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# PREPARATION AND CHARACTERIZATION OF CdS NANOWIRES BY POLYETHYLENE GLYCOL-ASSISTED SOLVOTHERMAL REACTION

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Cadmium sulfide nanowires have been successfully synthesized via polyethylene glycol-assisted solvothermal method at 200 °C for 24 h. The products were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), selected area electron diffraction (SAED), high resolution electron microscopy (HRTEM), transmission electron microscopy (TEM) and UV-Visible spectroscopy, respectively. The XRD and SAED results indicated that as-synthesized CdS samples are single phase with hexagonal structure. The SEM images show morphologies of CdS nanorods and nanowires for PEG-free and PVA-added in precursors with growth direction along [001] direction. The optical absorbance spectra of products showed that a strong absorption appeared at 487 nm for CdS nanorods and 480 nm for CdS nanowires.

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*Keywords:* Cadmium sulfide; Polyethylene glycol; Solvothermal method

## 1. Introduction

One-dimensional (1D) materials (nanowires, nanorods, nanoribbons and nanotubes) have attracted considerable research activities due to their immense potential for fundamental studies of the roles of dimensionality and size in their physical properties as well as for application in optoelectronic nanodevices and functional materials [1-3]. CdS is one of the most important groups II–VI semiconductors due to its wider band width (2.5 eV for the bulk hexagonal wurtzite structure and 3.53 eV for bulk cubic zinc blende structure) and non-linear optical properties [3-5]. CdS nanomaterials have already shown vital applications in light-emitting diodes, solar cell, or other optoelectronic devices [6-7]. Physical synthesis, such as chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD) and thermal evaporation, have been developed to synthesize 1D CdS nanostructures [8-13]. However, those methods usually require special instruments, high vacuum or high temperature. Compared to the chemical route, the solvothermal method is a facile, one-step, inexpensive, simple, morphology and size controlled and highly efficient synthetic approach for the preparation of 1D CdS nanostructures [14-17].

In this research, one-dimension CdS nanostructures were synthesized by PEG-assisted solvothermal. The products were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), selected area electron diffraction (SAED), high resolution electron microscopy (HRTEM), transmission electron microscopy (TEM) and UV-Visible spectroscopy, respectively.

## 2. Experiment

In a typical procedure, 0.005 moles of cadmium nitrate ($Cd(NO_3)_2$), and thiourea ($NH_2CSNH_2$) were mixed with 50 ml ethylenediamine (en). After that 0.0 and 0.5 g polyethylene glycol (PEG) M.W. 10,000 was added into the solution. Then it was put into a Teflon-lined

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autoclave. The autoclave was heated at 200 °C for 24 h. The products were filtered, washed with distilled water and absolute alcohol several times to remove the impurities and dried at 80 °C for 12 h, the yellow powders were collected for characterization.

X-ray powder diffraction (XRD) was recorded using a Siemens D500 x-ray diffractometer with graphite monochromatized Cu K$\alpha$ radiation with the scanning angle 2θ ranging from 15 ° to 60 °. Raman spectroscopy was recorded on HORIBA JOBIN YVON T64000 with a 50 mW Ar laser (514.5 nm). A scanning electron microscopy (SEM) of JEOL JSM-6335F was operated at 15 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and ), selected area electron diffraction (SAED) were performed with a JEOL, JEM-2010 microscope operated at 200 kV. The room temperature UV-visible spectra were obtained on a UV-Visible spectrometer Perkin Elmer LAMBDA 40 at wavelength range of 200-800 nm with scan rate 0.5 nm.sec$^{-1}$.

## 3. Results and discussion

Fig. 1a shows XRD patterns of the products. All the diffraction peaks can be indexed as (110), (002), (101), (102), (110), (103), (200), (112), (201) and (004) planes of hexagonal CdS structure with comparing to the JCPDS No. 41-1049 [18]. It can be seen that the intensities of (002) plane are higher than standard, which suggests that products have a preferential growth along the [002] direction.

