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Hybrid Solar Paint Based on TiO2/CdS Nanomaterials

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In this communication, surface modified CdS and TiO2 nanomaterials were synthesized by chemical route and sol-gel method respectively and characterized using XRD, UV-Visible and electron microscopy. A mixed phase of TiO2/CdS has been synthesized by a modified SILAR procedure with as-synthesized TiO2. As a result of the SILAR process, the properties of TiO2/CdS heterojunction prepared using a specific ratio of TiO2 and capped CdS will be different from those of TiO2/capped CdS heterojunction. Both materials will be subjected to solar cell applications.

Keywords: TiO2, CdS, capped CdS, photovoltaic effect.

1. Introduction

Energy demand is still on the rise throughout the world. Presently, fossil fuels and nuclear energy are the primary energy sources. One of the major problems is the limited availability of resources. A great deal of effort has been made in the past few decades to develop new alternative sources of energy in order to resolve these problems. Solar energy is one of these alternative energy sources and is reliable, clean, and free, and can be accessed worldwide. It is widely used for solar cell applications to convert sunlight directly into electricity by using photovoltaic cells. A significant part of the installed modules is silicon-based. There is a high cost associated with the production of silicon solar cells because higher energy needed for production and it takes a lot of time for preparation a single cell. Therefore thin film technique facilitate the process of producing solar cell by reducing material consumption, production costs and also reduce the preparation time. A variety of semiconductor assemblies and metal nanoparticles have received tremendous interest in the last decade, while significant efforts have been made to create systems that convert solar energy into electricity with high efficiency. [1-3][24]. for these techniques, inorganic semiconductors based nanoparticles such as CdX (X = Se, S and Te) and TiO_2 nanoparticles have been widely used. There has been a great deal of interest in TiO2 because it is affordable, abundantly available, safe, environmentally benign, as well as biologically and chemically stable [27][34][37]. Because of its large band gap energy of 3 – 3.2 eV, only 2–4% of solar light can be absorbed in the small UV fraction, thus preventing its efficient absorption of visible light [4-7][26][28]. To harvest photons in the visible spectrum, one important strategy is to sensitize TiO2 using dyes and metallic nanoparticles as sensitizers, which increase the photoactivity of TiO2[32][33]. The use of narrow band gap inorganic semiconducting materials in photovoltaic (PV) devices in order to increase their energy production has been proposed as a promising sensitizer [8-10][29][31][35]. When two semiconductor particles are combined, a semiconductor material with a large band gap and an energetically low-lying conduction band can be sensitized by a semiconductor material with a small band gap and a high conduction band [22]. It is possible to create a more efficient and longer charge separation by injecting charge into one semiconductor, which can be applied to photocatalysis and solar energy conversion [11-13][36]. Due to their size-tunable optical properties, cadmium chalcogenide semiconducting nanocrystals (CdX; X = S, Se, and Te) are highly desirable as sensitizers for TiO2 [14-16][25]. Particularly, CdS is a highly competent photoconductor and effective sensitizer material, as its energy level matches TiO2's. Nanocrystalline semiconductors have been extensively investigated as photoanodes in photoelectrochemical cells due to their suitable band gap, long lifetime, important optical properties, outstanding stability, and easiest fabrication. [21]. The use of such semiconductor sensitized electrodes with a low bandgap may offer advantages over dye-sensitized electrodes.

It is possible to optimize electron injection force through confinement effects. In addition, it is possible to produce high stability electrodes and ideal sensitizers by modifying their surfaces. A TiO2/CdS nanoparticles-based composite is mixed with a solvent to form a paste, which is applied as one-step paint to a transparent conducting material that produces electricity when illuminated [18]. It has already been reported that TiO2/CdS composites can be generated by a variety of methods. Preparation of CdS nanoparticles by the chemical precipitation method using Mercaptothanol as the capping agent. An approach to efficiently synthesize TiO2/CdS composite nanoparticles paste at room temperature by using the Modified SILAR method and making thin films by using the Doctor Blade method is outlined in this paper.

