

## Research Article

# The CdS/CdSe/ZnS Photoanode Cosensitized Solar Cells Based on Pt, CuS, Cu<sub>2</sub>S, and PbS Counter Electrodes

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Received 14 October 2013; Revised 25 December 2013; Accepted 25 December 2013; Published 27 February 2014

Academic Editor: Armin Gerhard Aberle

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Highly ordered mesoporous TiO<sub>2</sub> modified by CdS, CdSe, and ZnS quantum dots (QDs) was fabricated by successive ionic layer adsorption and reaction (SILAR) method. The quantity of material deposition seems to be affected not only by the employed deposition method but also and mainly by the nature of the underlying layer. The CdS, CdSe, and ZnS QDs modification expands the photoresponse range of mesoporous TiO<sub>2</sub> from ultraviolet region to visible range, as confirmed by UV-Vis spectrum. Optimized anode electrodes led to solar cells producing high current densities. Pt, CuS, PbS, and Cu<sub>2</sub>S have been used as electrocatalysts on counter electrodes. The maximum solar conversion efficiency reached in this work was 1.52% and was obtained by using Pt electrocatalyst. CuS, PbS, and Cu<sub>2</sub>S gave high currents and this was in line with the low charge transfer resistances recorded in their case.

## 1. Introduction

As an alternative to dye molecules, semiconductor quantum dots (QDs) like CdS, CdSe [1], PbS [2], InAs [3], InP [4], and others [5] as well as extremely thin inorganic absorber layers [6, 7] have been used. QDs are very attractive because of their size-dependent optical band gap, the possibility to design hierarchical multilayer absorber structures, and the potential to use them for multiexciton generation from a single photon. One potential method for improving the performance of quantum dots solar cells (QDSSCs) is by constructing desired energy band structures using multiple QDs. Niiitsoo and co-workers have firstly demonstrated that a desired cascade structure can be formed by sequential deposition of CdS and CdSe layers onto the TiO<sub>2</sub> nanoparticle films [8]. Recently, Lee et al. have also reported a self-assembled TiO<sub>2</sub>/CdS/CdSe structure that exhibited a significant enhancement in the photocurrent response [9, 10]. In addition, nanostructured CuS, PbS, Cu<sub>2</sub>S, and Pt have been used as electrocatalysts on the counter electrode. Alternative catalysts have been proposed by several researchers [9–12]. Metal sulfides are considered

a good choice. However, their deposition on plain FTO electrodes does not always produce materials with sufficiently high specific surface or with structural stability.

In this paper, we studied the effects of comodification by CdS, CdSe, and ZnS QDs on the photovoltaic response of mesoporous TiO<sub>2</sub> based QDSSC. The mesoporous TiO<sub>2</sub> were treated by SILAR of CdS, CdSe, and ZnS QDs and were used as photoanodes in QDSSC. We demonstrated that the comodified mesoporous TiO<sub>2</sub> possesses superior photovoltaic response compared to the single QD sensitized devices. Pt, CuS, PbS, and Cu<sub>2</sub>S have been used as electrocatalysts on counter electrodes. The final TiO<sub>2</sub>/CdS/CdSe/ZnS photoanode leads to high efficiency QDSSCs.

## 2. Experiment

**2.1. Materials.** Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (99%), Cu(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>S, Zn(NO<sub>3</sub>)<sub>2</sub>, Se powder, S powder, Na<sub>2</sub>SO<sub>3</sub>, and Brass foil were obtained from Merck. TiO<sub>2</sub> paste was obtained from Dyesol, Australia.

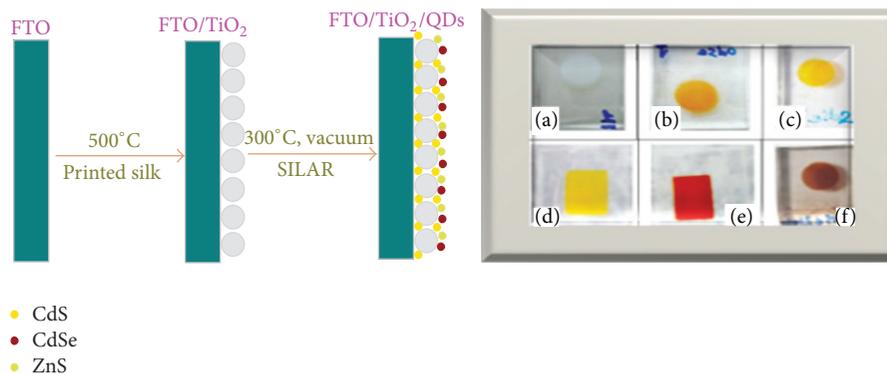


FIGURE 1: The diagram shows the process to prepare the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanode.

**2.2. To Prepare  $\text{TiO}_2$  Films.** The  $\text{TiO}_2$  thin films were fabricated by silk-screen printing with commercial  $\text{TiO}_2$  paste. Their sizes ranged from 10 to 20 nm. Two layers of film with thickness of  $8\ \mu\text{m}$  were measured by microscope. Then, the  $\text{TiO}_2$  film was heated at  $400^\circ\text{C}$  for 5 min and  $500^\circ\text{C}$  for 30 min. Afterwards, the film was dipped in 40 mmol  $\text{TiCl}_4$  solution for 30 min at  $70^\circ\text{C}$  and heated at  $500^\circ\text{C}$  for 30 min.

The specific surface area of the mesoporous  $\text{TiO}_2$  was investigated by using the  $\text{N}_2$  adsorption and desorption isotherms before and after the calcination. The surface area is  $120.6\ \text{m}^2\ \text{g}^{-1}$  (measured by BET devices). This result indicates that the synthesized material has wider mesoporous structure.

