



Structure, Optical and Photocatalytic Behavior of ZnO–CdS Nanocomposites

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Abstract

Composites nanomaterials are widely studied because of their important applications and unique structure that can be modified and controlled by different methods. In this work, three types of ZnO–CdS composites have been synthesized and applied as photocatalysts for the degradation of Rhodamine B dye in aqueous solutions. The optical and morphological properties of the prepared composites were characterized by different techniques. X-ray diffraction patterns used to identify the phase and to calculate the crystallites size of composites. The morphology and particle size of the composites were analyzed by transmission electron microscopy (TEM). Energy Dispersive X-Ray Analysis coupled with transmission electron microscopy used to measure the composites elemental content. Electronic and optical properties of the solid composites were analyzed by diffraction spectrophotometer. TEM results revealed that all ZnO–CdS composites have homogenous shape with (20–30 nm) particles size. XRD characterization indicates that the composites pattern belongs to wurtzite structure and the calculated crystallites size also in the nanometer. EDS results revealed that all ZnO–CdS composites contains only oxygen, Zinc, Cadmium and sulfur without impurities. UV-Vis measurements showed that the energy-gap of composites significantly decreased after heat treatment and all of prepared composites absorb visible light. The photocatalytic activity of prepared composites shows an excellent performance for RhB dye degradation in aqueous solutions.

Keywords: Composite, Nanoparticles, Optical, Photodegradation, Rhodamine B

1. Introduction

Nanomaterials have attracted and significant importance due to their optic, electronic, and catalytic properties which related to the quantum confinement effect [1]. They have many uses and applications in light emitting devices, solar cells, bio-imaging and, catalysis [2]. In order to modify the optical and electrical properties of semiconductor nanomaterials, the field of composite nanoparticles has been extensively recognized as one of the most rapidly and promising study area. The Promising applications of nanocomposites are includes many fields such as electronic and optical materials, coating technology, solid electrolytes, catalysis, sensors, separation science and device applications [3–4].

The nanocomposites of cadmium sulfide –zinc oxide have been widely studied because of their applications in the field of electronics, optics and photocatalysis[1][5–7]. ZnO–CdS nanostructures materials have important applications in biology and

chemical engineering [8–11][4][12]. Also, one dimensional nanocomposites of ZnO–CdS with tunable band gap have attractive optical properties, and suitable for transportation and fast photon absorption [13].

In the nanocomposites of ZnO–CdS, CdS represent the sensitizer for visible light while the wide band gap (3.34 eV) ZnO semiconductor suppresses the recombination process by charge separation [14].

Also, ZnO–CdS nanocomposites have superior physicochemical aspects compared with constituents. As example, nanorods composites of ZnO–CdS nanoparticles have better conductivity than that of pure ZnO nanorods [15].

Different attempts have made to improve the photocatalytic performance of ZnO which successfully enhanced visible light irradiation such as doping with metal and nonmetal ions [16–19], sensitization using dye and semiconductor quantum

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dots (QDs) [20–23].

CdS represent an interesting semiconductor and it is energy band gap value about (2.4 eV) with high optical absorption coefficient and having different applications in photosensitive devices or photovoltaic and optoelectronic (lasers, light emitting diodes, transistors, etc.), [24–25].

CdS able to transfer electrons for semiconductors with large band gap, which make it suitable photosensitizer for ZnO[26–27].

For this reason, the photocatalytic decomposition of water is the better when achieved using CdS –ZnO nanocomposites[28].

The current work includes preparation and characterization of ZnO-CdS nanocomposite. The as-prepared ZnO-CdS nanocomposite was calcined under vacuum at 250 °C for different times. The prepared ZnO-CdS nanocomposites exhibited excellent photocatalytic performance in degradation of Rhodamine B (RhB) as model organic pollutants.

2. Materials

All the chemical reagents (zinc acetate dehydrate, sodium sulfide, Rhodamine B and cadmium acetate) were purchased from sigma Aldrich and used without purification.

