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Dye-sensitized nanocrystalline CdS and ZnS solar cells with different organic dyes

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We have developed dye-sensitized nanocrystalline CdS and ZnS solar cells (DSSCs) based on crystal violet, methylene blue, and fluorescein photosensitizers. Nanocrystalline CdS and ZnS were synthesized by a green synthesis method using starch as the capping agent. Characterization of nanocrystalline CdS and ZnS was carried out by optical absorption and x-ray diffraction. The results indicate that CdS and ZnS prepared by this method may be used as photoelectrodes in photo-electro-chemical energy conversion systems. DSSCs have been built and their photocurrent, open-circuit voltage, fill factor, and efficiency have been measured under direct sunlight illumination (1000 Wcm^{-2}). The efficiency of the cells made from dye-CdS was much higher than that of the cells made from dye-ZnS. This can be attributed to the particle size effect. Among the prepared dye-sensitized solar cells, a DSSC based on fluorescein dye as the photosensitizer produced the highest overall light solar energy to electricity conversion efficiency.

I. INTRODUCTION

Recent research on solar cells has been aimed at lowering the fabrication cost to decrease the price of the energy obtained.¹ In this context, suitable materials should be easily preparable, inexpensive, and show stable behavior over long periods of operation. For these reasons, electrochemical photovoltaic cells composed of dye-sensitized oxides have been widely investigated. Grätzel and others have demonstrated that Ru-dye sensitized titanium dioxide (TiO_2) offers a respectably high solar energy-to-electricity conversion efficiency of up to 10%.² This raised the hope of fabricating a stable, highly efficient, electrochemical photovoltaic cell. Nanocrystalline metal sulfides such as ZnS and CdS are promising materials in this respect.³ They are used in a variety of applications, such as optical and optoelectronic devices, photocatalysis,⁴ and window layers for fabrication of solar cell, due to their high transmittivity and low resistivity.⁵ Several methods were documented for the synthesis of nanocrystalline CdS and ZnS. Some of these methods are metal-organic precursors, sol-gel, sonochemical, micro-wave assisted synthesis, and chemical bath deposition.⁶

In this paper we present our study on the synthesis and characterization of CdS and ZnS in nanocrystalline form to prepare the photoelectrochemical solar cell. On the other hand, there are few studies on the sensitization of

the nanocrystalline semiconductor electrode by organic dyes compared to those of metal complex.⁷ Therefore, this paper focuses on the sensitization of these metal sulfides with various organic dyes.

II. EXPERIMENTAL

A. Preparation of ZnS and CdS nanoparticles

The green synthesis method using starch as a capping agent was used to prepare ZnS and CdS nanoparticles.⁸ The green synthesis requires the related materials to be environmentally benign, nontoxic, and renewable. Starch as a green capping agent is one of the best candidates. Further, starch adopts a right-handed helical conformation in aqueous solution, in which the extensive numbers of hydroxyl groups can facilitate the complexation of metal ions to the molecular matrix.⁸ Cadmium chloride, zinc chloride, and sodium sulfide were purchased from BDH Chemical Ltd. Co. Starch, a commercially available material, was used as the capping agent. A dilute aqueous solution of sodium hydroxide was used to control the pH.

The synthesis of starch capped ZnS and CdS nanoparticles proceeds as follows: The mixture of aqueous solution of starch (0.05 wt%) and 0.1 mol dm^{-3} of cadmium was stirred at room temperature for about 1 h. Then the pH was adjusted to $\text{pH} = 8-9$ using a dilute solution of sodium hydroxide. When the homogeneous solution was obtained, an aqueous solution of 0.1 mol dm^{-3} of sodium sulfide was slowly added. The mixture was further stirred for about 5 h and aged to

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about 12 h. The final precipitate was filtered and washed three times with acetone and dried at 200 °C for 4 h to get rid of the starch. The ZnS was prepared in the same way. The CdS and ZnS are now ready to be applied as anodes in the cell and to be sensitized by dyes, which takes place immediately to prevent particle aggregation.