**2.3. To Prepare  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  Films.** The highly ordered  $\text{TiO}_2$  was sequentially sensitized with CdS, CdSe, and ZnS QDs by SILAR method. First, the  $\text{TiO}_2$  film was dipped in 0.5 mol/L  $\text{Cd}(\text{CH}_3\text{COO})_2$ -ethanol solution for 5 min, rinsed with ethanol, dipped for 5 min in 0.5 mol/L  $\text{Na}_2\text{S}$ -methanol solution, and then rinsed with methanol. The two-step dipping procedure corresponded to one SILAR cycle and the incorporated amount of CdS QDs was increased by repeating the assembly cycles for a total of three cycles. For the subsequent SILAR process of CdSe QDs, aqueous Se solution was prepared by mixing Se powder and  $\text{Na}_2\text{SO}_3$  in 50 mL pure water after adding 1 mol/L NaOH at  $70^\circ\text{C}$  for 7 h. The  $\text{TiO}_2/\text{CdS}$  samples were dipped into 0.5 mol/L  $\text{Cd}(\text{CH}_3\text{COO})_2$ -ethanol solution for 5 min at room temperature, rinsed with ethanol, dipped in aqueous Se solution for 5 min at  $50^\circ\text{C}$ , and rinsed with pure water. The two-step dipping procedure corresponds to one SILAR cycle. Repeating the SILAR cycle increases the amount of CdSe QDs (a total of four cycles). The SILAR method was also used to deposit the ZnS passivation layer. The  $\text{TiO}_2/\text{CdS}/\text{CdSe}$  samples were coated with ZnS by alternately dipping the samples in 0.1 mol/L  $\text{Zn}(\text{NO}_3)_2$  and 0.1 mol/L  $\text{Na}_2\text{S}$ -solutions for 5 min/dip, rinsing with pure water between dips (a total of two cycles). Finally, it was heated in a vacuum environment with different temperatures to avoid oxidation (see Figure 1). The thickness of  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanodes were measured by Microscopic. The results of the average thickness

of every layer of CdS, CdSe, and ZnS are 40 nm, 43.3 nm, 40 nm, respectively.

**2.4. Construction of the Counter Electrodes.** PbS films were deposited on fluorine doped tin oxide (FTO) conductive glass electrode by cyclic voltammetry (CV) from the solution of  $\text{Pb}(\text{NO}_3)_2$  1.5 mM and  $\text{Na}_2\text{S}_2\text{O}_3$  1.5 mM. CV experiments were carried out at various potential scan rates in a potential range 0.0 to  $-1.0\ \text{V}$  versus  $\text{Ag}/\text{AgCl}/\text{KCl}$  electrode, pH from 2.4 to 2.7, and ambient temperature. Pt films were fabricated by silk-screen printing with commercial Pt paste. Then, the Pt films were heated at  $450^\circ\text{C}$  for 30 min. CuS was also deposited on FTO electrodes by a SILAR procedure, by modifying the method presented in [13]. Precursor solutions contained 0.5 mol/L  $\text{Cu}(\text{NO}_3)_2$  in methanol and 1 mol/dm<sup>3</sup>  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in a 1:1 water:methanol mixture. An FTO electrode was immersed for 5 min in the metal salt solution, copiously washed with triple-distilled water, dried in an air stream, immersed for 5 min in the  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  solution, and finally washed and dried again. This sequence again corresponds to one SILAR cycle. 10 SILAR cycles were performed. Finally, the electrode with deposited CuS film was first dried and then it was put for 5 min in an oven at  $100^\circ\text{C}$ . The counter electrode was a  $\text{Cu}_2\text{S}$  film fabricated on brass foil. Brass foil was immersed into 37% HCl at  $70^\circ\text{C}$  for 5 min, rinsed with water, and dried in air. After that, the etched brass foil was dipped into 1 mol/L S and 1 mol/L  $\text{Na}_2\text{S}$  aqueous solution, resulting in a black  $\text{Cu}_2\text{S}$  layer forming on the foil [14].

**2.5. Fabrication of QDSSCs.** The polysulfide electrolyte used in this work was prepared freshly by dissolving 0.5 M  $\text{Na}_2\text{S}$ , 0.2 M S, and 0.2 M KCl in Milli-Q ultrapure water/methanol (7:3 by volume). The CdS/CdSe/ZnS cosensitized  $\text{TiO}_2$  photoanode and Pt counter electrode were assembled into a sandwich cell by heating with a Surllyn. The electrolyte was filled from a hole made on the counter electrode, which was later sealed by thermal adhesive film and a cover glass. The active area of QDSSC was  $0.38\ \text{cm}^2$ .

**2.6. Characterizations and Measurements.** The morphology of the prepared samples was observed using field-emission scanning electron microscopy (FE-SEM, S4800). The crystal

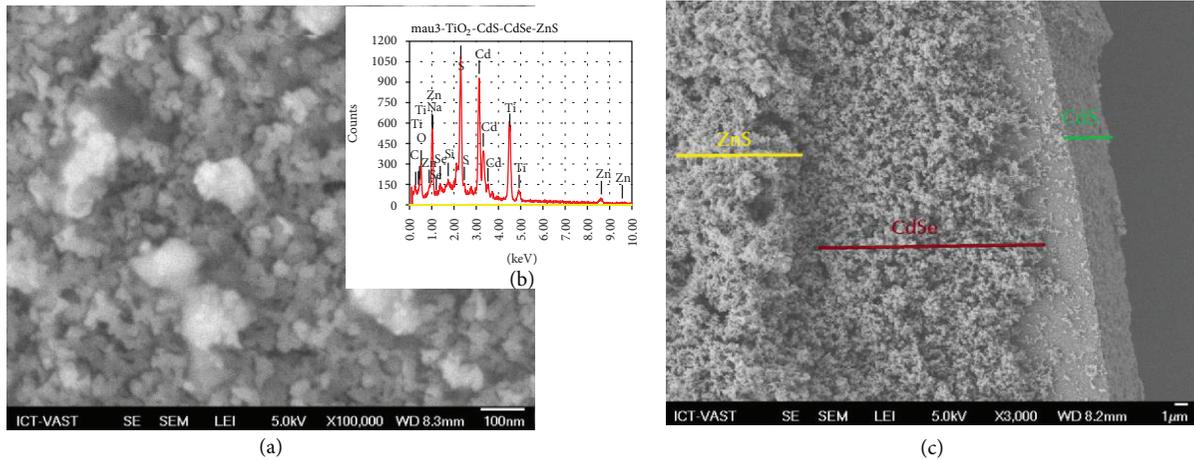


FIGURE 2: (a) FE-SEM images of the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanode, (b) energy dispersive analysis of X-ray spectra (EDAX) of the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanode, (c) cross-sectional view of the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanode.