3. Procedure

To synthesize CdS-ZnO nanocomposite, equal volumes (25 ml) of a (0.2 M) solutions of zinc acetate dehydrate and sodium hydroxide were mixed together and the mixture stirred to obtain homogeneous white solution. solution of cadmium acetate (0.2 M, 25 ml) was added to that mixture, and stirred carefully. Later, solution (0.2 M, 25 ml) of sodium sulfide was added with continuous stirrer to the mixture solution. The obtained solution mixture was placed in 60 ml Teflon coated stainless autoclave, and heated in hot air oven at 120 °C for 6 hours. Then, the resulted light yellow precipitate washed and dried at 120 °C for 2 h in a hot air oven. Later, the as-synthesized nanocomposite was transferred to a quartz tube opened from one end, and then treated in low vacuum drying oven at 250 °C for (3, 5 and 7 h), with heating rate(10 °C/min) at 250 °C. According to heating time, the synthesized composites samples were labeled as: ZnO-CdS3, ZnO-CdS5 and ZnO-CdS7.

Characterization

The morphology and particle size of the composites were analyzed by transmission electron microscopy (TEM ,Zeiss Libra @120). Energy

Dispersive X-Ray Analysis coupled with transmission electron microscopy measure the composites elemental content. The prepared nanocomposites were also analyzed by X-ray diffraction (XRD) using Bruker, 2dimensions Phaser advanced monochromatic (CuK α radiation $\lambda = 1.5406\text{\AA}$). The reflection spectra and electronic properties of the solid nanocomposites were analyzed by(Perkin Elmer) diffraction spectrophotometer..

4. Results and Discussion

Figure 1 shows the TEM images of ZnO-CdS3, ZnO-CdS5 and ZnO-CdS7 composites. All of the composites are regular particle aggregates with about (20–30 nm) particles size and ZnO-CdS7 composite greater particles size than the others.

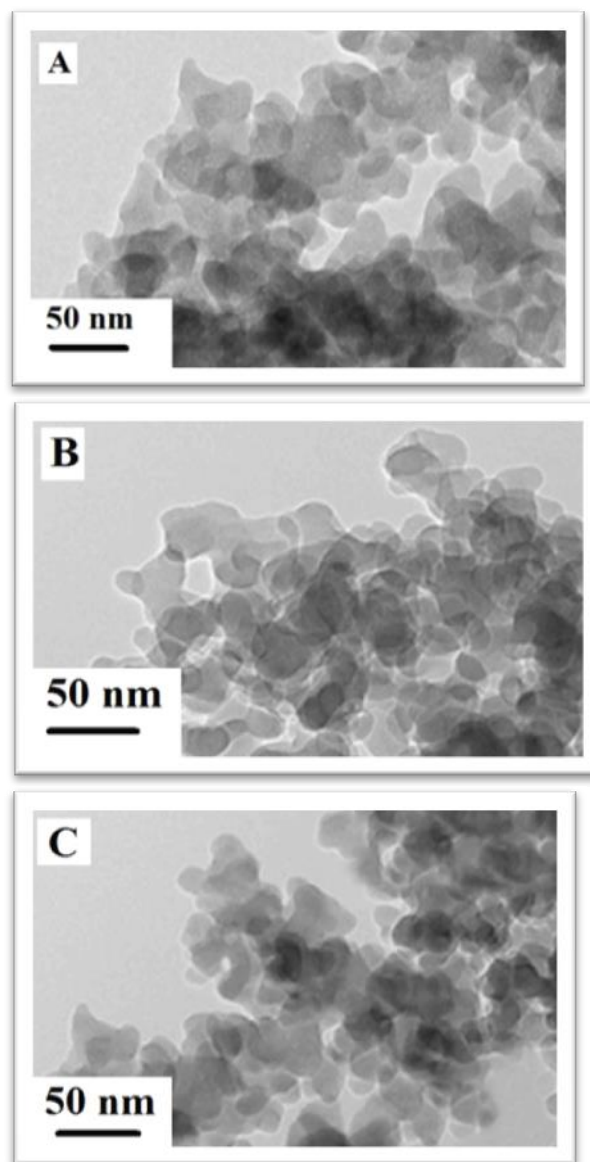


Fig. 1 TEM images (A) ZnO-CdS3(B) ZnO-CdS5(C) ZnO-CdS7

XRD analysis performed to predict the crystalline structure and phase of all prepared composites. Figure 2 shows the XRD patterns of ZnO–CdS3, ZnO–CdS5 and ZnO–CdS7 composites. The XRD patterns showed that all peaks in the CdS/ZnO composites related to wurtzite structure of CdS and ZnO nanoparticles. For ZnO–CdS7 composite, the peaks at $2\theta = 25.32^\circ$, 27.02° , 28.24° , 44.69° , and 54.91° were attributed to CdS (100) (002), (101), (110), and (112) reflection planes respectively.

