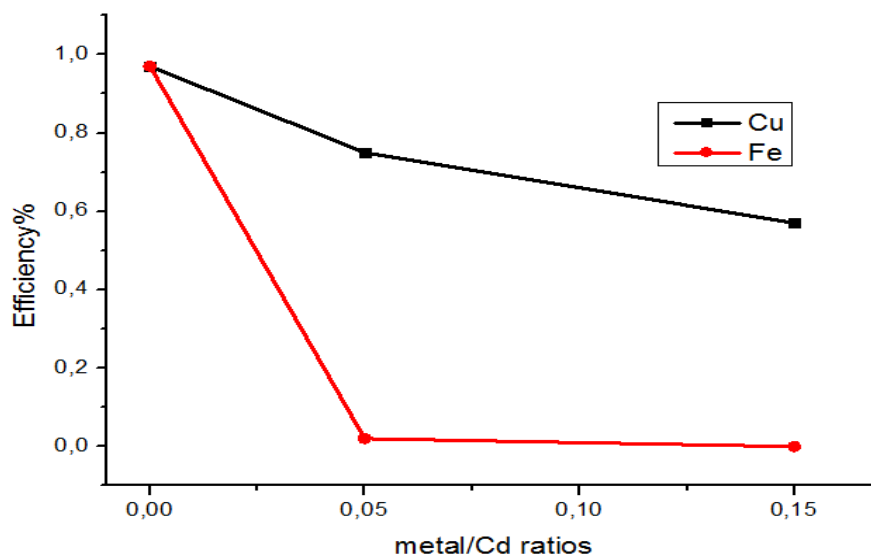


Figure 52. Efficiencies of the ti8 samples with different Co(II)/Cd(II) or Fe(III)/Cd(II) ratios.

Overall, Mn(II) is the only cation that increases the efficiency of the solar cell and the increase is quite significant, about 40%. The Fe(III) incorporated samples are the worst; even at 0.05 mole ratio measured current from cell disappears. The Cu(II) and Co(II) samples also display lower efficiencies but the Cu(II) samples are better than the Co(II) samples. Figure 53 compares all the measurements in the same graph.

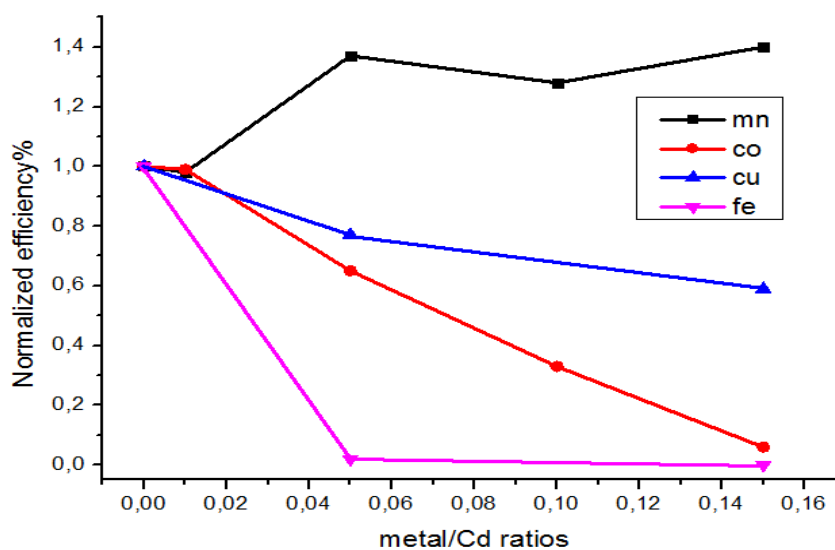


Figure 53. Efficiencies (normalized to the undoped ti8 sample) of the ti8 samples with different metal/Cd(II) ratios.

4.3.13.4. Zn(II) Incorporation into the Silica and Titania Systems

For the Zn(II) salt; there is another problem: instability while measuring the efficiency of the cell. ZnSe reacts with sulfide anion in the electrolyte to give ZnS and ZnS has a very high band gap, 2.7 eV; so the efficiency is nearly equal to zero (efficiency = 0.04%). When brown ZnSe film is put into electrolyte; suddenly its color turns to pale yellow, due to formation of ZnS. Figure 54 shows a set of photographs of these electrodes before and after dipping into electrolyte solution.

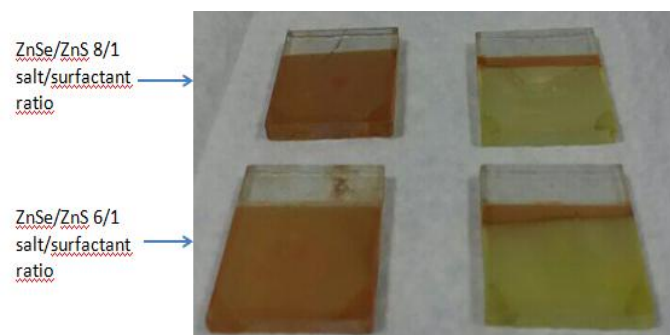


Figure 54. Picture of the meso-ZnSe-TiO₂-TiO₂ films before and after solar measurement.