B. Cell preparation

To form the CdS and ZnS photoanode structure, CdS and ZnS coating was first applied using a conventional method.⁹ The colloid CdS solution of 6 g was ground in a mortar with 2 mL of water and 0.2 mL of acetylacetone. A detergent (0.1 mL Triton X-100) was added to facilitate the spreading of the colloid on the substrate. Finally, the colloid was diluted by addition of 8 mL water. The colloid ZnS dispersion was prepared by the same method as the colloid CdS. The electrode was prepared by spreading a viscous dispersion of nanocrystalline CdS and ZnS on a conducting indium tin oxide (ITO)-coated glass substrate (transmission >70% in visible and sheet resistance 20 Ω/square). After air drying, the film electrodes were fired for 30 min at 200 °C. The resulting film thickness was about 20 μm.

The adsorption of dyes was carried out immediately after high-temperature annealing to avoid rehydration of the porous thin films. The ITO/CdS and ZnS film electrodes were dipped into a 10⁻³ mol L⁻¹ solution of the commercially available dyes crystal violet (CV; Fluka), methylene blue (MB; Fluka), and fluorescein (FL; Fluka) at room temperature for more than 12 h. After completion of the dye adsorption, the carbon counterelectrode was prepared by sputtering a thin layer of carbon on a transparent conducting glass support using a graphite rod. The carbon electrode was placed over the dye-coated electrode, and the edges of the cell were sealed. A redox electrolyte consisting of a mixture of iodide/triiodide in acetonitrile was injected by syringe into the space between the two electrodes. The area of the cell was 2 cm² (1 cm × 2 cm). A schematic diagram showing the construction of the cell is represented in Fig. 1.

The dye coated semiconductor film was illuminated through the conductive glass support. To measure the I-V characteristic, direct sunlight served as a light source. The intensity of the illumination source was measured using a power meter. The circuit used for this measurement is shown in Fig. 2. A load resistance was used and varied between the short-circuit and open-circuit conditions to give the full I-V curve. The voltage was recorded using a voltmeter and a Keithly Electrometer 614 was used for measuring the current.

C. Characterization of ZnS and CdS nanoparticles

Powder x-ray diffraction (XRD) was recorded on Diano Corporation USA diffractometer using Co-radiation

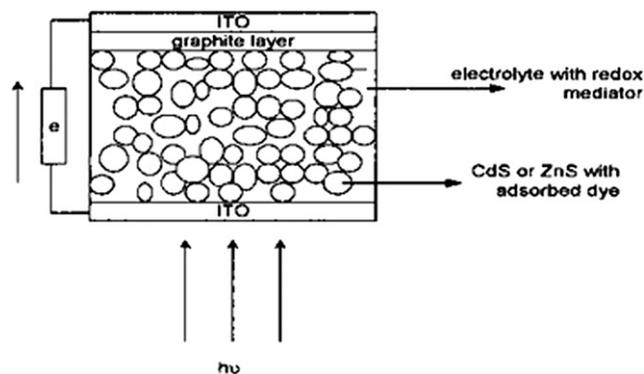


FIG. 1. Scheme configuration of dye-sensitized solar cell.

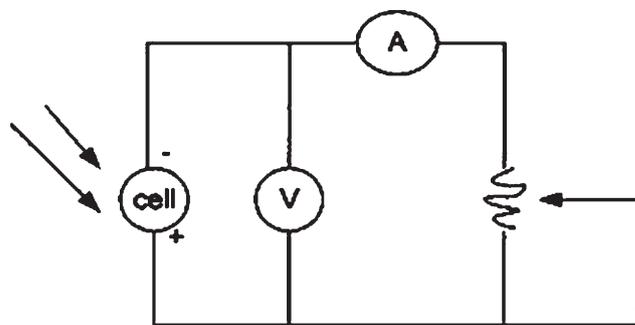


FIG. 2. The circuit used to measure I-V characteristic of cell.

($\lambda = 0.179$ nm). The absorption measurements were performed on a Perkin-Elmer Lambda 40 spectrophotometer.

III. RESULTS AND DISCUSSION

A. Structure characterization

XRD patterns of the synthesized CdS and ZnS powder are shown in Fig. 3. From which, it is clear that CdS shows diffraction peaks at 2θ positions of 27.2°, 44.3°, and 53.3°. The diffraction peaks at 2θ for ZnS were observed at 37°, 53.4°, and 66.7°. These three diffraction peaks for CdS and ZnS correspond to reflection from the (111), (220), and (311) planes of the cubic phase, respectively. These results agree with those reported in the literature.^{10,11} The average size of particles can be calculated from the full width at half maximum (FWHM) values of the diffraction peaks using the Scherrer formula¹²:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size, λ the x-ray wavelength, θ the diffraction angle, and β the FWHM. The calculated average particle size of the synthesized CdS was 11 nm derived from the FWHM of the peak corresponding to $2\theta = 27.2^\circ$. The average particle size for ZnS was 20 nm derived from the FWHM of peak corresponding to $2\theta = 37^\circ$.

