Sol-gel coupled hydrothermal synthesis of cactus structured TiO_2 for quantum dot sensitized solar cell

A. RANJITHA[a,*], M. THAMBIDURAI[b], N. MUTHUKUMARASAMY[c]
[a]*Department of Physics, Kongunadu Arts and Science College, Coimbatore, India*
[b]*School of Electrical and Electronic Engineering, The Photonics Institute (TPI), Nanyang Technological University, Singapore*
[c]*Department of Physics, Coimbatore Institute of Technology, Coimbatore, India*

Nanocrystalline TiO_2 thin films have been prepared by hydrothermal method. CdS quantum dots have been incorporated into TiO_2 thin films using simple precursors by SILAR method and the assembly of CdS quantum dots with TiO_2 thin films has been used as photo-electrode in quantum dot-sensitized solar cells. X-ray diffraction results showed the formation of rutile phase TiO_2. The absorption spectra reveals that the absorption edge of CdS quantum dot sensitized nanocrystalline TiO_2 thin films shifts towards longer wavelength side when compared to the absorption edge of TiO_2 thin films. The efficiency of the fabricated CdS quantum dot sensitized TiO_2 thin film based solar cell is 1.5%.

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1. Introduction

Titanium dioxide has received considerable attention over the past two decades owing to their unique optical and electrical properties. TiO_2 is an attractive material for many applications such as transparent electrodes [1], gas sensors [2], photocatalytic [3] photo-electrochemical cells [4], self cleaning glasses [5] etc. Nanocrystalline TiO_2 thin films is being used as n-type electrode in dye sensitized photo-electrochemical solar cells and is a promising material for quantum dot sensitized solar cells. However, TiO_2 absorbs only about 5% of the solar radiation, resulting in poor conversion efficiency when used in solar cell applications. Because of the high cost of the typical organic dyes such as N719, it is necessary to develop alternate inexpensive light harvesters. Quantum dot sensitized solar cells have established themselves as an alternative to conventional solar cells owing to their remarkable power conversion efficiency. The use of semiconductor quantum dots as sensitizer has some advantages when compared with the conventional systems. The band gap of the nanocrystals can be adjusted by changing their size so that the absorption spectrum can be tuned to match the spectral distribution of sunlight [6]. Also these quantum dots can use hot electrons or generate multiple charge carriers using a single photon [7]. CdS quantum dots with broad tunable band gap (2.4 – 4.2 eV) could give rise to new opportunities to harvest light in the visible region of solar spectrum [8], and inject the photo-induced electrons into the conduction band of wide band gap semiconductors, leading to the improvement of the energy conversion efficiency. For this purpose, CdS has been successfully deposited onto a mesoporous TiO_2 surface by chemical bath deposition [9], successive ionic layer adsorption and reaction [10], spray pyrolysis deposition [11] and photodeposition [12]. Xia et al [13] have prepared TiO_2 nanowires by thermal annealing of anodized Ti foil. They have reported that CdS quantum dot is a good candidate for sensitizing TiO_2 nano wires and has the potential to improve the solar energy conversion efficiency of TiO_2 based solar cells. Prabakar et al [14] have sensitized TiO_2 films using CdS quantum dots for solar cell applications by chemical bath deposition technique. They have reported that the increase of the dipping time of TiO_2 film in the CdS solution reduces the amount of quantum dots adsorbed on nanoporous TiO_2 and this in turn limits the redox reactions in the electrolyte. Highly porous TiO_2 networks with reduced grain boundary yield multiple carrier generation due to the quantum confinement.

In the present work, cactus structured TiO_2 was synthesized by two step process. Step 1 involves the formation of TiO_2 thin film by sol-gel method and Step 2 involves the hydrothermal treatment of the prepared TiO_2 thin film. The two step process was adopted, in order to increase the adhesion and film stability. CdS quantum dot sensitized TiO_2 based solar cells have been fabricated and their characterizations have been studied.