Also, the diffraction peaks at $2\theta = 36.59^\circ$, 47.57° , 57.32° , 63.74° , and 68.12° related to ZnO (101), (102), (110), (103), (112) planes respectively. All the composites showing similar XRD patterns and no peak owing to impurity were detected.

According to Debye–Scherrer equation, the crystallite size (D_p) of the composites were calculated from the full width at half maximum for the peaks at ($2\theta = 28.24^\circ$, 28.22° and 28.02° for ZnO–CdS7, ZnO–CdS5 and ZnO–CdS3 respectively). As showed in table 1, the crystallites size were 42.32, 31.07 and 28.3 nm for ZnO–CdS7, ZnO–CdS5 and ZnO–CdS3 respectively.

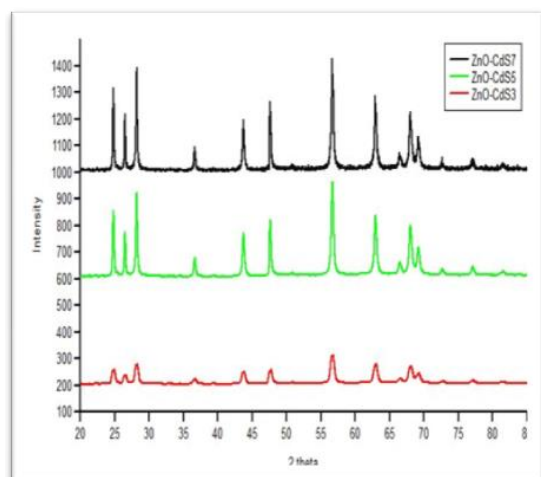


Fig. 2 XRD patterns of ZnO–CdS composites

Table 1. Calculated crystallite size (D_p)

composite	Peak position 2θ ($^\circ$)	FWHM	D_p (nm)
ZnO–CdS7	28.24	0.2021	42.3
ZnO–CdS5	28.22	0.2754	31.0
ZnO–CdS3	28.08	0.2977	28.7

To investigate the composition of the prepared composites, the EDS analysis has been performed and the results are showed in figure 3.

EDS spectrums of the ZnO–CdS3, ZnO–CdS5 and ZnO–CdS7 indicate that all the prepared composites consist of cadmium (Cd), zinc (Zn) and, sulfur (S) oxygen (O) elements and no impurity peaks have been detected.