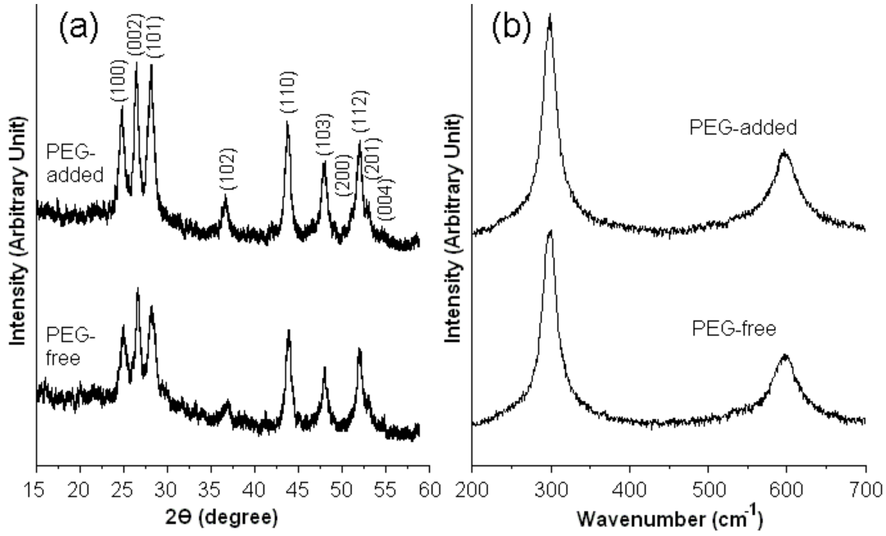

*Fig. 1 (a) XRD pattern and (b) Raman spectra of products were synthesized by solvothermal method at 200 °C for 24 h*

The hexagonal CdS have $C^4_{6v}$ space group. Its Raman actives are $1A_1 + 1E_1 + 2E_2$ ($E_{2H}$ and $E_{2L}$) but $2B_2$ modes are silent. The phonon polarization for the $A_1$ branch is in the z direction. But for the doubly degenerate $E_1$ and $E_2$ branches, the phonon polarizations are in the x–y plane. The wurtzite structure is noncentrosymmetric. Therefore, both $A_1$ and $E_1$ modes split into longitudinal optical (LO) and transverse optical (TO) components. Raman spectra of the products (Fig. 1b) show the same position of 1LO and 2LO for $A_1$ mode at 300 and 601 cm$^{-1}$, polarizing in the x–z face and strong coupling to the exciton along c-axis [19-21].

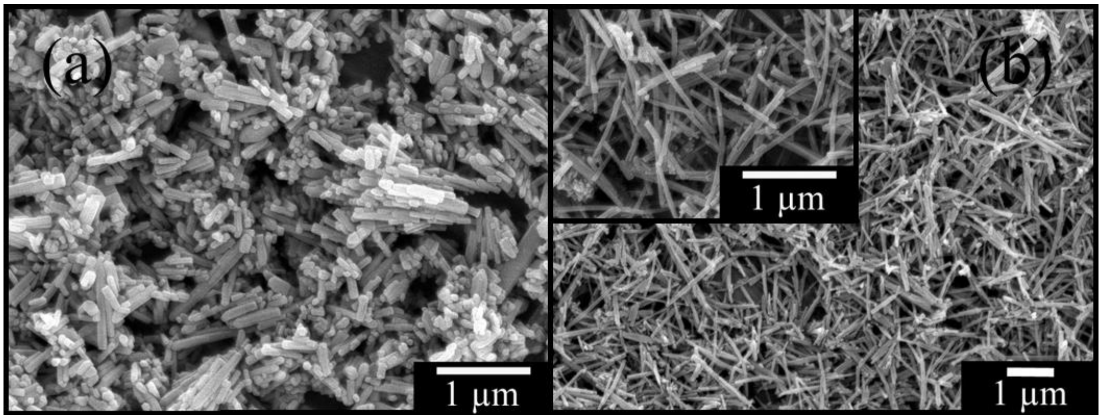

*Fig. 2 SEM image of as-synthesized CdS nanostructures synthesized by solvothermal method at 200 $^oC$ for 24 h with (a) PEG-free and (b) PEG-added.*

Fig. 2 shows the SEM images of as-synthesized CdS nanostructures without and with PEG-added. In PEG-free, CdS nanorods with an average length of 100-800 nm and a diameter of 60 nm were obtained. It was observed that the CdS nanorods transformed to nanowires by added PEG in precursor as shown in Fig. 2b. The product prepared in the presence of PEG is composed of CdS nanowires with an average length of 2-4 μm and a diameter of 20-30 nm. Therefore, CdS nanostructures with high aspect ratio were produced by PEG-added as capping reagent, resulting in the formation of CdS nanowires.