2. Experimental Procedure

2.1. Materials

Titanium tetra-isopropoxide($C_{12}H_{28}O_4Ti$) of M.W. = 284.215 g/mol., Cadmium Chloride ($CdCl_2$) of M.W. = 201.32 g/mol., Sodium Sulfide ($Na_2S.\ 9H_2O$) of M.W. = 240.18 g/mol., Mercaptoethanol (C_2H_6SO) of M.W. = 78.133 g/mol. had been used as starting materials. Ethanol and Distilled water have used as solvents.

2.2. TiO_2 Preparation Procedure

Titanium tetra-isopropoxide(TTIP) was used as a starting material to prepare TiO_2 nanoparticles by sol-gel method. 5 ml of TTIP was dropped in to 10 ml of ethanol and 20 ml distilled water was added to the solution under at room temperature under vigorous stirring until form a sols(white precipitate). To adjust the pH of the solution Nitric acid (HNO_3) was used. After that the solution is aged for one day for transform sols in to gels. In order to remove the water and organic matters the gels were dried under 120 ºC for 2 hours. Then the dried gels were annealed under 450 ºC for 2 hours to get the TiO_2 nano-crystalline material.

2.3. CdS Preparation Procedure

CdS nanoparticles were prepared in a aqueous medium by chemical precipitation method starting from cadmium chloride ($CdCl_2$) and sodium sulfide ($Na_2S.9H_2O$) using Mercaptoethanol (C_2H_6SO) as a capping agent. In this, 1M of $CdCl_2$ was added to 5 ml [20]. Mercaptoethanol (C_2H_6SO) under continuous stirring and maintains it for 30 minutes. Then 1M of $Na_2S.9H_2O$ was added slowly to the mixture under constant stirring for 1 hour.

2.4. TiO_2/CdS Paste Preparation

(a) By Modified SILAR method

The preparation of TiO_2/CdS was prepared by mixing 0.5 g of TiO_2 with 15 ml of ethanol/water in the ratio of 3:1 ratio under gentle stirring. After suspension, 100 µl of 0.1 M of sodium hydroxide was added to TiO_2 mixture. Then 2 ml of 0.1 M $CdCl_2$ was added to ethanol/water in the ratio of 1:1 and mixed with TiO_2 Slurry solution. After stirring, 30 min then the TiO_2 Slurry was added with 2 ml of 0.1 M Na_2S in ethanol/water in the ratio of 1:1. After that, the mixture was centrifuged at 7000 rpm. This cycle was repeated 8 times.

(b) Mechanical grinding of TiO_2 and capped CdS to form TiO_2/capped-CdS

In the preparation of TiO_2/capped-CdS, 0.5 g of TiO_2 and 0.5 g of capped-CdS were mixed and grinded well for few minutes. To the mixture, 1 ml of ethanol was added and made it as a slurry like paste material.

3. Results and Discussion

3.1. Characterization

The as-prepared materials TiO_2 and CdS are characterized by X-Ray Diffraction (XRD) using X-ray diffractometer XRD-6000: Shimadzu model with Cu radiation in the range of 20º- 70º for TiO_2 sample as shown in figure 1(a). It showed crystalline nature nanoparticles were synthesized with 2θ peaks lying at $2\theta = 25.4237^\circ$, $2\theta = 38^\circ$, $2\theta = 48.1621^\circ$, $2\theta = 55.36^\circ$, $2\theta = 63^\circ$, $2\theta = 75^\circ$. A good agreement was found between the diffraction data and JCPDS files # 21-1272 for all peaks in the XRD patterns. [19]. Crystallite size was obtained by Debye-Scherrer's formula given by equation.

$$D=K\lambda/ (\beta\cos\theta) \qquad \text{---------} \quad (1)$$

Where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the line width at half-maximum height. The average crystalline size obtained using this formula is about 5 to 10 nm.

