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Chemically deposited TiO_2/CdS bilayer system for photoelectrochemical properties

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Abstract. **In the present investigation, TiO_2, CdS and TiO_2/CdS bilayer system have been deposited on the fluorine doped tin oxide (FTO) coated glass substrate by chemical methods. Nanograined TiO_2 was deposited on FTO coated glass substrates by successive ionic layers adsorption and reaction (SILAR) method. Chemical bath deposition (CBD) method was employed to deposit CdS thin film on pre-deposited TiO_2 film. A further study has been made for structural, surface morphological, optical and photoelectrochemical (PEC) properties of FTO/TiO_2, FTO/CdS and FTO/TiO_2/CdS bilayers system. PEC behaviour of FTO/TiO_2/CdS bilayers was studied and compared with FTO/CdS single system. FTO/TiO_2/CdS bilayers system showed improved performance of PEC properties over individual FTO/CdS thin films.**

Keywords. **TiO_2/CdS bilayer; chemical methods; PEC performance.**

1. Introduction

In the present day scenario, solar energy is playing a high-flying role as a primary energy source. In the last decade, the development of assemblies using semiconductor structures and metal nanoparticles has received marvelous interest, while significant efforts have been undertaken to obtain high efficiency solar energy conversion devices (Oliver 2006; Kamat 2007, 2008). In this framework, one of the most important semiconductor, titanium dioxide (TiO_2), has attracted great interest due to cheap, abundantly available, safe, environmentally benign, biologically and chemically stable properties. However, because of its large bandgap energy of 3·0–3·2 eV, only about 2–4 % solar light can be consumed in the small UV fraction preventing its efficient visible light absorption. In order to harvest photons in the visible light, one important approach is to sensitize TiO_2 by diverse materials like dyes and metallic nanoparticles as sensitizers which increases the photoactivity of TiO_2 in the visible range (Yu *et al* 2003; Karkmaz *et al* 2004; Chen *et al* 2005; Aprile *et al* 2008). Narrow bandgap inorganic semiconducting materials have been considered as promising sensitizers to enhance the utilization of sunlight for energy production in photovoltaic (PV) devices (Plass *et al* 2002; Sant and Kamat 2002; Niitsoo *et al* 2006). Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small bandgap and energetically high-lying conduction band. Charge injection from one semiconductor into another can lead to efficient and longer charge separation, which is expected to have possible applications in photocatalysis and solar energy conversion (Nasr *et al* 1998; Kongkanand *et al* 2008; Lee *et al* 2009). In particular, cadmium chalcogenide semiconducting nanocrystals (CdX; X= S, Se and Te) belonging to II–VI semiconductors are very attractive as sensitizers for TiO_2 due to their size-tunable optical properties (Peng and Peng 2001; Bilgin *et al* 2005; Robel *et al* 2007). Specially, CdS is one of the most competent photoconducting and effective sensitizer material, because its energy level matches with those of TiO_2. It is the most extensively studied nanocrystalline semiconductor as a photoanode in photoelectrochemical cells because of its suitable bandgap, long lifetime, important optical properties, outstanding stability and simplicity of fabrication (Biswas *et al* 2008; Chi *et al* 2008). It is suggested that such low bandgap semiconductor sensitized electrodes offer advantages over dye sensitized electrodes. The driving force for electron injection may be optimized through confinement effects; ideal sensitizer and highly stable electrodes may be produced by appropriate surface modification. Therefore, the semiconductor combination of TiO_2 and CdS were investigated widely (Chen *et al* 2006; Jang *et al* 2006, 2007; Robert 2007). It is very difficult for the two conventional methods to obtain uniform distribution of nanocrystalline CdS on TiO_2 and this is unfavourable for the improvement of the photoelectrochemical properties of CdS/TiO_2 film. Recently, soft chemical synthesis methods have opened new routes for preparation and fixation of inorganic materials. These are very simple methods for large scale uniform coating to persuade clean, dense and strong adhesion to substrate thin films (Hodes 2002). In order to alleviate reaction conditions, environmental impact and decrease the economic cost, synthesis of this material through soft chemical solution method would be a priority if the properties of the material could be retained. Accordingly,

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CBD and SILAR methods are environment friendly, low cost and low temperature soft chemical solution methods. The SILAR method is relatively a new and less investigated method, which is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which is used to deposit nanocrystalline thin films. CBD method is well suited for producing large-area thin films. Considering the current interest in the nanoparticles, CBD is an excellent method to deposit nanostructured films (Mane and Lokhande 2000; Pathan and Lokhande 2004; Patil *et al* 2009). In the present investigation, we report on the synthesis of novel nanocrystalline distinct TiO_2/CdS bilayers electrode by low temperature chemical methods and their structural, surface morphological, optical and PEC properties were studied. Enhanced PEC properties of TiO_2/CdS electrode as compared to bare FTO/CdS electrode has been observed and reported.