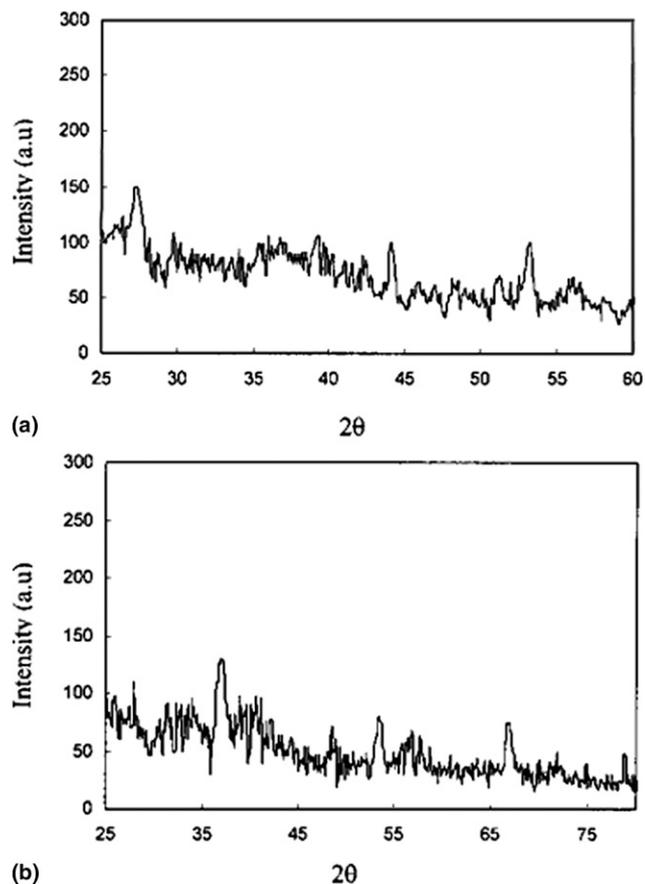


FIG. 3. X-ray diffraction patterns of (a) CdS and (b) ZnS powder.

Figure 4 shows the absorption spectra of CdS and ZnS nanoparticles. We can see from Fig. 4(a) that the onset of the absorption peak for CdS is located at nearly 480 nm which represents a blue shift of approximately 35 nm with respect to the band gap of 515 nm for bulk CdS.⁸ Additionally, the UV-vis spectrum also shows a shoulder peak at 320 nm, which can be assigned as an excitation peak.⁸ The absorption spectrum of ZnS is shown in Fig. 4(b). It can be noted that the prepared ZnS showed a maximum at 317 nm with a blue shift in the absorption edge compared to bulk ZnS. This blue shift in absorption edge for CdS and ZnS is a result of quantum confinement effects.¹³

The optical band gaps (E_g) of the prepared CdS and ZnS were calculated using the relation:

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (2)$$

where α is the optical absorption coefficient derived from the absorption data, $h\nu$ is the photon energy, A is a constant, and n depends on transition type. The plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) showed linear behavior for $n = 1/2$, Fig. 5. This can be taken as evidence for direct transition in these samples. The optical band (E_g) can be calculated from extrapolating the straight line to zero