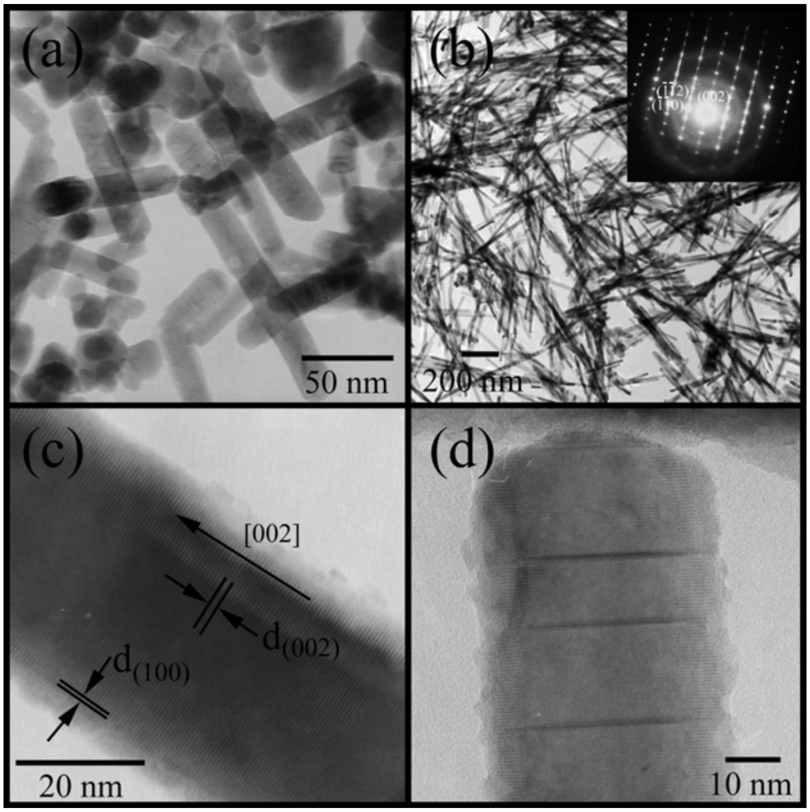

*Fig. 3 TEM image, SAED pattern and HRTEM image of as- synthesized CdS nanostructures synthesized by solvothermal method at 200 $^oC$ for 24 h with (a) PEG-free and (b-d) PEG-added.*

Fig. 3 shows the TEM image, SAED patterns and HRTEM image of CdS without and with PEG-added prepared by solvothermal at 200 °C for 24 h. The product (Fig. 3a) is composed of CdS nanorods with length of 50-200 nm and diameter of length about 15-20 nm. While the product produced by PEG-added at 200 °C for 24h (Fig. 3b), the aspect ratio of 1D CdS nanostructure was increased from 8-50 of CdS with PEG-free to 100-250 of CdS with PEG-added. The diameter and length of CdS nanowires were about 20-30 nm and 2-4 µm. That result indicates that the PEG has influence on the formation of CdS nanowires. SAED pattern as inserted in Fig. 3b displayed a bright spot pattern which indicated that products are single crystalline. It can be indexed to (-1-10), (-1-1-2) and (00-2) planes of hexagonal CdS structure with [-110] as zone axis. HRTEM image shows lattice fringes which are parallel and perpendicular to the growth direction of single nanowires with the spaces of 0.358 and 0.336 nm. They correspond with those of (100) and (002) planes of hexagonal CdS phase. HRTEM image of single CdS nanowire as shown in Fig. 3d found a straight traverse stripes on the nanowire which may be attributed to defects during the growth process. Stacking faults as planar defect are the most frequently observed planar defects in 1D wurtzite semiconductor nanomaterials [22-25]. Stacking faults are formed by a change in stacking sequence of atomic planes. In the wurtzite semiconductor nanomaterialse, there are three possible types of stacking faults as I1, I2, and E in bulk materials, which are produced by extracting one layer, extracting two layers, and inserting a layer, respectively. In this case, it found the stacking defect along [0001] direction was due to the shape effect of the planar defects in *c* plane. The atom arrangement of perfect hexagonal CdS structure is a ABABAB stacking sequence parallel to the (001) plane [22]. However, a new sequence identified as to be ...ABABCACABAB... as I1 and an I2 stacking faults can be formed in growth stage. The ABABAB stacking sequence changes to ABCABC in some local areas as shown in Fig. 3d, corresponding to the formation of the zinc blende CdS phase in the wurtzite-matrix [22-24].