2. Experimental

The growth of TiO_2 thin film was carried out by SILAR method at room temperature. The schematic of SILAR method for the deposition of TiO_2 thin film is shown in figure 1. The source of cationic precursor was aqueous solution of 0·1 M Ti(III)Cl_3, 30 % HCl and anionic was 0·01 M NaOH. The well-cleaned fluorine-doped tin oxide (FTO) coated glass substrates were immersed in cationic precursor for 20 s, where complexed titanium species are adsorbed on it. To remove loosely bound titanium species from the FTO coated glass substrate, it was rinsed with double distilled water for 5 s. The FTO coated glass substrate was then immersed in an anionic precursor for 20 s, where NaOH reacts with adsorbed titanium species to form TiO_2 onto the FTO coated glass substrate. To remove excess or unreacted species or powdery deposit, again FTO coated glass substrate was rinsed with double distilled water for 5 s. In order to remove hydroxide from as-deposited film and to improve the crystallinity, films were heat treated at 673 K for 2 h. Figure 2 shows schematic of the chemical bath deposition

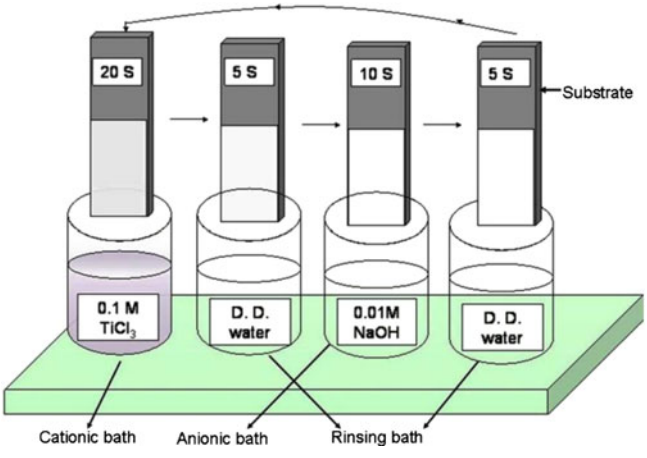

Figure 1. Schematic experimental set up of SILAR method for deposition of TiO_2 thin films.

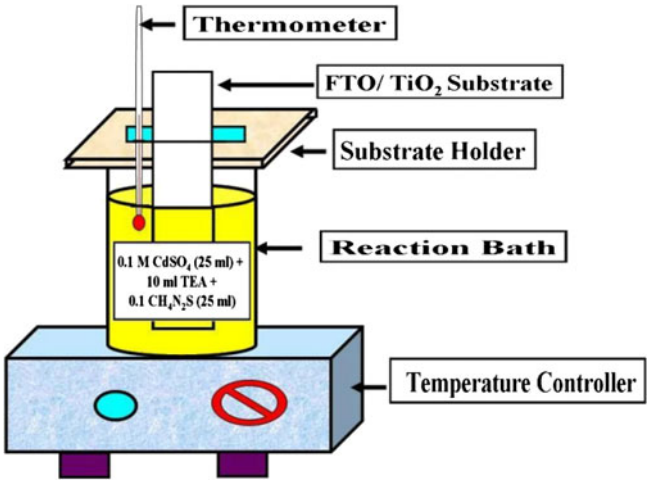

Figure 2. Schematic experimental set up of CBD method for deposition of CdS thin films.

(CBD) method for the deposition of CdS, on the previously deposited TiO_2 thin film on FTO substrate. The CdS thin films were prepared by CBD method. The bath composition was prepared as 25 ml (0·1 M) $CdSO_4$ + 10 ml triethylamine (TEA), the pH of the solution maintained at 12·0 by drop wise addition of liquor ammonia. The resultant solution was mixed with 25 ml (0·1 M) thiourea. The solution was stirred for a few seconds and then transferred into another beaker containing cleaned FTO coated glass and FTO/TiO_2 coated glass substrates. The prepared bath was heated at 353 K with constant stirring and well adherent, uniform deposition of CdS was carried out after 30 min.