structure was analyzed with an X-ray diffractometer (Philips, PANalytical X'pert,  $\text{CuK}\alpha$  radiation). The absorption properties of the nanotube array samples were investigated using a diffuse reflectance UV-Vis spectrometer (JASCO V-670). Photocurrent voltage measurements were performed on a Keithley 2400 sourceMeter using a simulated AM 1.5 sunlight with an output power of  $100 \text{ mW}/\text{cm}^2$  produced by a solar simulator (Solarena, Sweden).

### 3. Results and Discussion

Shown in Figures 2(a) and 2(b) are the FESEM images of  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanode film. Figure 2(a) shows highly uniform porous morphology with the average inner diameter of nanostructure around 60 nm. For photovoltaic applications, the structure of QDs adsorbed  $\text{TiO}_2$  should meet at less two criteria. First, the QDs should be uniformly deposited onto the  $\text{TiO}_2$  surface without aggregation, so that the area of  $\text{TiO}_2/\text{QDs}$  can be maximized. Second, a moderate amount the QDs should be deposited so that  $\text{TiO}_2$  is not blocked.

Figure 2(c) is a cross-sectional image showing that the QDs are well deposited onto the  $\text{TiO}_2$  with an average thickness of about  $12 \mu\text{m}$  by the microscope. Figure 2(b) is the energy dispersive X ray spectroscopy of the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  film. It shows that the Ti and O peaks are from the  $\text{TiO}_2$  film; and Cd, Se, Zn, and S peaks, clearly visible in the EDS spectrum, are from the QDs. The Si is from the FTO and C is from the solvent organic. That shows that the QDs are well deposited onto the  $\text{TiO}_2$ .

The structure of the  $\text{TiO}_2/\text{QDs}$  photoelectrodes for photovoltaic applications, shown in Figure 3(a), is studied by the XRD patterns. It reveals that the  $\text{TiO}_2$  has an anatase structure with a strong (101) peak located at  $25.4^\circ$ , which indicates that the  $\text{TiO}_2$  films are well crystallized and grow along the (101) direction (JCPDS Card number 21-1272). Three peaks can be observed at  $26.4^\circ$ ,  $44^\circ$  and  $51.6^\circ$ , which can be indexed to

(111), (220), and (331) of cubic CdS (JCPDS Card number 41-1049) and CdSe (JCPDS Card number 75-5681), respectively. Two peaks can be observed at  $48^\circ$  and  $54.6^\circ$ , which can be indexed to (220) and (331) of cubic ZnS, respectively. It demonstrates that the QDs have been crystallized onto the  $\text{TiO}_2$  film. Figure 3(b) is the Raman spectrum of the  $\text{TiO}_2/\text{QDs}$  photoelectrodes. It shows that an anatase structure of the  $\text{TiO}_2$  films has five oscillation modes corresponding wave numbers at  $143$ ,  $201$ ,  $395$ ,  $515$ , and  $636 \text{ cm}^{-1}$ . In addition, two peaks can be observed at  $201$ ,  $395$ , and  $515 \text{ cm}^{-1}$ , which can be indexed to the cubic structure of CdS and CdSe. The results of the Raman are likely similar to the results of the XRD. The optical performance of the QDs coated  $\text{TiO}_2$  film is characterized by absorbance. Figure 3(c) shows the UV-Vis absorption spectra of the sensitized electrodes measured after each cycle of SILAR. As expected, the absorbance increased with the deposition cycles of CdS, CdSe, and ZnS. However, only absorption spectra with SILAR cycles of the electrode  $\text{TiO}_2/\text{CdS}(3)/\text{CdSe}(3)/\text{ZnS}(2)$  show the best photovoltaic performance as discussed in the following section. In short-wavelength region ( $380\text{--}550 \text{ nm}$ ), the increase of absorbance is due to the fact that more CdS was loaded on  $\text{TiO}_2$  film and the coabsorption of CdS, CdSe, and ZnS. In long-wavelength region ( $550\text{--}629 \text{ nm}$ ), the deposition of higher amounts of CdSe and ZnS on  $\text{TiO}_2/\text{CdS}$  electrode results in the increase of absorbance. Moreover, the increasing successive deposition cycles also trigger a red shift of absorption spectrum which is due to a slight loss of quantum confinement effect [15]. The evaluated sizes of CdS and CdSe are consistent with the sizes measured from the FE-SEM images. The effect of deposition cycles of CdS, CdSe, and ZnS can be clearly seen on the energy band gap values of CdS/CdSe/ZnS cosensitized  $\text{TiO}_2$  films. The estimated band gaps vary from  $1.97 \text{ eV}$  to  $2.7 \text{ eV}$ , which are higher than the values reported for CdS and CdSe in bulk ( $2.25 \text{ eV}$  and  $1.7 \text{ eV}$  resp. [16]), indicating that the sizes of CdS, CdSe, and ZnS on  $\text{TiO}_2$  films are still within the scale of QDs. The diameter of QDs was calculated from  $2 \text{ nm}$  to  $6 \text{ nm}$  by (1). A higher absorption is thus obtained because

