



A FACILE ROUTE FOR PREPARATION OF CdS NANOPARTICLES

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ABSTRACT

CdS nanoparticles have been synthesized by a chemical reaction route using ethylenediamine as a complexing agent. The nanoparticles were characterized using techniques such as X-ray powder diffraction (XRD), scanning electron microscope (SEM), UV–VIS absorption spectroscopy, and photoluminescence spectroscopy. The Absorption edge for the bulk hexagonal CdS is at 512 nm (2.42 eV). Comparing with the bulk CdS, it is believed that the blue shift in the absorption peak was caused by the quantum confinement effect. Photoluminescence measurements indicate CdS nanoparticles show fluorescence band with a maximum close to 315 nm.

Key words: Cadmium sulfide, Nanoparticle, X-ray diffraction, Absorption spectroscopy, Photoluminescence spectroscopy.

INTRODUCTION

Nanocrystalline semiconductor materials such as PbS and CdS have attracted considerable attention due to their unique properties, which are not present in bulk materials. These nanoparticles exhibit size dependent properties (size quantization effects) such as a blue shift of absorption onset, a change of electrochemical potential of band edge, and an enhancement of photocatalytic activities, with decreasing crystallite size CdS, in particular, have been extensively studied due to their potential applications such as field effect transistors, light emitting diodes, photocatalysis and biological sensors. Many synthetic methods have been employed to prepare CdS nanoparticles including soft chemical reaction, solid-state reaction, sol-gel process, so no chemical preparation microwave heating photoetching and reverse micelle. In this investigation, we have developed a new method to produce CdS nanoparticles of small sizes using chemical reaction.

The nanoparticles are synthesized by reaction of ethylenediamine (C₂H₈N₂) aqueous solution of cadmium acetate dehydrate (C₄H₆O₄Cd·2H₂O) with Na₂S. The prepared particles were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), UV–VIS absorption spectroscopy, photoluminescence (PL) spectroscopy.

EXPERIMENTAL

Cadmium acetate dehydrate ($C_4H_6O_4Cd_2H_2O$), ethylenediamine ($C_2H_8N_2$) were obtained from Merck.

Double distilled water and ethanol was used for washing the particles. A typical procedure for the Cd nanoparticles synthesis is as follows: appropriate amount of analytically pure Cd (CH_3COO) $_2$ \cdot 2H $_2$ O was dissolved into a deaerated 35 mol. % aqueous solution of ethylenediamine in a flask at room temperature.

Then under vigorous stirring, analytical pure Na $_2$ S was quickly added to this solution, and a milk-white sol was formed soon. Next, the resultant milk-white sol was heated to 100°C, and kept on stirring at this temperature for about 6 hours until the milk white reaction mixture gradually turned to a yellow colour.

The final product was then collected and washed with distilled water and ethanol. The X-ray powder diffraction (XRD) pattern was recorded on Philips B.V (CuK- radiation $\lambda = 0.154$ nm), employing scanning rate of 0.02 deg/s in range from 20° to 60°. The SEM images were recorded on Philips XL30 scanning electron microscope.

The sample used or SEM observations were prepared by transferring the particles that at first was dispersed in the ethanol to the SEM stage. After allowing the evaporation of ethanol from the stage, the particles on the stage were coated with a thin layer of gold. UV-VIS absorption spectrum

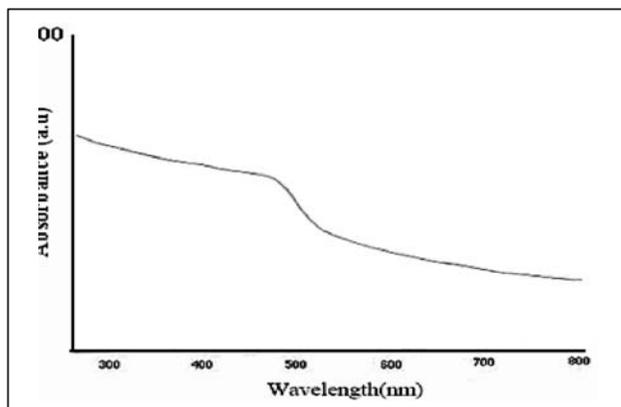


Fig. 1: UV-VIS absorption spectrum of CdS nanoparticles obtained by the offered route