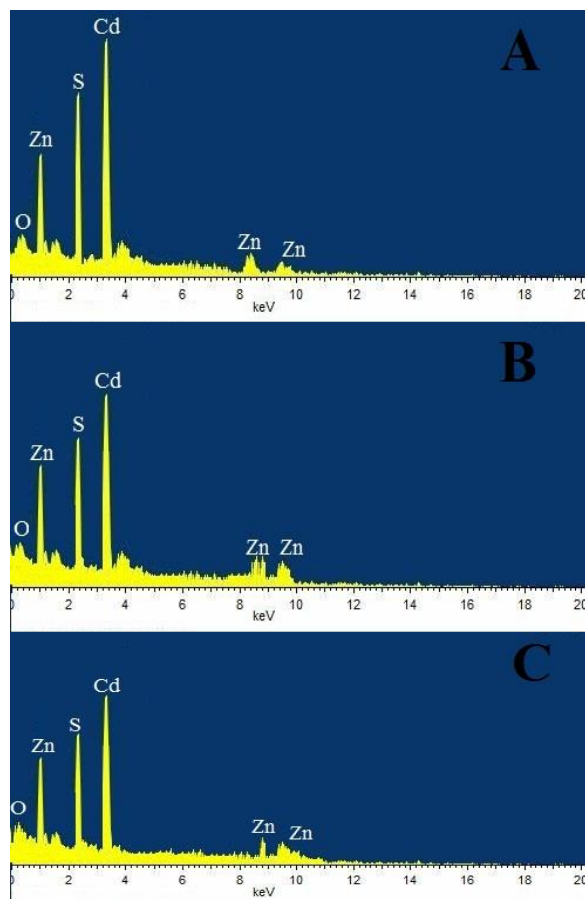


Fig. 3. EDS spectrum of (A) ZnO–CdS3 (B) ZnO–CdS5 (C) ZnO–CdS7

The optical properties for the prepared ZnO–CdS composites were furthermore studied by the (UV–Visible) diffuse reflectance spectroscopy (DRS) and the obtained absorption spectra showed in Figure 4(a). The optical energy gap E_g of ZnO–CdS composites is calculated from Tauc relation. The optical energy gap for all prepared composites was estimated from the reflectance spectra using Tauc relation and the results showed in Figure 4 (b). Based on these results, the energy gap of ZnO–CdS7 were 2.5, 2.6 and 2.83 eV for ZnO–CdS7, ZnO–CdS5 and ZnO–CdS3 respectively.

5. Photocatalytic activity

The photocatalytic activity of prepared composites was evaluated as catalysts using Rhodamine B dye. Photocatalytic degradation measurements were performed using Photochemical immersion well reactor (400W medium pressure mercury lamp, light output 5×10^{19} Photons/s). The degradation efficiency was monitored using UV–Vis spectra in the range (200– 800 nm) after separating the composite catalyst from the aqueous solution by centrifugation for 30 min. Then, the degradation percentages were calculated by the equation:

$$(\text{Degradation } \%) = (A_0 - A / A_0) \times 100$$

Where, A and A_0 represent the absorbance of Rhodamine B dye at reaction times t and 0 respectively. For the photocatalytic activity test, we use ZnO-CdS7 composite as catalyst because it has the smaller energy gap.

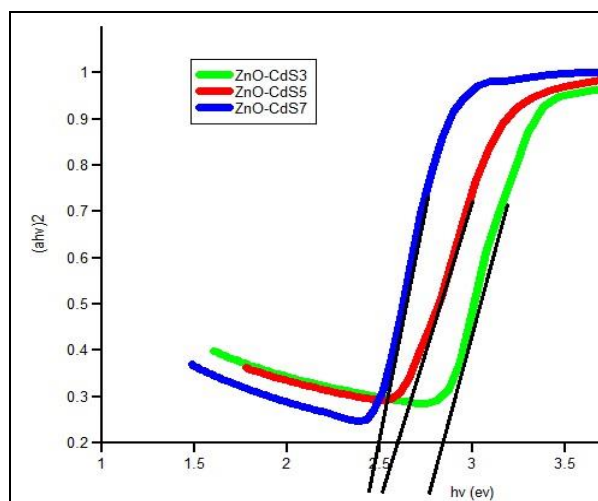
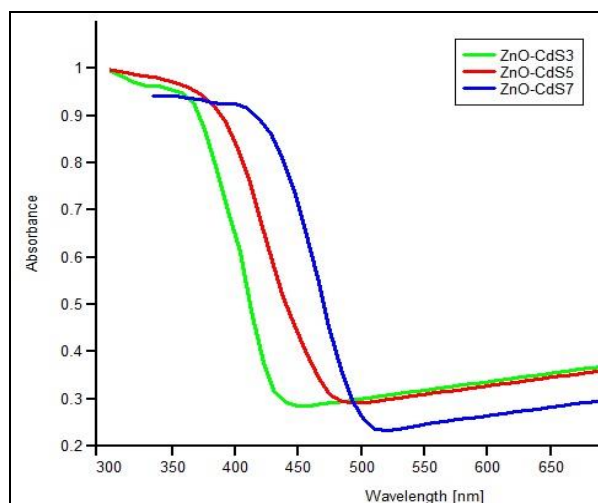


Fig.4 DRS spectra (Top) and Tauc plot (Down)

5.1. Influence of RhB dye concentration

The effect of initial concentration of dye (5, 10, 15 and 20 mg/L) at constant catalyst dosage (1 g) on the photocatalytic efficiency was performed under visible light irradiation and shown in Figure 5.

As can be observed, with increasing the dye concentration, the percentage of degradation decreased.

At constant catalyst content, the number of active sites in the catalyst decreased via dye adsorption over the surface of the catalyst which results in declining the production of ($\cdot\text{OH}$, $\cdot\text{O}_2^-$ and $\cdot\text{OH}_2$) active radicals therefore reducing the photo-degradation efficiency.

More increase in the initial MO dye concentrations means more dye molecules are adsorbed on the surface of the ZnO-CdS catalyst therefore large

amount of radiations are shielded by the dye itself rather than the absorption by catalyst.