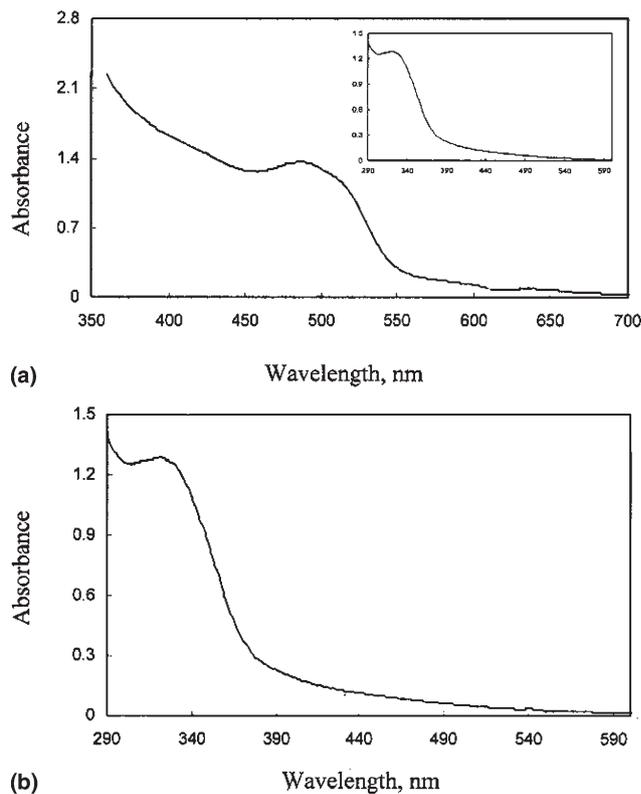


FIG. 4. Absorption spectra of (a) CdS and (b) ZnS.

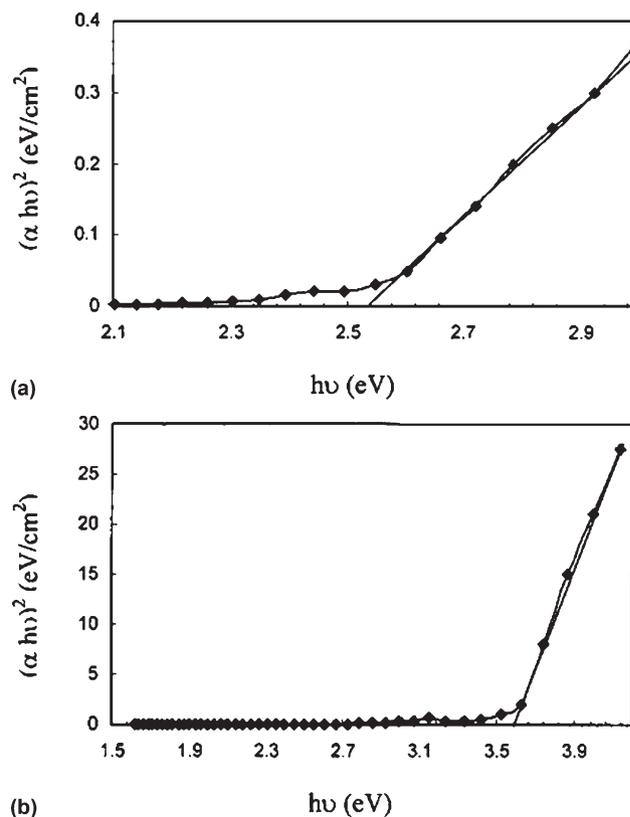


FIG. 5. Determination of band gap energy for (a) CdS and (b) ZnS.

photon energy. It is evident from the plot that CdS and ZnS have band gaps of 2.54 eV and 3.63 eV, respectively. The band gap values were found to be higher compared to the bulk value.^{6,13}

The average size of CdS and ZnS particles can also be calculated by employing the Brus equation,¹³

$$E = [E_g^2 + 2(\hbar)^2 E_g (\pi/r)^2 / m^*]^{1/2} \quad (3)$$

where E is the energy gap, E_g the bulk band gap, r the particle radius, and m^* the effective mass of an electron. The average particle diameter corresponding to the energy gap, 2.54 eV for CdS and 3.63 eV for ZnS, is 10 and 18 nm, respectively. This agreed well with the nanocrystallite sizes as determined from the x-ray studies and the shift in the band gap.

These results indicate that the CdS and ZnS prepared by this method can be used as photoelectrodes in dye-sensitized solar cells.

B. Photovoltaic properties of DSSCs based on nanocrystalline CdS and ZnS

The synthesized CdS and ZnS were used as the electrode in a dye sensitized solar cell. Figure 6 represents the molecular structures of three efficient photosensitizers for DSSCs. The absorption of a photon by a dye molecule happens via an excitation between its electronic states. The electron transfer mechanism is strongly dependent on the electronic structure of the adsorbed dye molecule and the energy level matching between the excited state of the dye and the conduction band of the CdS and ZnS.