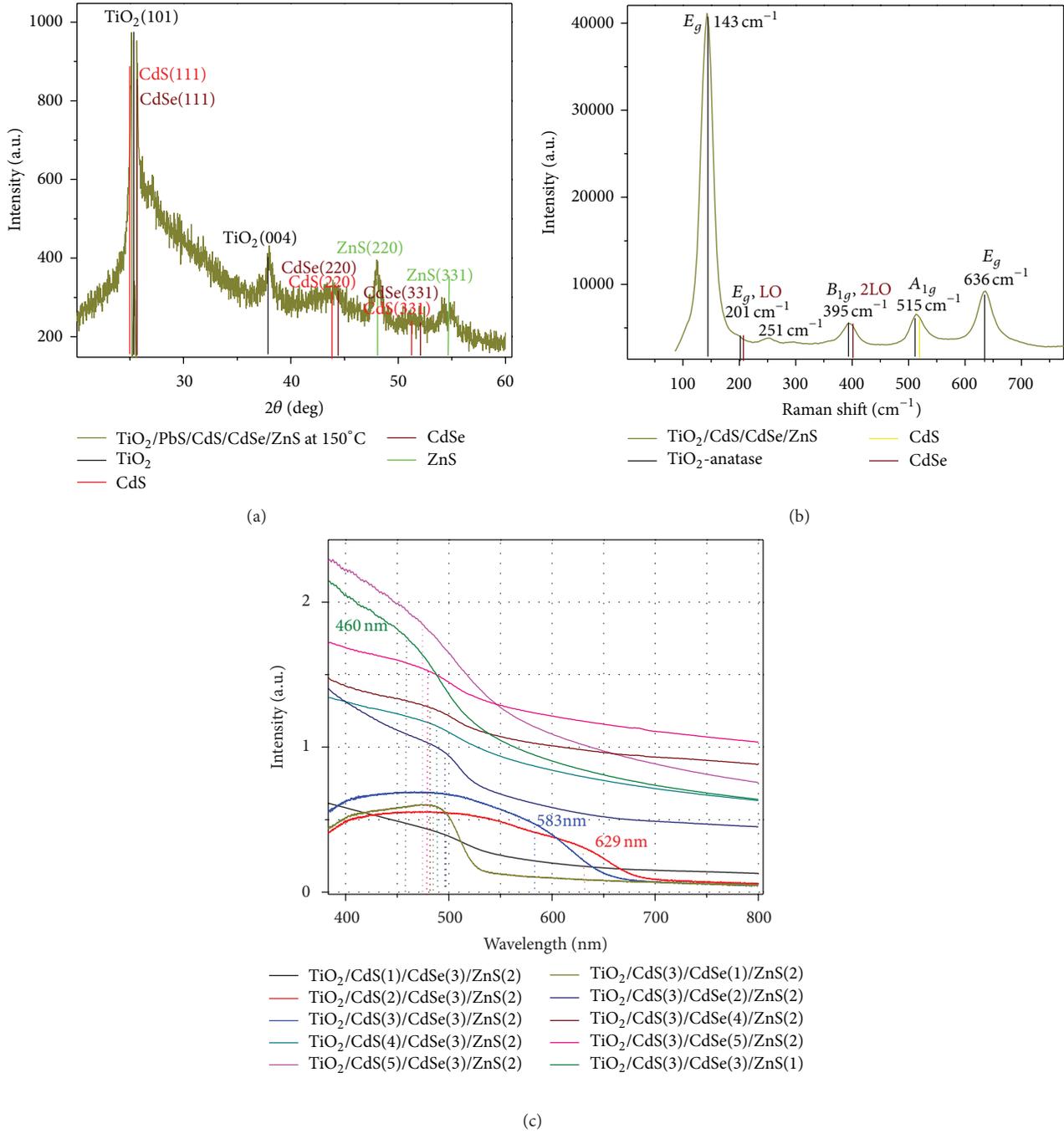


FIGURE 3: XRD (a), Raman (b), and UV-Vis (c) of the  $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$  photoanodes.

the absorption spectrum of ZnS complements those of the CdSe and CdS QDs. Furthermore, ZnS acts as a passivation layer to protect the CdS and CdSe QDs from photocorrosion [17]. Consider the following equation by Yu et al. [18] group:

$$D = 1.6122 \cdot 10^{-9} \lambda^4 - 2.6575 \cdot 10^{-6} \lambda^3 + 1.6242 \cdot 10^{-3} \lambda^2 - 0.4277 \lambda + 41.57. \quad (1)$$

The XRD patterns were used to characterize the crystal structure of the obtained products. As shown in Figure 4(a), it can be seen that the XRD pattern of the PbS counter electrode is in conformity with cubic ( $a = b = c = 5.93 \text{ \AA}$ ). The observed peaks could be assigned to diffraction from the (111), (200), (220), (311), and (222) faces and there is no characteristic peak for other impurities. This indicates that pure crystalline PbS was formed via the cyclic voltammetry process. Figure 4(b) illustrates the XRD pattern of the synthesized  $\text{Cu}_2\text{S}$  after