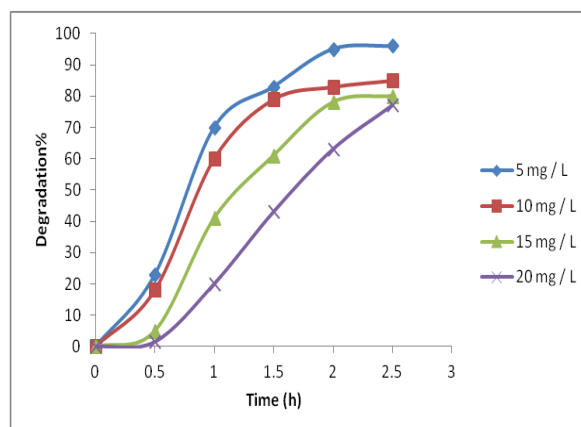


Fig.5. Effect of RhB dye concentration on the degradation of RhB

5.2. Influence of catalyst amount

In order to evaluate the effect of catalyst dosage on the RhB dye degradation efficiency, different amounts of photocatalyst (0.25, 0.5, 0.75 and 1 g) were added to 5 mg RhB dye aqueous solution and the results shown in figure 6.

The results showed that the degradation rate tended to increase gradually as the catalyst dosage increased. It is well known that the catalyst active sites increased as the catalyst dosage in the solution increased therefore increasing the RhB dye molecules that adsorbed on the catalyst and finally enhancing degradation efficiency.

Nevertheless, high amounts of catalyst slightly reduce the degradation efficiency which due to agglomeration and accumulation of the catalyst particles in the photoreaction system therefore scattering the photons.

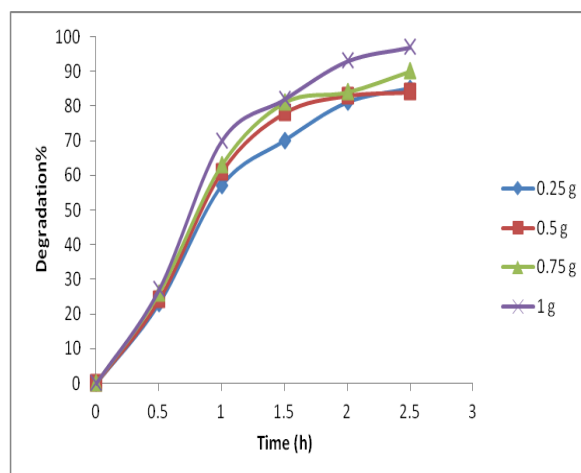


Fig.6. Effect of photocatalyst amount on the degradation of RhB.

5.3. Effect of pH

pH represent one of the important parameters affecting the degradation of RhB dye. The photodegradation percentage studied at different pH values (2.5, 5, 7 and 12) and the results showed in figure7. It can be observed that the degradation percentage of RhB dye in low acidic-natural medium (pH 5 and pH 7) larger than degradation percentage in the high acidic-basic medium (pH 2.5 and pH 12).

However, the reduction in degradation activity at high acidic mediums (pH<5) attributed to the electrostatic repulsions between the RhB cationic molecules and catalyst nanoparticles.

Compared with other method that studied ZnO-CdS as photocatalyst, composites prepared in this study showed high degradation performance for RhB photodegradation[29].

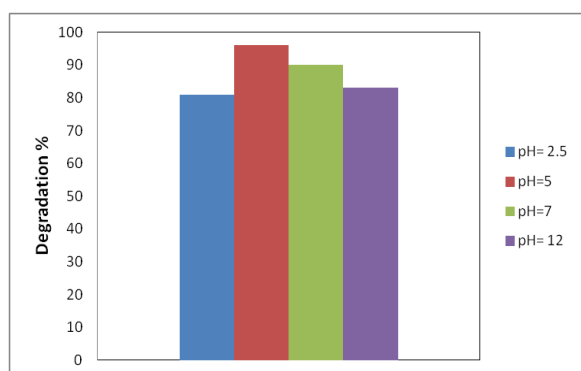


Fig.7. Effect of pH on the photocatalytic degradation of RhB

6. Conclusions

In this study, three ZnO-CdS composite have been synthesized and treated at different temperatures (3, 5, and 7 hours). TEM images revealed that the prepared composites have homogenous shape and the particles size in the range (20-30 nm). The XRD characterization improves that the composites pattern belongs to wurtzite structure and the calculated crystallites size also in the nanometer. EDS technique revealed the prepared composites contains only oxygen, Zin, Cadmium and sulfur without any impurities. The optical properties measured via UV-Vis DRS show that the energy-gap of composites decreased in the order (ZnO-CdS3> ZnO-CdS5 >ZnO-CdS7) and all of prepared composites absorb visible light. The photocatalytic activity of prepared composites shows an excellent performance for RhB dye degradation in aqueous solutions.