2. Experimental

2.1. Step 1

TiO_2 thin films have been synthesized by sol-gel dip coating method. The sol has been formed by mixing titanium tetra iso-propoxide and acetyl acetone and poly ethylene glycol 400 (PEG 400) in the molar ratio 2:1:0.5 in ethanol. Acetyl acetone slows down the hydrolysis and poly condensation reactions while PEG 400 was used as

stabilizer. The solution was magnetically stirred for two hours. Then cleaned glass plates have been dipped into the sol and dried at 100°C for 30 minutes. The obtained TiO_2 films were then annealed at 500°C for one hour to obtain TiO_2 thin films. The prepared film was used as a template for hydrothermal method.

2.2. Step 2

To a mixture of concentrated HCl and deionised water (1:1), required amount of titanium (IV) butoxide was added and stirred for one hour. The solution was then transferred to autoclave. The TiO_2 film prepared by sol-gel dip coating method was placed in the teflon-lined stainless steel autoclave containing the solution. Then it was hydrothermally treated at 180°C for five hours. The film was then rinsed in deionised water and dried at 100°C for 30 minutes.

CdS quantum dots have been deposited onto TiO_2 thin film by successive ionic layer adsorption and reaction (SILAR) method. 0.1M of cadmium nitrate in ethanol was taken as cationic pre-cursor solution and 0.1M of sodium sulfide in ethanol was taken as anionic pre-cursor. The hydrothermally treated TiO_2 thin film was dipped in cationic solution for 15 seconds for adsorption of cadmium ions and rinsed in deionised water to remove loosely bounded Cd-species. Then it was dipped in anionic solution for 15 seconds and rinsed in deionised water. The sulfide ions react with adsorbed cadmium ions forming CdS on nanocrystalline TiO_2 thin film. The obtained film was then dried at 100°C.

X-ray diffraction pattern have been recorded using XPERT-PRO diffractometer system operating with Cu K_α radiation. Surface morphology of the films has been studied using JEOL-6390 scanning electron microscopy. Optical absorption spectra have been recorded using JASCO-UV-VIS-NIR spectrophotometer (JASCO V570). Sandwich type photoelectrochemical solar cell has been fabricated using the CdS quantum dot sensitized TiO_2 thin film as photoelectrode. Pt coated ITO was used as the counter electrode. 0.1 M lithium iodide and 0.03M iodine were dissolved in acetonitrile and was used as the electrolyte solution. The J-V characteristic of the cell was recorded using a Keithley 4200-SCS meter. A xenon lamp source (Oriel, USA) with an irradiance of 100 mW/cm^2 was used to illuminate the solar cell (equivalent to AM1.5 irradiation).

3. Results and discussion

Fig. 1 (a, b) shows the x-ray diffraction pattern of TiO_2 thin film and hydrothermally treated TiO_2 thin film respectively. Figure 1a shows the formation of anatase TiO_2(JCPDS card No. 894203), whereas rutile phase has been observed for hydrothermally treated TiO_2 thin film. The hydrothermal process has activated the phase transformation of TiO_2 from anatase to rutile phase at a low temperature. Observation shows that the width of the diffraction peak slightly becomes wide with hydrothermal treatment, indicating enhancement in crystallization of TiO_2 with formation of larger TiO_2 crystallites. The inset of Fig. 1 shows the x-ray diffraction pattern of CdS quantum dot. All the diffraction peaks in the pattern correspond to the hexagonal phase of CdS(JCPDS card No.890440). The grain size has been calculated using Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the x-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The grain size of CdS is found to be 5 nm.

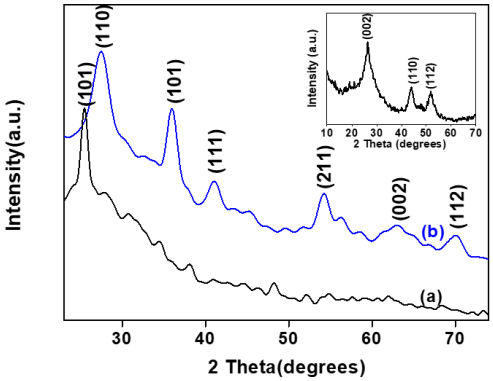

Fig. 1. X-ray diffraction pattern of (a) TiO_2 thin film (b) hydrothermally treated TiO_2 thin film Inset - CdS quantum dot