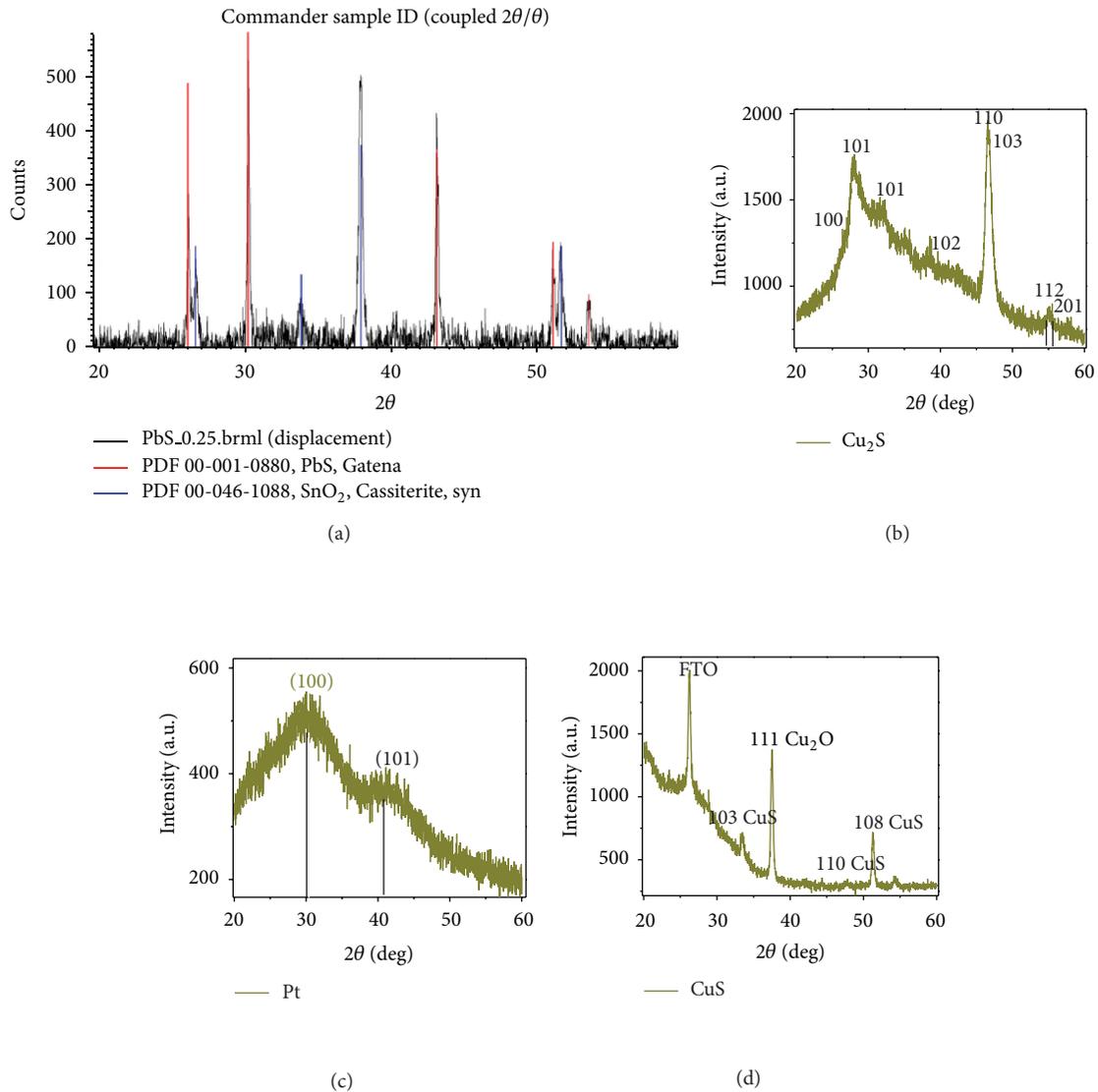


FIGURE 4: XRD of the PbS, Cu<sub>2</sub>S, Pt, and CuS counter electrodes.

1 h by chemical bath deposition (CBD) method. The peaks of corresponding crystal planes were indexed in the figure, matching to the hexagonal phase chalcocite  $\beta$ -Cu<sub>2</sub>S (JCPDS card number 46-1195,  $a = 3.96 \text{ \AA}$ ,  $c = 6.78 \text{ \AA}$ ). Figure 4(c) illustrates that the XRD pattern of the Pt films were fabricated by silk-screen printing with commercial Pt paste. The peaks of corresponding crystal planes were indexed in the figure, matching to the hexagonal phase. As shown in Figure 4(d), it can be seen that the XRD pattern of the CuS counter electrode is in conformity with the hexagonal phase. It is in agreement with the reported data for CuS (JCPDS Card. number 79-2321).

A relative energy level of different components is shown in Figure 5(a). According to the data reported in the literature [16, 19], the band gap of TiO<sub>2</sub> (3.2 eV) limits its absorption range below the wavelength of about 400 nm. CdSe has a higher conduction band (CB) edge than TiO<sub>2</sub>, which is favorable for electron injection. However, with a band gap

of 1.7 eV, the absorption of bulk CdSe is also limited below approximately 760 nm. The conduction band of CdSe is slightly lower than that of TiO<sub>2</sub>, so the electrons would flow from CdSe to TiO<sub>2</sub> [20]. In addition, we have coated two layers of ZnS QDs, which could be attributed to several reasons. First, as the absorption edge of ZnS is at about 345 nm, a higher absorption can be obtained due to the complement of the absorption spectrum of the ZnS with that of the CdSe and CdS QDs. Second, ZnS acts as a passivation layer to protect the CdS and CdSe QDs from photocorrosion. Thus, the photoexcited electrons can efficiently transfer into the conduction band of TiO<sub>2</sub>. Third, the outer ZnS layer can also be considered to be a potential barrier between the interface of QDs materials and the electrolyte. ZnS has a very wide band gap of 3.6 eV; it is much wider than that on the CdS and CdSe QDs. As a result, the leakage of electrons from the ZnS, CdSe, and CdS QDs into the electrolyte can be inhibited. As a result, an ideal model for the cosensitized