Figure 7 shows the steps in the conversion of a photon to current. Dye adsorbed on the CdS and ZnS surface absorbs the incident photon and is then excited from the ground state to the excited state owing to the intramolecular $\pi-\pi^*$ transition. The electron of the excited state is immediately injected into the conduction band of the CdS and ZnS electrode before it is deactivated by emission and subsequent formation of the oxidized dye. Injected electrons in the conduction band of CdS and ZnS are transported toward the back contact transparent conducting glass support (TCO) and consequently reach the counterelectrode through the external load and wiring. The oxidized dye accepts electrons from the Γ redox mediator, regenerating the ground state of the dye, and Γ^- is oxidized to I_3^- . The oxidized redox mediator, I_3^- , is regenerated to Γ^- at the counterelectrode. This means that electric power is generated without permanent chemical transformation. We concern ourselves here only with the effect of the chemical structure of the dye present upon the solar cell operation. All other factors, such as the concentrations of dye, electrolyte, type of solvent, and sealing stay fixed for all solar cells investigated.

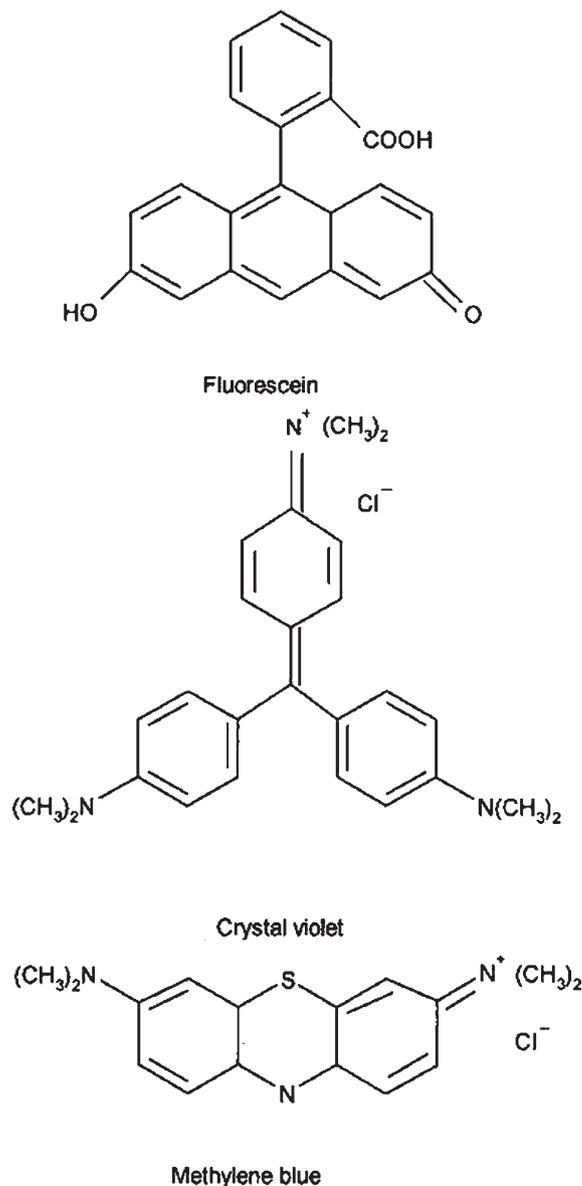


FIG. 6. The structure of investigated dyes.

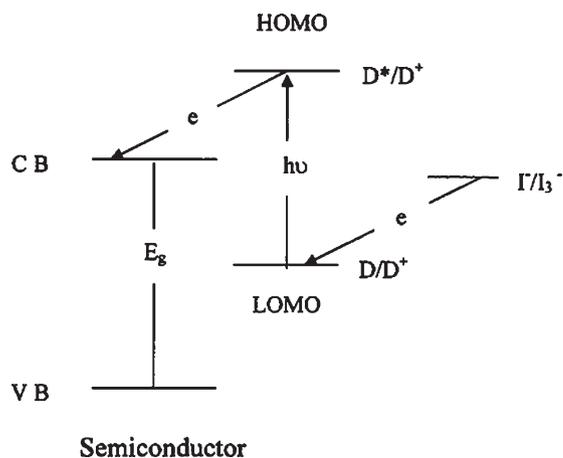


FIG. 7. Schematic energy diagram for a DSSC.