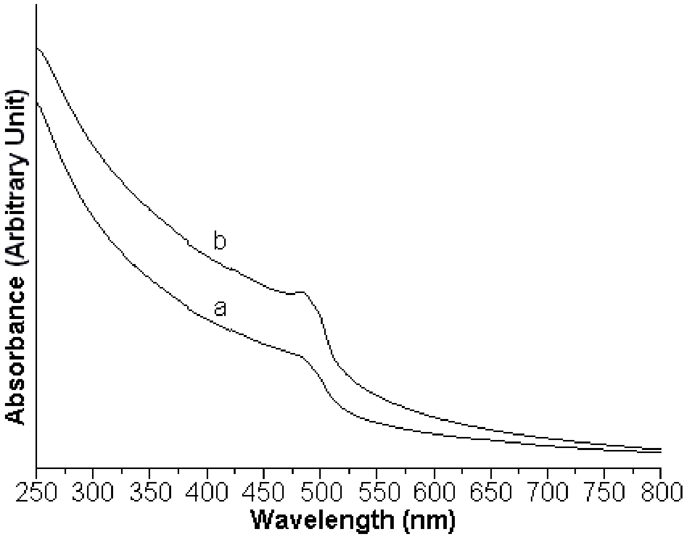

*Fig. 4 UV-Visible spectra of as-synthesized CdS nanostructures synthesized by solvothermal method at 200 °C for 24 h with (a) PEG-free and (b) PEG-added.*

The possible formation mechanism of 1D CdS has two possible routes. Firstly, the $Cd^{2+}$ ions can complex with thiourea (Tu) to form $[Cd–Tu]^{2+}$ complexes. After that Cd–Tu complexes decompose under solvothermal condition to produce 1D CdS nanostructures with grow along [002] direction due to the minimum surface energy effect [3, 25, 26, 27]. The process can be expressed as the following equation (1):

$$Cd^{2+} + 2Tu\square\rightarrow\ [Cd(Tu)_2]^{2+}\square\rightarrow\ CdS \qquad (1)$$

However, en has often been used as a complexing agent to the synthesis of 1D materials in the solvothermal process because of its strong chelate-forming ability. The coordination ability of en is much stronger than Tu and the complex ion $[Cd(en)_2]^{2+}$ will form in solution instead of $[Cd(Tu)_2]^{2+}$. The Tu reacts with a small amount of $H_2O$ in the system to produce $S^{2-}$. Finally, CdS nanorods nucleated and grew by the following reactions as below [3, 5, 25, 27] :

$$Cd^{2+} + 2en \rightarrow Cd(en)_2^{2+} \tag{2}$$

$$NH_2CSNH_2 + H_2O \rightarrow NH_2CONH_2 + H_2S \tag{3}$$

$$Cd(en)_m^{2+} + S^{2-} \leftrightarrow CdS(en)_m \leftrightarrow CdS(en)_{m-n} + n(en) \tag{4}$$

The reaction rate is relatively slow due to the slow release rate of $S^{2-}$ ion as a precursor to form complex with en, and $S^{2-}$ ion also has a relatively weak intermolecular coordinating to $Cd^{2+}$ ion ($\log \beta_2 = 10.09$, and $\beta_2$ is a constant of the complex ion $Cd(en)_2^{2+}$) [3, 20, 25]. The slow reaction rate can play a role in the crystal growth towards 1D CdS nanostructure. The CdS nucleate grow along the {001} plane according to closed-packing effect which causes it to form 1D CdS nanostructure [3]. When a PEG was added in the solution at the same condition, the length of CdS increased several times and formed to nanowires. The strong interaction of PEG with the side faces of CdS nanorods is higher than that with their ends along c-axis. Therefore, PEG inhibited the growth of side faces by capping them heavily, in comparison to the end faces with less capping by PEG, remaining as highly active for the continuous growth [2, 20]. As a result, the orientation growth along *c*-axis was advantaged. Therefore, PVA has the influence on 1D growth of CdS nanostructures.

The UV-Visible spectra of CdS nanostructures is shown in Fig. 4. It can be observed that a strong absorption appeared at 487 nm for CdS nanorods and 480 nm for CdS nanowires which are assigned to the first excitation of CdS [28]. The band gap energy of product was calculated by the Planck’s equation [29]. The calculated band gap energies from UV-visible absorption for CdS nanorods and nanowires are 2.54 eV and 2.58 eV, respectively. In comparison to the CdS bulk material with 2.42 eV band gap and maximum absorption 512 nm [28, 30], CdS nanowires and nanorods showed a blue shift due to quantum confinement effect of the small diameter.

## 4. Conclusions

One-dimension CdS with high aspect ratio was synthesized using cadmium nitrate and thiourea in ethylenediamine as a solvent by PEG-assisted solvothermal method. Comparing the aspect ratio between CdS with PEG-free and PEG-added, the aspect ratio increased form 8-50 of CdS with PEG-free to 100-250 of CdS with PEG-added. The experiment results indicated that PEG play an important role in controlling growth of 1D CdS nanostructures.