The structural, surface morphological and optical properties were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical absorption. To study the structural properties of the films, X-ray diffraction analysis was performed on Philips (PW-3710) diffractometer with copper target ($\lambda = 1{\cdot}5440$ Å). The surface morphological studies of the films were carried out by scanning electron microscopy using model JEOL-JSM 6360 (JAPAN). Optical studies were carried out by systronics-119 spectrophotometer over a wavelength range of 300–850 nm. PEC studies of CdS and TiO_2/CdS films deposited on FTO coated glass substrate was studied by linear sweep voltammetry (LSV) using the 273 A EG&G Princeton Applied Research Potentiostat.

3. Results and discussion

3.1 *Structural study*

Figure 3 shows XRD patterns of (a) FTO, (b) FTO/TiO_2 and (c) FTO/TiO_2/CdS. The XRD pattern of FTO/TiO_2/CdS [figure 3] is not of much significance for the structural study as the background peaks of FTO are more dominant which makes it difficult to analyse. However, intensity of the FTO background peaks decreases as the layer of TiO_2 and CdS loaded on the FTO substrate increases. The broader peak of

the FTO is attributed to the existence of amorphous/poorly crystalline TiO_2/CdS bilayers. However, Chi *et al* (2008) reported crystalline nature of electrodeposited TiO_2 over ITO substrate. Whereas, in our synthesis, SILAR and CBD methods allow formation of amorphous/poorly crystalline TiO_2/CdS bilayers system over the FTO substrate. Chen *et al* (2006) reported similar amorphous nature of CdS over TiO_2 nanotube.

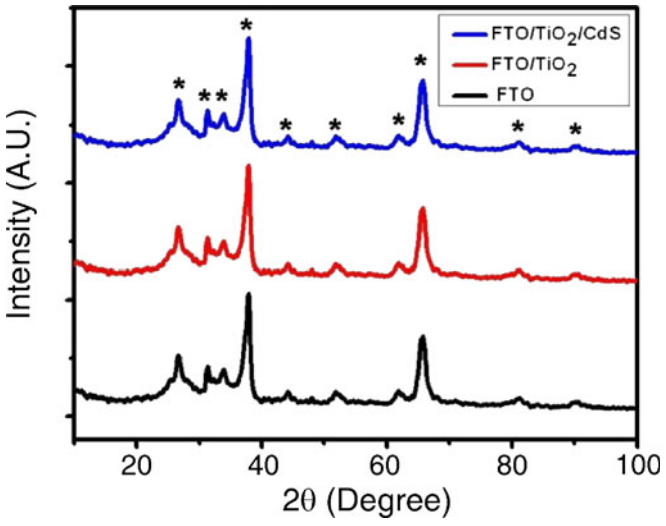

Figure 3. X-ray diffraction patterns of FTO as reference pattern, FTO/TiO_2 and FTO/TiO_2/CdS bilayers thin films.

3.2 *Morphological study*

Figures 4(a), (b) and (c) show SEM micrographs of bare TiO_2, CdS and TiO_2/CdS bilayers thin films on FTO coated glass substrates, respectively. The micrographs of TiO_2 thin films visualized in figure 4(a) shows that the FTO coated glass substrate is entirely covered with spherically nanograined TiO_2 particles. Such type of morphology provides large surface area, finds useful application in PEC solar cells (Mane *et al* 2005a, b). Figure 4(b) shows rose like morphology of CdS thin film. This morphology is unique than that of usually observed spherically grained particles (Mane and Lokhande 1997; Mane *et al* 2005a, b). Interestingly, change in morphology was observed from rose like to spherical grained CdS particle against TiO_2 coated substrate as revealed by figure 4(c). The change in morphology was observed due to the TiO_2 granular particles, which act as a nucleation centre for CdS deposition. Such type of morphology possesses large surface area, which is more suitable for PEC studies. The cross section image of TiO_2/CdS bilayer shown in figure 4(d), demonstrates distinct layers of TiO_2 and CdS. Chi *et al* (2008) reported similar nanograined morphology over ITO substrate.