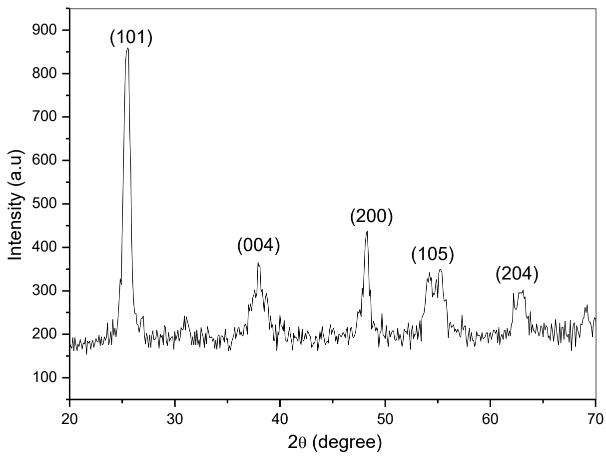

Figure 1(a). XRD Pattern of crystalline anatase-TiO_2

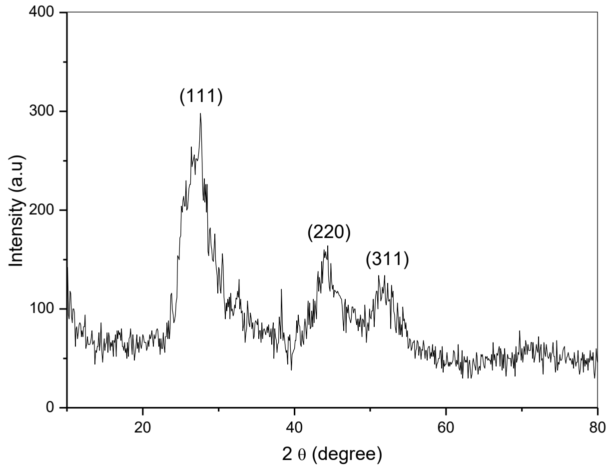

Figure 1(b). XRD Pattern of capped-CdS

In the figure 1(b) shown XRD pattern of CdS sample in that XRD peaks was found to be very broad while indicate the very fine grain size with 2θ peaks laying at 2θ = 32.0672º, 2θ = 45.8183º and 2θ = 84.3963º. The crystallite size was obtained by Debye-Scherrer's formula as given by equation 1. The average crystalline size obtained using this formula is about 1 to 5 nm.

UV-VIS spectra were recorded using a Spectro UV-VIS Double Beam UVD 3500. Figure 2 shows the absorption spectrum of TiO_2, and thiol capped CdS nanocrystalline samples. The absorption band onset were estimated around 365 nm for TiO_2 and 439 nm for CdS samples and the corresponding energy band gaps are 3.4 eV for TiO_2 and 2.51 eV for CdS samples respectively. The band gap of the semiconductors has been found to be particle size dependent. A decreasing particle size leads to an increasing band gap and a shifting of the absorption edge to a higher energy (blue shift). Figure 3 shows the absorption profile of TiO2/CdS heterojunctions prepared by SILAR and TiO2/capped-CdS heterojunctions prepared by grinding the two components in particular ratios. The peak positions around 365 and 440 nm in the mixed profile confirm the hetero-junctions mixed component