Fig. 2 (a) shows the SEM image of cactus structured TiO_2 nanorods. Initially formed TiO_2 nuclei act as building blocks for the formation of cactus like structures. With hydrothermal treatment, the TiO_2 nuclei act as energetically favored sites for further deposition of incoming TiO_2 species, leading to the formation of cactus like TiO_2 nanorods in large quantity via chemical growth process. The hydrothermal treatment allows the deposition of TiO_2 to follow more energetically favorable directions, resulting in growth of agglomerates. Branches would protrude from the surface of the agglomerates and extend in length, forming the observed cactus like structure. Fig. 2 b shows the SEM image of CdS quantum dot sensitized cactus structured TiO_2 thin film. Fig. 3 shows the EDX spectrum of CdS quantum dot sensitized TiO_2 thin film. The presence of Ti, O, Cd and S in the sample is clearly observed from the EDX spectrum.

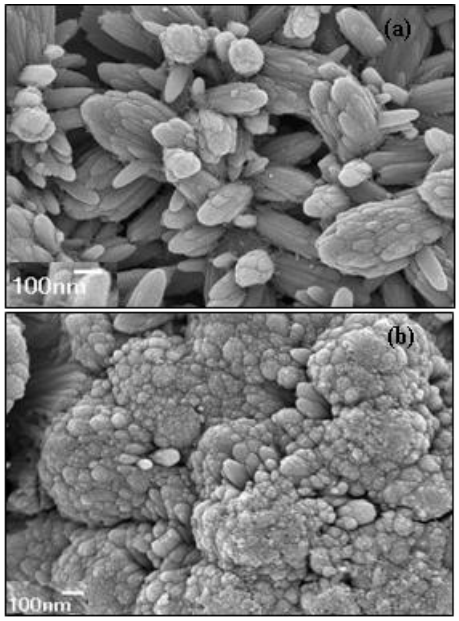

Fig. 2. SEM image of (a) Hydrothermally treated TiO_2 thin film (b) CdS quantum dot sensitized hydrothermally treated TiO_2 thin film

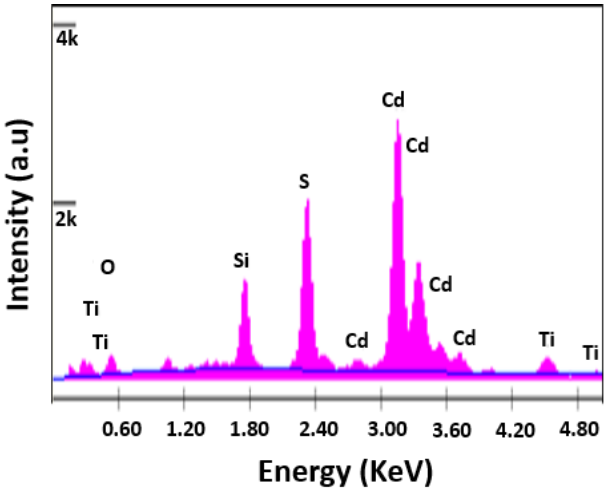

Fig. 3. EDAX spectrum of CdS quantum dot sensitized TiO_2 thin film

Optical absorption spectra of TiO_2 and CdS quantum dot sensitized TiO_2 thin films are shown in Fig. 4. The optical absorption spectra shows that the absorption edge of CdS quantum dot sensitized TiO_2 is shifted towards longer wavelength side (red shift) when compared to TiO_2 thin films.

The optical band gap energy has been calculated using the equation,

$$\alpha h\upsilon = A\,(E_g - h\upsilon)^n \qquad (2)$$

where, α is the absorption co-efficient, υ is the frequency of the incident radiation, A is a constant, E_g is the band gap of the material, h is the Planck's constant and n is equal to ½ for direct transition. Figure 5 shows the plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of TiO_2 and CdS quantum dot sensitized TiO_2 thin films. The band gap energy has been calculated and is found to be 3.7 eV and 3.6 eV for TiO_2 and CdS quantum dot sensitized cactus like TiO_2 respectively. The increase in absorption of light is ascribed to the change in surface morphology of the prepared thin film.