3.3 *Optical study*

The consequence of CdS sensitization was explored by optical absorbance measurements in the wavelength range, 300–850 nm. Figure 5 shows optical absorption spectra for FTO/TiO_2 and FTO/TiO_2/CdS thin films at room

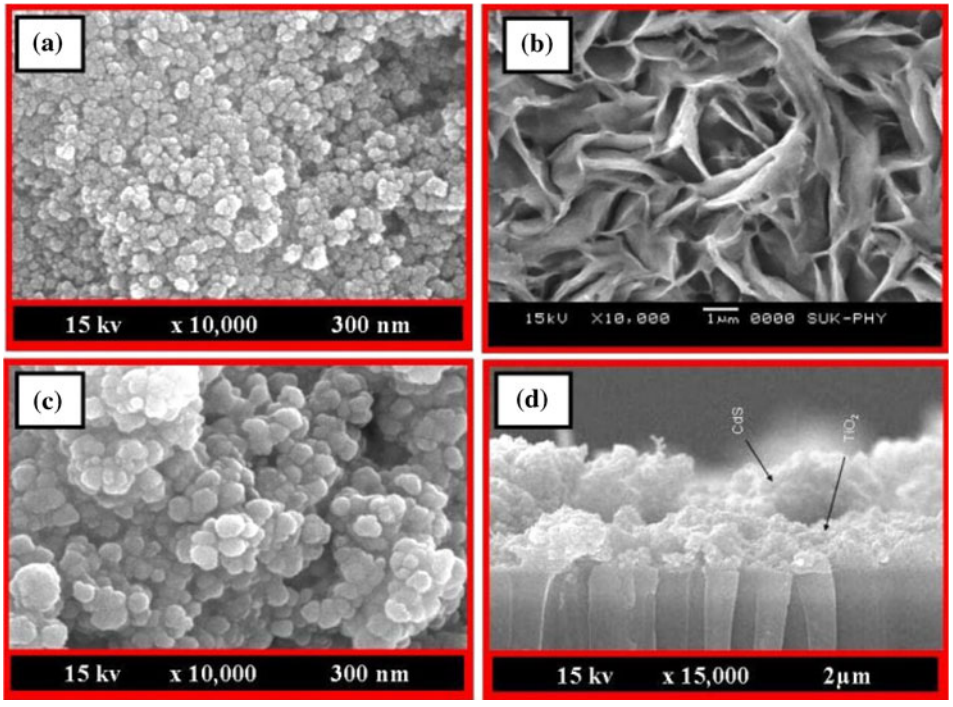

Figure 4. SEM micrographs of (**a**) FTO/TiO_2, (**b**) FTO/CdS and (**c**) FTO/TiO_2/CdS bilayers thin films, respectively. **(d)** shows cross-section image of FTO/TiO_2/CdS bilayers.

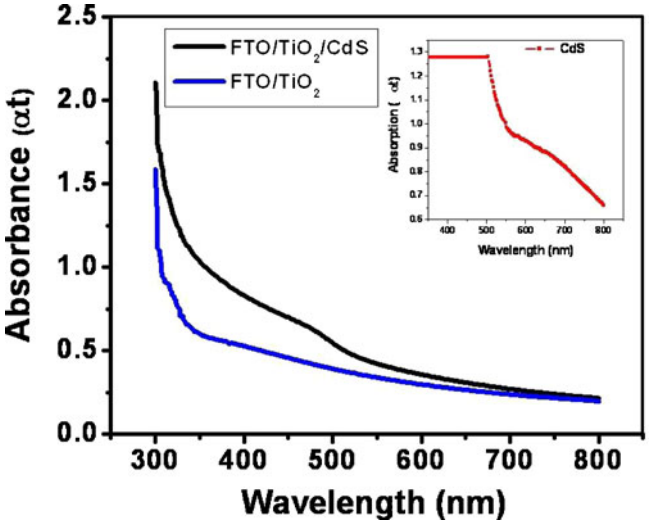

Figure 5. Optical absorption spectra for FTO/TiO_2 and $FTO/TiO_2/CdS$ thin films at room temperature. Inset of figure 5 shows CdS deposited on FTO coated glass substrate having characteristic absorption edge at 500 nm.