The I-V characteristics of a dye sensitized solar cell based on crystal violet (CV), methylene blue (MB), and fluorescein (FL) under direct sunlight (1000 Wcm^{-2}) are shown in Figs. 8 and 9. The open circuit voltage (V_{oc}) and short circuit current (J_{sc}) were obtained from x and y intercepts, respectively. The fill factor (FF) was calculated using the following relation:

$$FF = \frac{V_m J_m}{V_{oc} J_{sc}}, \quad (4)$$

where V_m and J_m are voltage and current, respectively, for maximum power output. The overall energy conversion yield (η_y) was defined by the following relation:

$$\eta_y = \frac{J_{sc} V_{oc} FF}{P_{in}}, \quad (5)$$

where P_{in} is the power of the incident white light.

The values of fill factor and efficiency (η) are given in Table I. As shown in Table I, the J_{sc} values for all the DSSCs based on CdS nanoparticles were higher than for ZnS. This is probably due to the extent of adsorbed dye. This led to the question of comparing the amount of

adsorbed dye with J_{sc} of corresponding DSC. Figures 10 and 11 represented the absorption spectroscopy of the dye solution before and after absorption from the CdS and ZnS electrodes. The maximum wavelength before and after adsorption from CdS and ZnS and percent of adsorbed dyes are summarized in Table II. This table shows that the position of the maximum absorption peak

TABLE I. Photovoltaic parameters of crystal violet (CV), methylene blue (MB), and fluorescein (FL) dye-sensitized nanocrystalline ZnS and CdS solar cells.

Samples	J_{sc} ($\mu\text{A}\cdot\text{cm}^{-2}$)	V_{oc} (mV)	J_m ($\mu\text{A}\cdot\text{cm}^{-2}$)	V_m (mV)	FF	$\eta \times 10^{-2}\%$
FL/CdS	90	570	65	335	0.42	2.2
MB/CdS	70	500	50	300	0.43	1.5
CV/CdS	40	445	25	250	0.35	0.6
FL/ZnS	8	103	6.3	75	0.47	0.5
MB/ZnS	5	103	3.5	72	0.49	0.3
CV/ZnS	3	96	1.3	70	0.31	0.1

J_{sc} : Short circuit current. FF: Fill factor. V_{oc} : Open circuit voltage. η : overall energy conversion yield. J_m : Maximum current. V_m : Maximum voltage.

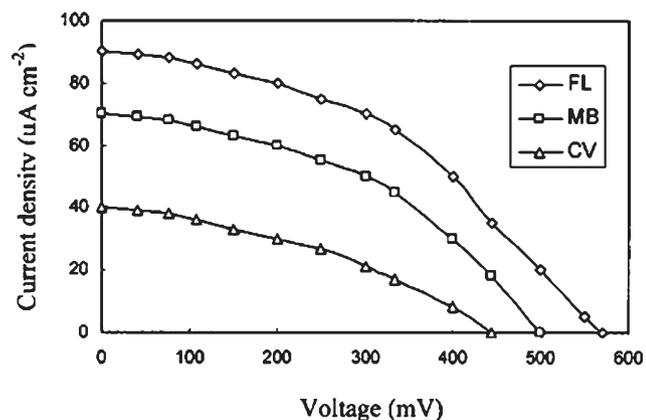


FIG. 8. Current-voltage curves for FL, CV, and MB sensitized CdS electrodes.

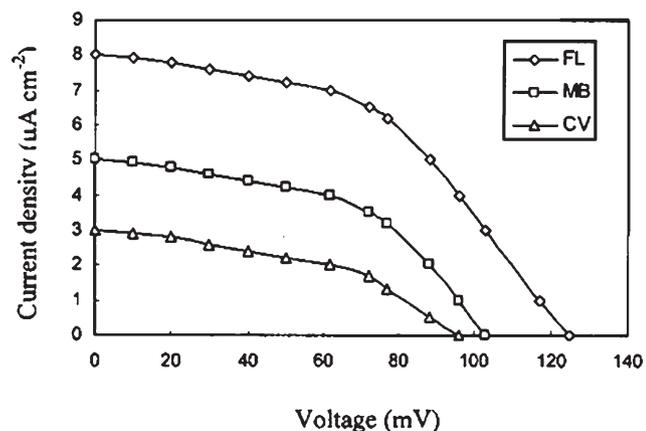


FIG. 9. Current-voltage curves for FL, CV, and MB sensitized ZnS electrodes.