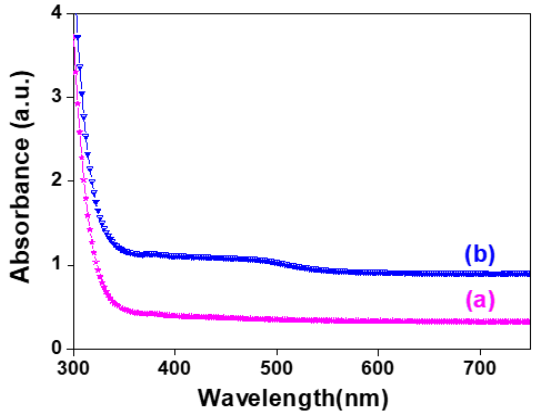

Fig. 4. Absorption spectra of (a) TiO_2 thin film (b) CdS quantum dot sensitized TiO_2 thin film

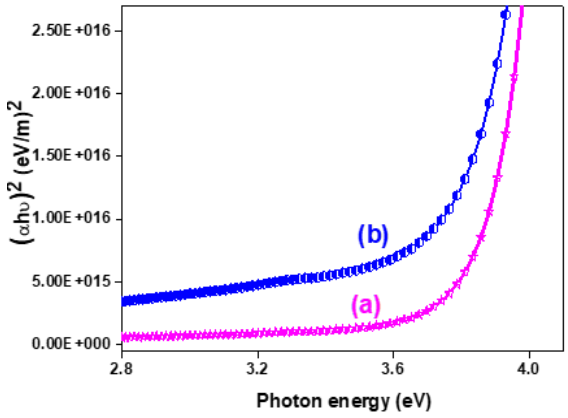

Fig. 5. Plot of $(\alpha h\upsilon)^2$ versus hυ of (a) TiO_2 thin film (b) CdS quantum dot sensitized TiO_2 thin film

The current density–voltage (J–V) characteristics of CdS quantum dot sensitized TiO_2 photoanodes are shown in Fig. 6. The CdS quantum dot sensitized TiO_2 shows an efficiency of 1.5% with short-circuit current density (J_{sc}) of 6.1 $mAcm^{-2}$, open-circuit voltage (V_{oc}) of 0.56 V and fill-factor (FF) of 0.44. The obtained power conversion efficiency was 1.5% for CdS quantum dot sensitized TiO_2 solar cell. CdS quantum dot sensitized TiO_2 thin film shows shift in absorption spectra which greatly influenced the absorption of solar energy, because of large extinction co-efficient, CdS quantum dot generates multiple electron-hole pairs per photon. The TiO_2 nanorods forms heterojunction with CdS quantum dots which leads to separation and transportation of electron – hole pairs to the

respective electrodes, ultimately leading to enhanced efficiency.

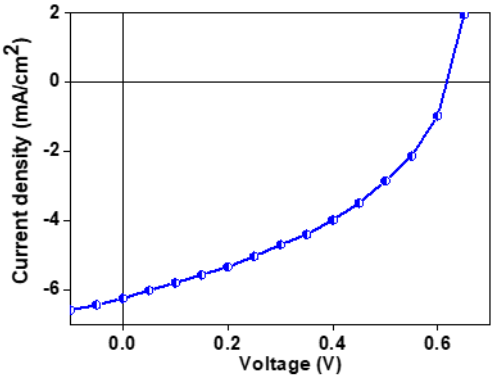

Fig. 6. J–V characteristics of CdS quantum dot sensitized TiO_2 thin film solar cell

4. Conclusion

Cactus structured TiO_2 nanorods were prepared by sol–gel coupled hydrothermal method. X-ray diffraction analysis reveals the formation of rutile phase TiO_2. The formation of cactus structured TiO_2 nanorods have been confirmed using SEM image. The CdS quantum dot sensitized cactus structured TiO_2 nanorods exhibited a power conversion efficiency of 1.5%.

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*Corresponding author: ranjichitra@Yahoo.co.in