7. Conflicts of interest

The authors declare no conflict of interest.

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9. References

- [1] Edvinsson, T., 2018, Optical quantum confinement and photocatalytic properties in two-, one- and zero-dimensional nanostructures. Royal society open science, 5(9), 180387.
- [2] HasanTuhmaz, H., 2020, The Thermo-Optical Treatment of Cancer by Laser Light with Ag Nanoparticles. University of Thi-Qar Journal of Science, 7(2), 84-86.
- [3] Alhameedawi, F.A.H., Challab, M.K. and Khathi, M.T., 2020, Use Activated Carbon Prepared from Some Palm Waste to Remove Co (II) and Cu (II) from Sewage Water. University of Thi-Qar Journal of Science, 7(2), 101-105.
- [4] Nayak, J., Sahu, S.N., Kasuya, J. and Nozaki, S., 2008, CdS–ZnO composite nanorods: synthesis, characterization and application for photocatalytic degradation of 3, 4-dihydroxy benzoic acid. Applied Surface Science, 254(22), 7215-7218.
- [5] Panda, S.K., Chakrabarti, S., Satpati, B., Satyam, P.V. and Chaudhuri, S., 2004, Optical and microstructural characterization of CdS–ZnO nanocomposite thin films prepared by sol–gel technique. Journal of Physics D: Applied Physics, 37(4), 628.
- [6] Fang, F., Zhao, D.X., Li, B.H., Zhang, Z.Z., Zhang, J.Y. and Shen, D.Z., 2008, The enhancement of ZnO nanowalls photoconductivity induced by CdS nanoparticle modification. Applied Physics Letters, 93(23), 233115.
- [7] Vasa, P., Taneja, P., Ayyub, P., Singh, B.P. and Banerjee, R., 2001, Photoconductivity in sputter-deposited CdS and CdS–ZnO nanocomposite thin films. Journal of Physics: Condensed Matter, 14(2), 281.
- [8] Wang, X., Liu, G., Lu, G.Q. and Cheng, H.M., 2010, Stable photocatalytic hydrogen evolution from water over ZnO–CdS core–shell nanorods. international journal of hydrogen energy, 35(15), 8199-8205.
- [9] Meng, X.Q., Zhao, D.X., Zhang, J.Y., Shen, D.Z., Lu, Y.M., Fan, X.W. and Wang, X.H., 2007, Photoluminescence properties of single crystalline ZnO/CdS core/shell one-dimensional nanostructures. Materials letters, 61(16), 3535-3538.
- [10] Rajeshwar, K., de Tacconi, N.R. and Chenthamarakshan, C.R., 2001, Semiconductor-based composite materials: preparation, properties, and performance. Chemistry of Materials, 13(9), 2765-2782.
- [11] Alivisatos, A.P., 1996, Semiconductor clusters, nanocrystals, and quantum dots. science, 271(5251), 933-937.
- [12][12] Anderson, M.A., Gorer, S. and Penner, R.M., 1997, A hybrid electrochemical/chemical synthesis of supported, luminescent cadmium sulfide nanocrystals. The Journal of Physical Chemistry B, 101(31), 5895-5899.
- [13] Caruso, F., 2001, Nanoengineering of particle surfaces. Advanced materials, 13(1), 11-22.
- [14] Thambidurai, M., Muthukumarasamy, N., Arul, N.S., Agilan, S. and Balasundaraprabhu, R., 2011, CdS quantum dot-sensitized ZnO nanorod-