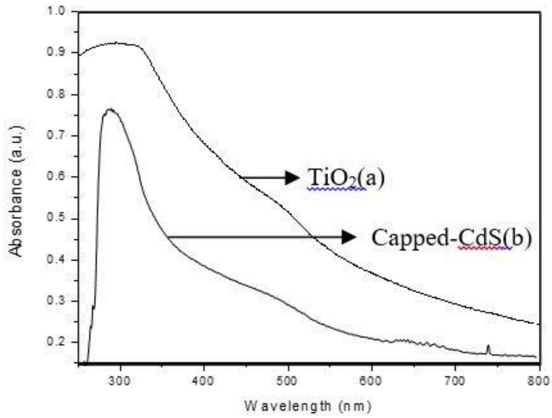

Figure 2. UV-Vis. spectra of TiO2 and capped-CdS

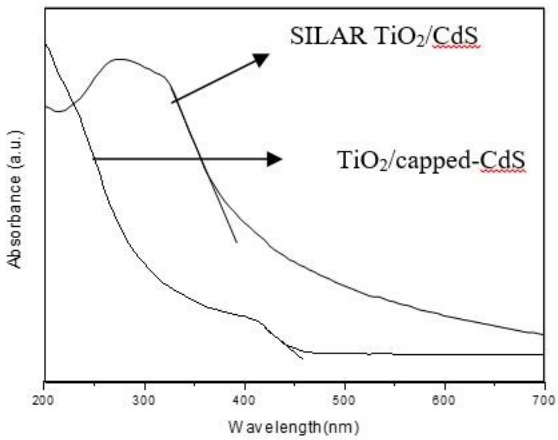

Figure 3. UV-Vis. spectra of TiO2/capped-CdS and SILAR TiO2/CdS

The morphology and size of capped CdS nanoparticles were observed by HR-TEM using JEOL JEM 2100 HR-TEM instrument. Figure 4 shows a sphere shaped CdS nanoparticles. It clearly shows that the particles size of <10nm and interplanar spacing of 0.33nm assigned to the (111) plane of the cubic CdS structure [23]. Inset shows SAED profile of electron diffraction ring pattern confirms the CdS nanoparticles in cubic crystalline structure.

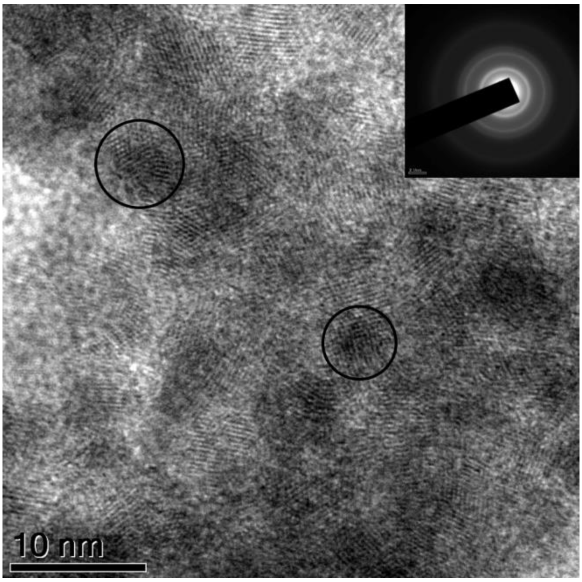

Figure 4. HR-TEM image of capped-CdS nanoparticles

Photoelectronic performance of the TiO_2/CdS nanocomposite films is an important issue to be investigated for these mixed hetero-junctions materials for the solar cell applications based on solar paint [17]. Initial steps have been taken in order to make hetero-junction based mixed TiO_2/CdS nanocrystalline material; (i) a thin film has been deposited on the glass plate by Doctor Blade method for two different TiO_2/CdS hetero-junction mixed nanocrystalline materials as shown in Figure 5- a huge difference in their color indicate their different particle size as well as its compositions of the thin film coating of TiO_2/capped CdS and SILAR TiO_2/CdS by doctor blade method.

(a) (b)

Figure 5. Doctor Blade coating of (a) TiO_2/capped CdS and (b) SILAR TiO_2/CdS

4. Conclusions:

Nanocrystalline TiO_2 and thiol capped CdS have been synthesized by sol-gel and chemical techniques respectively and characterized by XRD, UV-Vis, and TEM. TiO_2/CdS nanocrystalline hetero-junction has been synthesized by addition of $CdCl_2$ to a synthesized TiO_2. By grinding in a particular ratio of as-synthesized TiO_2 and capped CdS nanocrystalline material, it leads to form TiO_2/capped CdS hetero-junction. Combining with a suitable paint, these hetero-junction composites will exhibit characteristics suitable for flexible solar cell applications using screen printing techniques.

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