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## References

[1] D.P. Wang, D.B. Sun, H.Y. Yu, Z.G. Qiu, H.M. Meng, Mater. Chem. Phys. **113**, 227 (2009).
[2] H. Wang, P. Fang, Z. Chen, S. Wang, J. Alloy. Compd. **461**, 418 (2008).
[3] M. Maleki, S. Mirdamadi, R. Ghasemzadeh, M.S. Ghamsari, Mater. Lett. **62**, 1993 (2008).
[4] H. Cao, G. Wang, S. Zhang, X. Zhang, D. Rabinovich, Inorg. Chem. **45**, 5103 (2006).
[5] A. Phuruangrat, T. Thongtem, S. Thongtem, Mater. Lett. **63**, 1562 (2009).

[6] W. Qingqing, X. Gang, H. Gaorong, J. Solid State Chem. **178**, 2680 (2005).
[7] W. Qingqing, Z. Gaoling, H. Gaorong, Mater. Lett. **59**, 2625 (2005).
[8] X.P. Shen, A.H. Yuan, F. Wang, J.M. Hong, Z. Xu, Solid State Commun**.** **133**, 19 (2005).
[9] Y. Wang, C.Y. To, D.H.L. Ng, Mater. Lett. **60**, 1151 (2006).
[10] S.A. Mahmoud, A.A. Ibrahim, A.S. Riad, Thin Solid Films **372**, 144 (2000).
[11] L. Xu, Y. Su, D. Cai, Y. Chen, Y. Feng, Mater. Lett. **60**, 1420 (2006).
[12] R.A. Berrigan, N. Maung, S.J.C. Irvine, D.J. Cole-Hamilton, D. Ellis, J. Cryst. Growth **195**, 718 (1998).
[13] H. Ren, L. Zhang, X. Wan, Y. Bi, Y. Zhang, Thin Solid Films, **518**, 3700 (2010).
[14] W.S. Kim, H.C. Kim, S.H. Hong, J. Nanopart. Res. **12**, 1889 (2010).
[15] X. Liu, J. Cui, L. Zhang, W. Yu, F. Guo, Y. Qian, Nanotechnology 16, **1771** (2005).
[16] K. Aandan, V. Rajendran, J. Non-Oxide Glass. **2**, 83 (2010).
[17] W. Cai, Y. Zhao, J. Hu, J. Zhong, W. Xiang, J. Mater. Sci. Technol. **27**, 559 (2011).
[18] Powder Diffract. File, JCPDS Internat. Centre Diffract. Data, PA 19073–3273, U.S.A.(2001).
[19] A. Phuruangrat, N. Ekthammathat, T. Thongtem, S. Thongtem, J. Alloy. Compd**.** **509**, 10150 (2010).
[20] A. Phuruangrat, T. Thongtem, S. Thongtem, J. Exp. Nanosci. **4**, 47 (2010).
[21] A. Phuruangrat, T. Thongtem, S. Thongtem, Chalcogenide Lett. **7**, 605 (2010).
[22] Y. Ding, Z.L. Wang, J. Phys. Chem. B **180**, 12280 (2004).
[23] C. Ma, D. Moore, Y. Ding, J. Li, Z.L. Wang, Int. J. Nanotechnology **1**, 431 (2004).
[24] K.T. Yong, Y. Sahoo, H. Zeng, M.T. Swihart, J.R. Minter, P.N. Prasad, Chem. Mater. **19**, 4108 (2007).
[25] J.F.A. Oliveira, T.M. Milao, V.D. Araujo, M.L. Moreira, E. Longo, M.I.B. Bernardi, J. Alloy. Compd. **509**, 6880 (2011).
[26] A.V. Murugan, B.B. Kale, A.V. Kulkani, L.B. Kunde, V. Saaminathan, J. Mater. Sci. **16**, 295 (2005).
[27] S.H. Yu, J. Yang, Z.H. Han, Y. Zhou, R.Y. Yang, Y.T. Qian, Y.H. Zhang, J. Mater. Chem. **9**, 1283 (1999).
[28] S. Yan, L. Sun, P. Qu, N. Huang, Y. Song., Z. Xiao, J. Solid State Chem. **182**, 2941 (2009).
[29] U. Sirimahachai, S. Phongpaichit, S. Wongnawa, Songklanakarin J. Sci. Technol. **31**, 517 (2009).
[30] S. Yan, D. Hu, J. Wu, J. Qian, Y. Wang, Z. Xiao, Solid State Sci. **15**, 1507 (2010).