- based photoelectrochemical solar cells. *Journal of Nanoparticle Research*, 13(8), 3267-3273.
- [15] Lee, G.J., Lee, Y., Lim, H., Cheong, H., Kil, B.H. and Han, S.H., 2011, Photoluminescence and nonlinear optical properties of semiconductor nanocomposites consisting of ZnO nanorods and CdS nanodots. *Journal of the Korean Physical Society*, 58(5), 1290-1294.
- [16] Nayak, J., Sahu, S.N., Kasuya, J. and Nozaki, S., 2008, CdS–ZnO composite nanorods: synthesis, characterization and application for photocatalytic degradation of 3, 4-dihydroxy benzoic acid. *Applied Surface Science*, 254(22), 7215-7218.
- [17] Luo, L., Tao, W., Hu, X., Xiao, T., Heng, B., Huang, W., Wang, H., Han, H., Jiang, Q., Wang, J. and Tang, Y., 2011, Mesoporous F-doped ZnO prism arrays with significantly enhanced photovoltaic performance for dye-sensitized solar cells. *Journal of Power Sources*, 196(23), 10518-10525.
- [18] Pawar, B.N., Cai, G., Ham, D., Mane, R.S., Ganesh, T., Ghule, A., Sharma, R., Jadhava, K.D. and Han, S.H., 2009, Preparation of transparent and conducting boron-doped ZnO electrode for its application in dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 93(4), 524-527.
- [19] Park, Y.C., Kong, E.H., Chang, Y.J., Kum, B.G. and Jang, H.M., 2011, Tertiary hierarchically structured TiO₂ for CdS quantum-dot-sensitized solar cells. *Electrochimica Acta*, 56(21), 7371-7376.
- [20] Chen, Y., Tao, Q., Fu, W., Yang, H., Zhou, X., Zhang, Y., Su, S., Wang, P. and Li, M., 2014, Enhanced solar cell efficiency and stability using ZnS passivation layer for CdS quantum-dot sensitized actinomorphic hexagonal columnar ZnO. *Electrochimica Acta*, 118, 176-181.
- [21] Lai, Y., Lin, Z., Zheng, D., Chi, L., Du, R. and Lin, C., 2012, CdSe/CdS quantum dots co-sensitized TiO₂ nanotube array photoelectrode for highly efficient solar cells. *Electrochimica Acta*, 79, 175-181.
- [22] Zhai, T., Fang, X., Bando, Y., Dierre, B., Liu, B., Zeng, H., Xu, X., Huang, Y., Yuan, X., Sekiguchi, T. and Golberg, D., 2009, Characterization, cathodoluminescence, and field-emission properties of morphology-tunable CdS micro/nanostructures. *Advanced Functional Materials*, 19(15), 2423-2430.
- [23] Mondal, S.P. and Ray, S.K., 2009, Enhanced broadband photoresponse of Ge/CdS nanowire radial heterostructures. *Applied Physics Letters*, 94(22), 223119.
- [24] Xu, F., Yuan, Y., Han, H., Wu, D., Gao, Z. and Jiang, K., 2012, Synthesis of ZnO/CdS hierarchical heterostructure with enhanced photocatalytic efficiency under nature sunlight. *CrystEngComm*, 14(10), 3615-3622.
- [25] Ding, M., Yao, N., Wang, C., Huang, J., Shao, M., Zhang, S., Li, P., Deng, X. and Xu, X., 2016, ZnO@ CdS core-shell heterostructures: fabrication, enhanced photocatalytic, and photoelectrochemical performance. *Nanoscale research letters*, 11(1), 1-7.
- [26] Wang, X., Liu, G., Lu, G.Q. and Cheng, H.M., 2010, Stable photocatalytic hydrogen evolution from water over ZnO–CdS core–shell nanorods. *international journal of hydrogen energy*, 35(15), 8199-8205.
- [27] Chankhanittha, T., Watcharakitti, J. and Nanan, S., 2019, PVP-assisted synthesis of rod-like ZnO photocatalyst for photodegradation of reactive red (RR141) and Congo red (CR) azo dyes. *Journal of Materials Science: Materials in Electronics*, 30(19), 17804-17819.
- [28] Senasu, T. and Nanan, S., 2017, Photocatalytic performance of CdS nanomaterials for photodegradation of organic azo dyes under artificial visible light and natural solar light irradiation. *Journal of Materials Science: Materials in Electronics*, 28(23), 17421-17441.
- [29] Xu, F., Yuan, Y., Han, H., Wu, D., Gao, Z. and Jiang, K., 2012, Synthesis of ZnO/CdS hierarchical heterostructure with enhanced photocatalytic efficiency under nature sunlight. *CrystEngComm*, 14(10), 3615-3622.