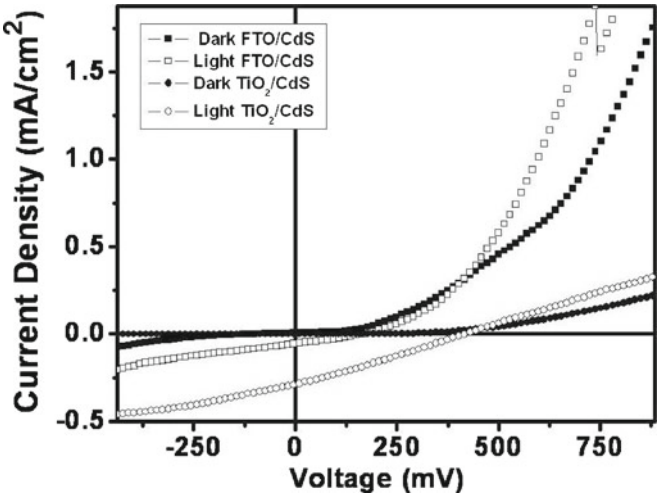

Figure 6. $I - V$ characteristic of typical FTO/CdS/polysulphide/graphite and $FTO/TiO_2/CdS$/polysulphide/graphite cell in dark and under illumination.

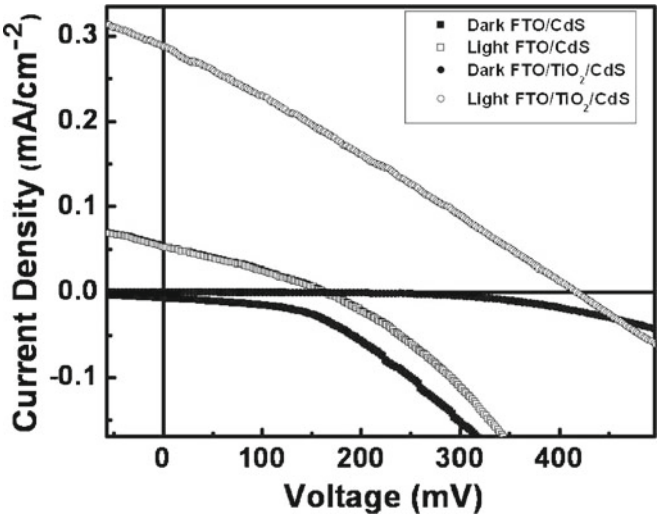

Figure 7. I–V curves of bare FTO/CdS electrode and $FTO/TiO_2/CdS$ bilayers film electrode.

temperature without taking into account reflection and transmission losses. The spectrum (I) reveals that TiO_2 films have low absorbance in the visible region and the characteristic absorption wavelength is <350 nm. However, it is observed that the absorption edge of the deposited $FTO/TiO_2/CdS$ film is strongly expanded to visible light region, which is shown in spectrum (II). Interestingly, $FTO/TiO_2/CdS$ film showed two absorption edges at 350 nm (TiO_2) and 475 nm (CdS), therefore, this may be attributed to existence of bilayer system, rather than the mixed phase (Kale *et al* 1996; Sankapal *et al* 2000; Hsu *et al* 2005). The CdS deposited on FTO/TiO_2 substrate showed the band edge absorption at 475 nm, while the CdS deposited on FTO coated glass substrate having characteristic absorption edge at 500 nm (shown in the inset of figure 5). Interestingly the "blue shift" has been observed in the CdS deposited on TiO_2 substrate against that deposited on the FTO coated glass substrate, indicating obvious size quantization effect of the nanoparticles (Hsu *et al* 2005). Similar optical properties for CdS over TiO_2 nanoparticles and nanotubes were reported by Chi *et al* (2008) and Chen *et al* (2006).

3.4 *I–V characteristics*

The I–V curves of FTO/CdS and $FTO/TiO_2/CdS$ electrode formed on the FTO substrate were tested for their nature in the 1 M polysulphide electrolyte. The I–V characteristic of typical FTO/CdS/polysulphide/graphite and $FTO/TiO_2/CdS$/polysulphide/graphite cell in dark and under illumination is shown in figure 6. For dark, the nonlinear nature of I–V curves predicts that the FTO/CdS and $FTO/TiO_2/CdS$ make rectification contact with the polysulphide electrolyte. The semiconductor–electrolyte junction is analogous to the Schottky barrier junction. The I–V characteristics of $FTO/TiO_2/CdS$ under dark, attributes to TiO_2 as buffer layer to CdS layer. PEC cell performances were studied under light illumination of 70 mW/cm^2. The 'back wall' (SE-illumination) cell made to avoid the absorption of light due to electrolyte, in such a manner, the light was allowed to pass through $FTO/TiO_2/CdS$/electrolyte. It has to be noted that the photons with energies less than bandgap energy of TiO_2 can reach n-TiO_2/CdS interface and produce electron hole pairs [EHP], which will be separated out by the potential drop obtained between the electrolyte and the surface of the semiconductor which creates an electric field, which is distributed in a charge polarized surface layer (space charge layer) and represented by a so-called band bending. Electrons will be driven in the conduction band of TiO_2 and holes