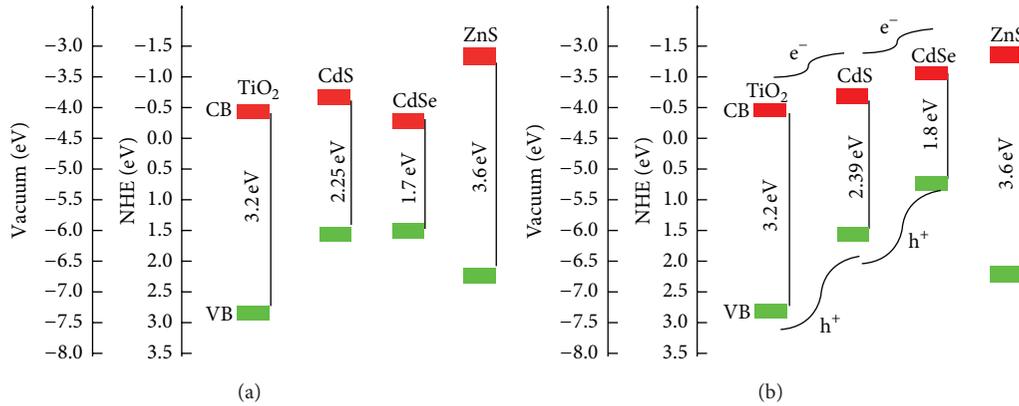


FIGURE 5: (a) Relative energy levels of TiO<sub>2</sub>, CdS, CdSe, and ZnS in bulk phase, (b) the proposed energy band structure of the TiO<sub>2</sub>/CdS/CdSe/ZnS nanostructure interface. All the energy levels are referenced to NHE scale. CB and VB are conduction band and valence band [16, 19].

TiO<sub>2</sub> electrode is shown in Figure 5(b). After CdSe and ZnS QDs are sequentially deposited onto a TiO<sub>2</sub>/CdS film, A cascade type energy band structure is constructed for the cosensitized photoanode. The best electron transport path is from the conduction band of ZnS and finally reaching the conduction band of TiO<sub>2</sub>. Meanwhile, this stepwise structure is also favorable for the hole transport.

We prepared the photoanodes with many different layers of QDs. Firstly, we have prepared CdS or CdSe films. However, the results were of very low performance. Therefore, we decided covering with ZnS layer for the following reasons. Firstly, extend peak adsorption spectrum in the visible light region. Secondly, the ZnS layers which acted as the agent passivated the surface of QDs. Moreover, they protected the light corrosion. Thus, the conversion excited electrons through the conduction band of TiO<sub>2</sub> better. Thirdly, ZnS layers separated the surfaces of the CdS and CdSe with electrolyte. The ZnS has a very wide band gap of about 3.6 eV, much larger than other CdS and CdSe QDs. As a result, electrons move from CdS, CdSe, and ZnS to the electrolyte can be inhibited. Figure 6(a) shows that the power conversion efficiencies of QDSSCs are increasing with the SILAR cycle number of CdS, CdSe, and ZnS at 3, 3, and 2, respectively. It is noted that lower power conversion efficiency was obtained for those cells with either less than 3 CdS and CdSe SILAR cycles or more than 3 CdS and CdSe SILAR cycles (Figure 6(b)). The TiO<sub>2</sub>/CdS(3)/CdSe(3)/ZnS device shows an open-circuit voltage ( $V_{OC}$ ) of 0.76 V, a short-circuit current density ( $J_{sc}$ ) of 4.79 mA/cm<sup>2</sup>, fill factor (FF) of 0.41, and an energy conversion efficiency of 1.52%. When the deposition cycles of CdS and CdSe increase, slight changes in  $V_{OC}$  and FF values were obtained. Remarkably, the  $J_{sc}$  decreases, which results in a substantial reduction of efficiency from 1.52% to 0.45% (Table 1). These results indicate that although better light absorption performance was obtained when more CdSe was loaded on TiO<sub>2</sub>/CdS, the excessive CdSe on TiO<sub>2</sub>/CdS films may lead to an increase of recombination in photoanodes. On the contrary, the increase of ZnS leads to the increasing generation of photoelectron

and is helpful to collect excited electrons from ZnS, CdSe, and CdS to TiO<sub>2</sub> film.

FF is determined from measurement of the IV curve and is defined as  $FF = V_{max} \cdot I_{Max} / V_{OC} \cdot I_{sc}$ . FF depending on  $V_{OC}$  values, the junction quality (related with the series  $R_s$ ), and the type of recombination in a solar cell. From Table 1,  $V_{OC}$  values change according to the film thickness from 0.29 to 0.76, corresponding to the change in FF from 0.26 to 0.41. Therefore, the FF is the low value because  $V_{OC}$  is low. On the other hand,  $V_{OC}$  values depend on the recombination process; they are particularly large;  $V_{OC}$  gives low open-circuit voltages. In addition, FF is effected by  $R_s$ . The equations of  $R_s$  can be calculated by Thongpron and coworkers [21] as follows:

$$R_s = \frac{V_1 - V_2}{I_2 - I_1} - \frac{1}{\lambda (I_2 - I_1)} \ln \left[ \frac{I_{ph} + I_o - I_1}{I_{ph} + I_o - I_2} \right]. \quad (2)$$

Two operating points are ( $I_1, V_1$ ) and ( $I_2, V_2$ ) on a single  $I$ - $V$  curve.  $\lambda = q/nKT$ ;  $I_{ph}$ ,  $I_o$  are the photocurrent and the diode reverse saturation current.  $R_s$  values are calculated from 55 to 158 mΩcm<sup>2</sup>. This result indicate that fill factor will decrease when VOC increase.