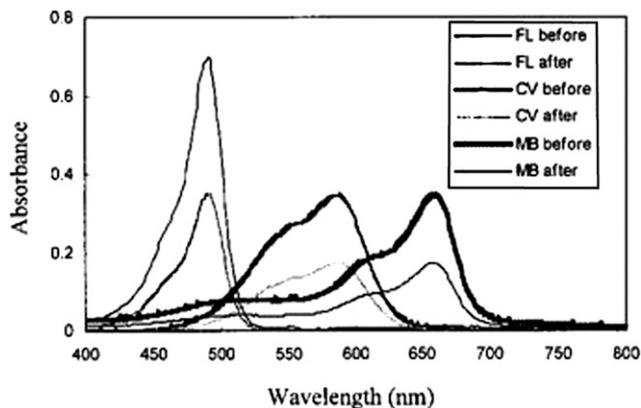


FIG. 10. The change in absorption spectra of FL, MB, and CV in ethanol solution before and after adsorption on the surface of CdS.

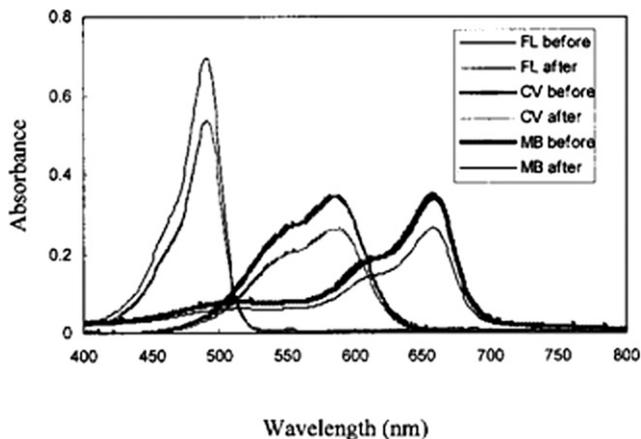


FIG. 11. The change in absorption spectra of FL, MB, and CV in ethanol solution before and after adsorption on the surface of ZnS.

TABLE II. The values of absorption at maximum wave length before and after adsorption from CdS and ZnS.

Samples	Adsorption	λ_{\max} (nm)	A	* %	
CdS	FL	before	488	0.69	52
		after	487	0.33	
	CV	before	580	0.33	48
		after	580	0.17	
	MB	before	655	0.34	50
		after	653	0.17	
ZnS	FL	before	488	0.68	25
		after	488	0.51	
	CV	before	580	0.31	19
		after	580	0.25	
	MB	before	655	0.33	24
		after	655	0.25	

*Percent of absorption.

was the same for each dye before and after adsorption, while a difference in absorption intensity was observed. In the case of CdS, the percent of adsorbed dye is higher than ZnS. This means that a larger amount of dye is adsorbed by CdS than by ZnS. This could be attributed to the small particle size of CdS compared to ZnS. The results also show that the percent of adsorbed FL is higher than CV and MB. The absorption of the dye to the semiconductor surface usually takes place via special anchoring groups. Assuming that the carboxylic group of the FL dye worked as anchoring group, the presence of this acidic group ensures the successful adsorption of this dye on the surface of CdS and ZnS, and increased the electron-injection yield.⁶ Therefore, it is thought that a DSSC based on FL shows the highest solar cell performance and thus the highest photocurrent. In the case of CV and MB, the anchoring groups are amino groups (basic dyes).¹⁴ It is possible that the amino groups were hardly adsorbed on the CdS and ZnS surface. This causes a slight resistance in the electron transfer from the excited state to the conduction band of CdS and ZnS and may suppress sensitization in the MB and CV cells compared to FL cells. This is advantageous to light harvesting and consequently favorable to photoelectric conversion.

Another explanation is also possible on the basis of the formation of aggregates of FL, CV, and MB on the ZnS and CdS surface. It is considered that the arrangement of adsorbed dyes on the ZnS and CdS surfaces was probably different from one dye to another, and the difference of the dye arrangement influenced the solar cell efficiencies. In the case of CV and MB cells, a disorder of the packing of the dye chromophores caused the decrease of efficiency.¹⁵ The formation of this aggregate could be caused by a decrease of the quantum yield and the fluorescence lifetime due to the self-quenching of the excited state in the aggregate.¹⁵ Therefore, it is surmised that the disorder of alignment of the chromophores in the aggregates and the self-quenching

in the aggregate might be responsible for the low efficiency of CV and MB.