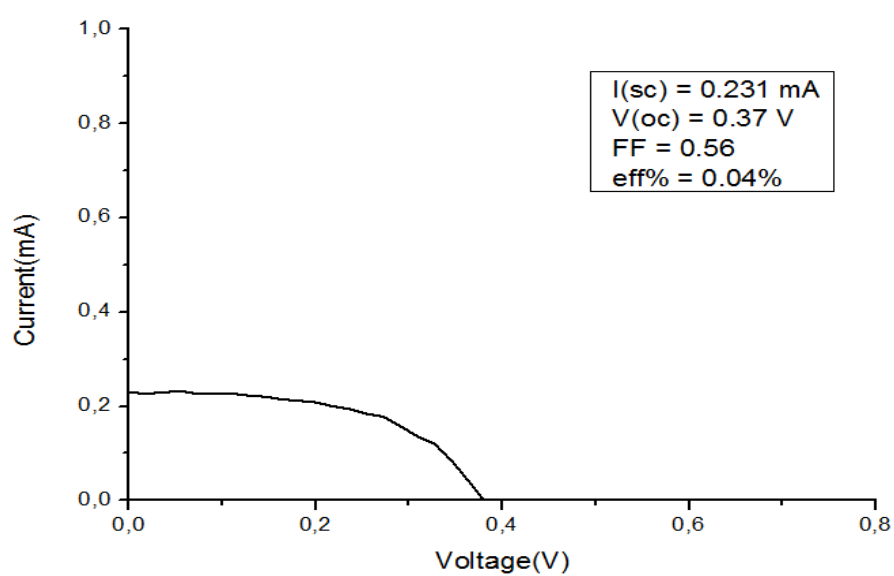


Figure 55. I-V curve of the meso-ZnSe-TiO₂-TiO₂ film at 6 Zn/surfactant ratio.

Chapter 5:

Conclusion

Molten salt self-assembly and solid-gas reaction processes has been employed, using cadmium salt-silica/titania-surfactant system and H_2Se reactions, to prepare anode materials for quantum dot sensitized solar cells. For this purpose, 3 different films were prepared: meso-CdSe-SiO₂-P25, meso-CdSe-TiO₂-P25 and meso-CdSe-TiO₂. The XRD diffraction around $1.5\text{-}2^\circ$, 2θ , shows the surfactant domains are organized in mesophases upon coating the MASA solution. Annealing around 450°C generates mesopores and these mesoporous structures react effectively with the H_2Se gas to produce the CdSe nanoparticles. We found out that the silica samples are more reactive than the titania samples; because in silica samples, CdO reacts directly with H_2Se , however in titania samples, CdTiO_3 reacts with H_2Se to produce CdSe and TiO₂. The 4, 6, 8 and 10 Cd/surfactant mole ratio silica and titania samples were prepared and based on the EDX results, the maximum CdSe amount has been obtained from the 8 mole ratio in both silica and titania systems. In titania systems, the H_2Se reaction produces more selenium (Se) as a byproduct than in the silica systems. The solar cell measurements were carried mostly using the samples prepared using P25; because the P25 samples have 2 times better absorbance. The P25 samples use 52% of the solar light, but the samples without P25 can absorb only 25% of the light. Therefore the maximum efficiency of the P25-free sample is around 0.68%. In order to have comparable results (to have the same thickness of film), the solar measurements

were made by spin coating method, instead of doctor blading method. The following parameters were optimized to determine their effects; the i) electrolyte must be freshly prepared, because sulfide/poly sulfide couple is not stable in solution and this can decrease the efficiency almost to half, ii) the mesoporosity increases the efficiency almost 2 times; so usage of surfactant is so important, iii) coating the anode film with a protecting layer is also important, coating with ZnS or CTAB eliminates some the shortcuts in circuit and increase efficiency around 50%, iv) the optimum calcination temperature is 450°C in both titania and silica systems, in the silica system even at 250°C and 350°C efficiencies are very close to 450°C, but in titania system, the film is not stable at 250°C and at 350°C and 550°C efficiencies are lower than 450°C, v) number of loading is another important parameter that second loading increases efficiency about 40%, third loading is not as effective as second loading (efficiency remains the same or decreases) and it can be conclude that loading twice is optimum, vi) the samples prepared using 6 and 8 Cd/surfactant mole ratio samples of both silica and titania systems show greater efficiencies. Efficiency is not proportional with the Cd/surfactant ratio; there is an optimum point around 6 and 8 mole ratio. This result can be supported by the Raman results.

In the Raman measurements over the conductance FTO, it has been shown that the samples were light-sensitive and the CdSe peak intensity decreases over time. Decreasing of the CdSe peak intensity is an indication of that CdSe is donating the electrons to TiO₂ and then to FTO effectively. The CdSe amount is the greatest in 8 Cd(II) ratio samples but the optimum amount is around 6-8 Cd(II)

ratio for a better solar performance. Since, CdSe amount, in the silica samples, is always more than in the titania samples, the silica systems have slightly better efficiency than the titania systems. Even though, the silica samples have more CdSe, Raman peak intensities show that electron transfer in titania samples is easier. Having more CdSe and transferring electron from CdSe are competed variables. Removing silica with HF etching reaction doesn't affect the efficiency and it shows that silica layer does not prevent the electron transfer. Doping metal ions effect the efficiency; Mn(II) increases and Co(II), Fe(III), Cu(II) and Zn(II) decreases the efficiency. In titania system, Mn(II) doping increases 40% of efficiency and it can be conclude that Mn(II) is very adaptable with titania system.

Overall, the MASA process works well in preparing anode electrodes for the quantum dot sensitized solar cells and further optimizations are necessary to increase the solar cell performance of these materials.

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