Four main types of counter electrodes have been studied. Their synthesis is detailed in experiment and method. The FESEM images of the corresponding electrocatalytic films are shown in Figure 7 (inset). In the first case, PbS films were deposited on fluorine doped tin oxide (FTO) conductive glass electrode by cyclic voltammetry (CV) from the solution of Pb(NO<sub>3</sub>)<sub>2</sub> 1.5 mM and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 1.5 mM. CV experiments were carried out at various potential scan rates in a potential range 0.0 to -1.0 V versus Ag/AgCl/KCl electrode, pH from 2.40 to 2.70, and ambient temperature. CuS was also deposited on FTO electrodes by a SILAR procedure, by modifying the method presented in [13]. The electrode with deposited CuS film was first dried and then it was put for 5 min in an oven at 100°C. The counter electrode was a Cu<sub>2</sub>S film fabricated on brass foil. Brass foil was immersed into 37% HCl at 70°C for 5 min and then rinsed with water and

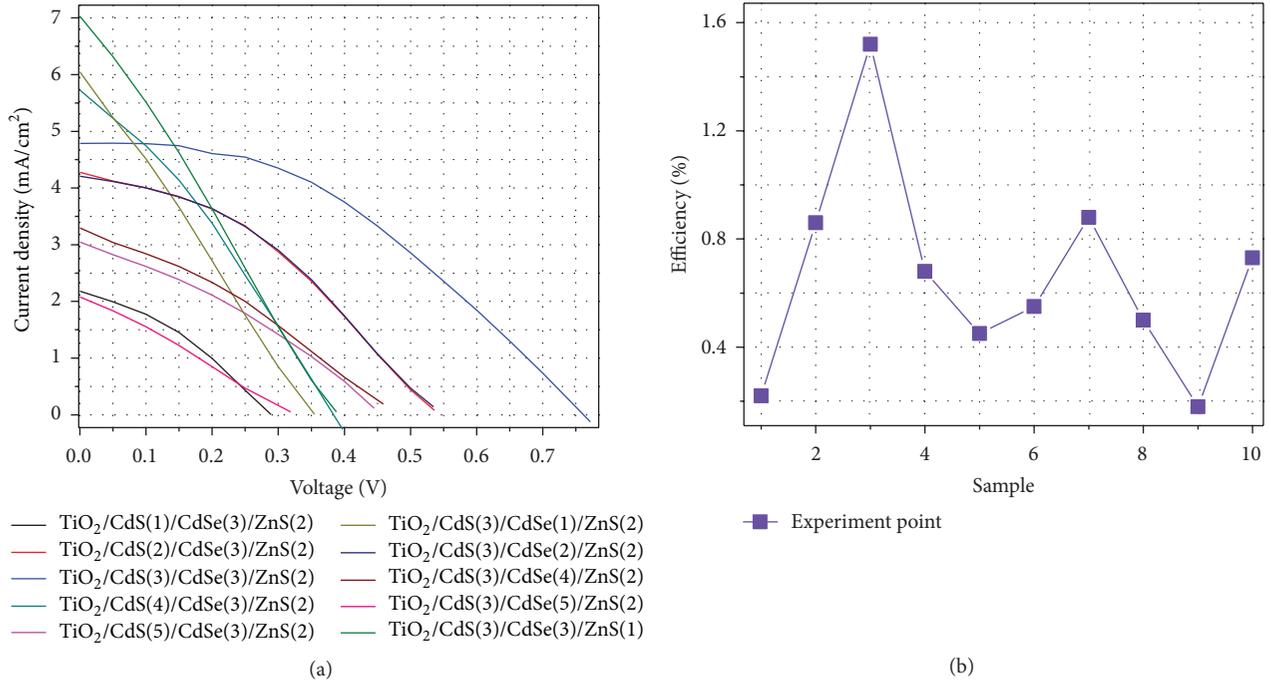


FIGURE 6: (a) The  $J$ - $V$  curves of the QDSSCs with different photoanodes under one sun illumination and (b) diagram shows the values efficiency of solar cells.

TABLE 1: Photovoltaic performance parameters of QDSSCs based on different photoanodes.

Solar cells	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	Fill factor FF	Efficiency $\eta$ (%)
TiO <sub>2</sub> /CdS(1)/CdSe(3)/ZnS(2)	2.18	0.29	0.35	0.22
TiO <sub>2</sub> /CdS(2)/CdSe(3)/ZnS(2)	4.28	0.54	0.37	0.86
TiO <sub>2</sub> /CdS(3)/CdSe(3)/ZnS(2)	4.79	0.76	0.41	1.52
TiO <sub>2</sub> /CdS(4)/CdSe(3)/ZnS(2)	5.73	0.39	0.31	0.68
TiO <sub>2</sub> /CdS(5)/CdSe(3)/ZnS(2)	3.05	0.45	0.32	0.45
TiO <sub>2</sub> /CdS(3)/CdSe(1)/ZnS(2)	6.05	0.356	0.256	0.55
TiO <sub>2</sub> /CdS(3)/CdSe(2)/ZnS(2)	4.21	0.55	0.38	0.88
TiO <sub>2</sub> /CdS(3)/CdSe(4)/ZnS(2)	3.30	0.48	0.31	0.50
TiO <sub>2</sub> /CdS(3)/CdSe(5)/ZnS(2)	2.08	0.33	0.27	0.18
TiO <sub>2</sub> /CdS(3)/CdSe(3)/ZnS(1)	7.03	0.39	0.26	0.73

TABLE 2: Photovoltaic parameters of solar cell modified by various cathodes.

Solar cells	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	Fill factor FF	Efficiency $\eta$ (%)
PbS cathode	6.14	0.43	0.24	0.63
CuS cathode	5.72	0.38	0.31	0.68
Cu <sub>2</sub> S cathode	4.2	0.55	0.376	0.87
Pt cathode	4.79	0.76	0.41	1.52

dried in air. After that, the etched brass foil was dipped into 1 mol/L S and 1 mol/L Na<sub>2</sub>S aqueous solution, resulting in a black Cu<sub>2</sub>S layer forming on the foil [14]. Figures 4(a), 4(b), and 4(c) show the image of PbS, CuS, Cu<sub>2</sub>S films that present a rough nanostructure, which are suitable for counter electrodes. The similar Pt films were fabricated by silk-screen

printing with commercial Pt paste. Then, the Pt films were heated at 450°C for 30 min. In the high magnification image of Figure 4(d), one can distinguish the big blocks of FTO covered with Pt nanoparticles [22]; Figure 4 and Table 2 show that the maximum efficiency reached in the present work, that is, 1.52%, was obtained with Pt on the counter