These results indicate that the prospects are good for using organic dye as photosensitizers in DSSCs.

IV. CONCLUSIONS

In this study, crystal violet, methylene blue, and fluorescein dyes were used as sensitizers for nanocrystalline CdS and ZnS electrodes. Nanocrystalline CdS and ZnS were prepared by the green synthesis method using starch as the capping agent. X-ray diffraction measurements indicated a cubic phase for both CdS and ZnS nanoparticles with an average particle size of 11 and 20 nm, respectively. Optical absorption measurements revealed a blue shift in the absorption spectrum due to quantum confinement effects. This paper shows a low cost method for the fabrication of sensitized solar cells. The obtained results showed that the short circuit photocurrent density (J_{sc}) of the cells made from dye-CdS was much higher than that made from dye-ZnS. This is due to particle size effect. Our results also show that the DSSCs based on fluorescein dye as the sensitizer exhibited higher photovoltaic performance than CV and MB.

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REFERENCES

1. N. Fathy and M. Ichimura: Photoelectrical properties of ZnS thin films deposited from aqueous solution using pulse electrochemical deposition. *Sol. Energy Mater. Sol. Cells* **87**, 747 (2005).
2. M. Grätzel: Dye-sensitized solar cell. *J. Photochem. Photobiol.* **4**, 145 (2003).
3. A. Olea and P.J. Sebastian: (Zn,Cd) S porous layers for dye-sensitized solar cell application. *Sol. Energy Mater. Sol. Cells* **55**, 149 (1998).
4. W. Dae and R.K. Mehra: Cysteine-capped ZnS nanocrystallites: Preparation and characterization. *J. Inorg. Biochem.* **70**, 125 (1998).
5. I.K. Battisha, H.H. Afify, G. Abd El-Fattah, and K. Bader: Raman and photoluminescence studies of pure and Sn-enriched thin films of CdS prepared by spray pyrolysis. *Fizika* **1**, 31 (2002).
6. V.P. Singh, R.S. Singh, G.W. Thompson, V. Jayaraman, S. Sanagapalli, and V.K. Rangari: Characteristics of nanocrystalline CdS films fabricated by sonochemical, microwave and solution growth methods for solar cell applications. *Sol. Energy Mater. Sol. Cells* **81**, 293 (2004).
7. K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, and H. Arakawa: Efficient sensitization of nanocrystalline TiO₂ films with cyanine and merocyanine organic dyes. *Sol. Energy Mater. Sol. Cells* **80**, 47 (2003).
8. Q. Wei, S.Z. Kang, and J. Mu: Green synthesis of starch capped CdS nanoparticles. *Colloids Surf., A* **247**, 125 (2004).
9. K.G.U. Wijayantha, L.M. Peter, and L.C. Otley: Fabrication of CdS quantum dot sensitized solar cells via a pressing route. *Sol. Energy Mater. Sol. Cells* **83**, 363 (2004).

10. A. Cortes, H. Gómez, R.E. Marotti, G. Riveros, and E.A. Dalchiele: Grain size dependence of band gap in chemical bath deposited CdS thin films. *Sol. Energy Mater. Sol. Cells* **82**, 21 (2004).
11. P. Yang, M. Lü, D. Xü, D. Yuan, C. Song, and G. Zhou: The effect of Co^{+2} and Co^{+3} on photoluminescence characteristics of ZnS nanocrystallines. *J. Phys. Chem. Solids* **62**, 1181 (2001).
12. S. Kumar and R. Chandra: Temperature dependent studies of CdS nanoparticles in viscous matrix. *Opt. Mater.* **27**, 1346 (2005).
13. S.K. Mandal, S. Chaudhuri, and A.K. Pal: Optical properties of nanocrystalline ZnS films prepared by high pressure magnetron sputtering. *Thin Solid Films* **350**, 209 (1999).
14. N.M. Dimitrijevic, K. Takahashi, and C.D. Jonah: Visible absorption spectra of crystal violet in supercritical ethane-methanol solution. *J. Supercrit. Fluids* **24**, 153 (2002).
15. K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa: Dye-sensitized nanocrystalline TiO_2 solar cells based on novel coumarin dyes. *Sol. Energy Mater. Sol. Cells* **77**, 89 (2003).