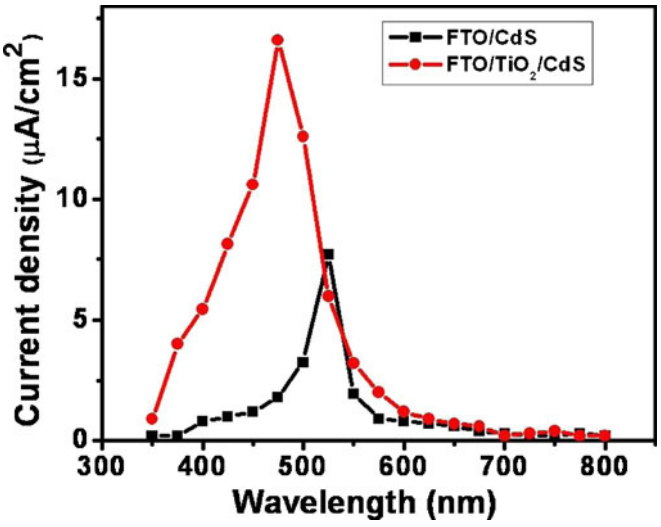

Figure 8. Spectral response of FTO/TiO_2/CdS bilayers and bare FTO/CdS layer.

will be pushed out towards the counter FTO through an electrolyte resulting in current generation. Drifted hole reduces to electrolyte and redox process takes place (Gratzel 2001). Both FTO/CdS and FTO/TiO_2/CdS films exhibit photoactivity in polysulphide with *n*-type behaviour. Figure 7 shows *I–V* curves of bare FTO/CdS electrode and FTO/TiO_2/CdS bilayers film electrode. We found that the cell performances dramatically enhanced by using FTO/TiO_2/CdS bilayers as the electrode, compared with bare FTO/CdS electrode. The photocurrent produced by FTO/TiO_2/CdS was 5·6 times that of by bare FTO/CdS electrode. The conversion efficiency for bare FTO/CdS and FTO/TiO_2/CdS bilayers system was 0·035% and 0·78% with fill factors 0·25 and 0·40, respectively. The enhancement in photoconversion efficiency occurred for FTO/TiO_2/CdS bilayers with respect to bare CdS thin layer. This enhancement is due to increase in surface area of CdS loaded on TiO_2 and retarding the rapid recombination losses of EHP in CdS (Mane *et al* 1999).

3.5 *Spectral response*

Spectral response of PEC cell was carried out by electrodes illuminated with continuous monochromatic light under potentiostatic conditions in two-electrode system. Monochromatic filters with a wavelength difference 25 nm were used to check spectral response of FTO/TiO_2/CdS bilayers and bare FTO/CdS layer. The photocurrent is registered as a function of wavelength (λ). The short circuit current "I_{sc}" of cell increases with increase in wavelength attaining a maximum and decreases with increase in wavelength (λ). Decrease in "I_{sc}" in low wavelength region is due to high surface recombination of photogenerated carriers by surface states and small "I_{sc}" in high wavelength region may be attributed to the transition between defect levels (Rajpure and Bhosale 2000). Figure 8 shows peak photocurrent for bare FTO/CdS and FTO/TiO_2/CdS bilayers obtained at 525 and 475 nm, respectively. The peak photocurrents were observed at the wavelength, where optical edges were found for bare FTO/CdS and FTO/TiO_2/CdS layers.

4. Conclusions

FTO/TiO_2, FTO/CdS and FTO/TiO_2/CdS photoelectrodes were successfully prepared by using low temperature chemical methods. SEM micrographs reveal change in morphology of CdS on TiO_2 surface from rose like to spherical grains. Optical studies showed the distinct transitions of FTO/TiO_2/CdS bilayers certifying two separate layers of TiO_2 and CdS. Spectral response studies support the blue shift for CdS deposited on TiO_2 surface than FTO substrate. The enhancement in photoconversion efficiency increases because of large surface area and decrease in rapid loss of EHP recombination by TiO_2. It became clear that there is room for further improvement of the cell performance.

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