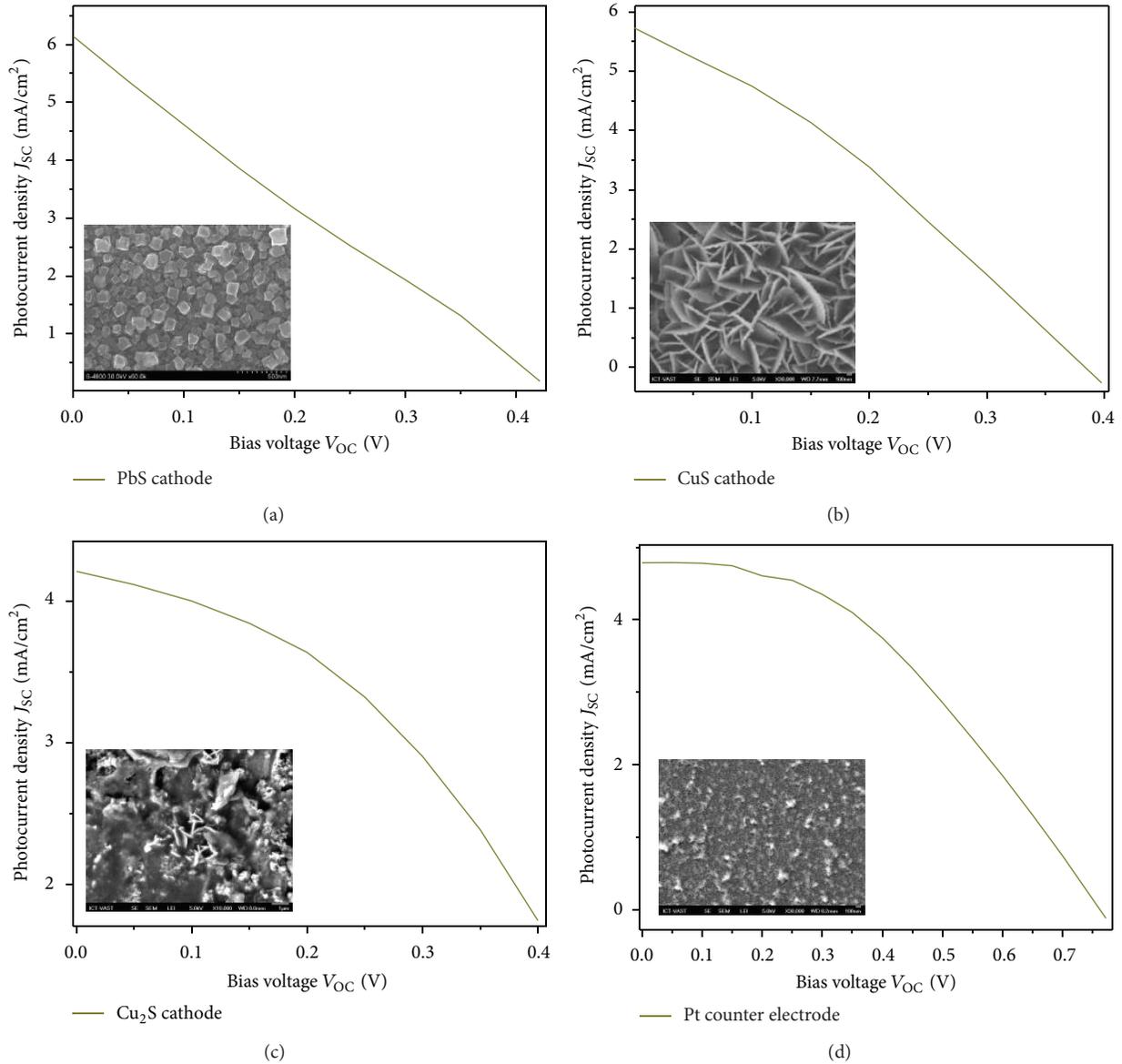


FIGURE 7:  $J$ - $V$  curves of solar cells modified by various cathodes.

electrode. The Pt electrocatalysts, that is,  $\text{Cu}_2\text{S}$ ,  $\text{CuS}$ , and  $\text{PbS}$ , gave higher current densities than Pt but lower  $V_{\text{OC}}$  than Pt. On the contrary, open-circuit voltage values were practically not affected by the electrocatalyst. The major problem encountered in the present work was with the value of the fill factor (FF). It remained below 0.42 and this limited the overall efficiency, even though, the current densities presently recorded were high. The search for a higher FF is an open question and has occupied many other researchers. It is believed that higher FFs will be obtained with even better electrocatalysts and more functional counter electrodes.

#### 4. Conclusions

QDSSCs have been constructed and optimized by combining  $\text{TiO}_2$  with  $\text{CdS}$ ,  $\text{CdSe}$ , and  $\text{ZnS}$  nanostructure on the anode

electrode.  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$ , and Pt were used as electrocatalysts on counter electrodes in combination with a polysulfide electrolyte. The maximum solar conversion efficiency of 1.52% was obtained with a Pt counter electrode. The most important finding of this work is the importance of the first nanostructure layer deposited on the mesoporous  $\text{TiO}_2$  film, which affected the quantity and the quality of the subsequent QDs layers and the ensuing cell efficiency. High current densities were obtained with all cells having optimized anode electrodes. Among them, the highest currents were obtained with Pt electrocatalysts.

#### Conflict of Interests

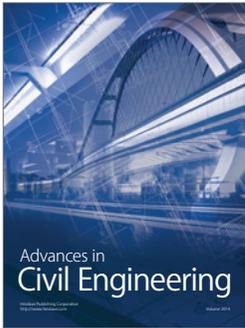
The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

This work was supported by Vietnam National University with the name of the project being B 2012-18-05TD, the University of Science of Ho Chi Minh City, and Dong Thap University.

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