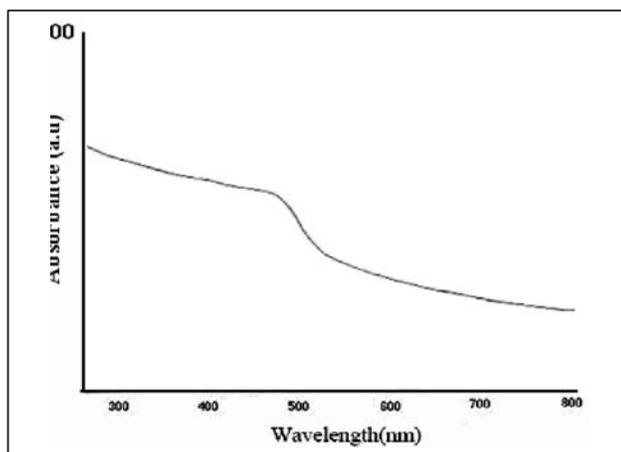


Fig. 2

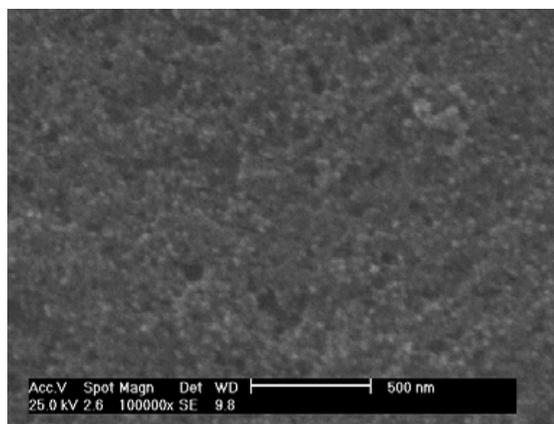


Fig. 3: SEM images of Cd prepared by the offered route. nanoparticles of the sample was recorded employing a double beam, Hitachi, Japan, applying quartz cuvettes of the optical path length 1 cm. The PL spectrum was achieved using Hitachi X530 fluorescence spectrophotometer with a 220 nm excitation line

RESULTS AND DISCUSSION

The UV-VIS absorption spectrum for the colloidal CdS nanoparticles is shown in Fig. 1. According to mass approximation method, the size of colloidal nanoparticles 3-4 nm has been estimated. The sample was dispersed in absolute ethanol by an ultrasonic disperser.

The absorption edge for the bulk hexagonal CdS is at 512 nm (2.42 eV). Comparing with the bulk CdS, it is believed that the blue shift in the absorption peak was obviously caused by the quantum confinement effect.

The XRD pattern of the precipitated nanoparticles was illustrated in Fig. 2. It can be attributed to hexagonal CdS (JCPDS – file No. 10-0454). The broadened peaks are indicating that the sizes of the particles are in nanorange. In order to achieve more confirmative information, the Debye–Scherer formula [12] $L = 0.9\lambda / B \cos\theta = 34 \text{ nm}$ has been applied to calculate the size of the nanoparticles. Here, L is the coherent length, λ is the wavelength of X-ray radiation, B is the full-width at a half-maximum (FMWH) of the peak, and θ is the angle of diffraction. In the case of spherical crystallites, the corresponding crystallite size of nanoparticles obtained in this way is 34 nm which confirms our findings in SEM image (Fig. 3).

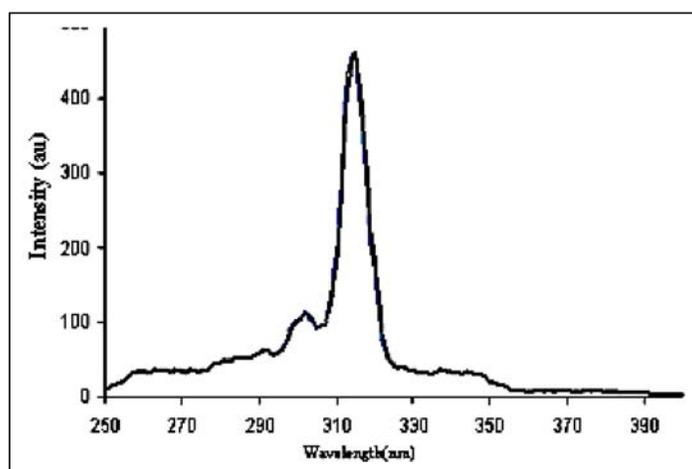


Fig. 4: PL emission spectrum of an absolute ethanol solution

Containing CdS nanoparticles that are obtained by the offered route. The pattern consists of one strong and narrow emission at 340 nm using a 220 nm excitation wavelength. The luminescence at 340 nm may be attributed to a higher level transition in CdS crystallites.

It was reported that this kind of band-edge luminescence is caused by the recombination of excitons and/or shallowly trapped electron-hole pairs¹³. The apparent blue shift and the strong peak are also indicative of size quantization in as-prepared Cd nanoparticles. In our synthetic system, the investigations of CdS nanoparticles formation indicated that the nucleation and growth were well controlled.

Firstly, ethylenediamine, as a strongly bidentating solvent, was ready to form relatively stable Cd²⁺ complexes^{14,15}. Next, the Na₂S generate S²⁻ ions slowly and homogeneously. The S²⁻ ions will react with the Cd²⁺ ions that has chelated with ethylenediamine in a reversible and effective pathway to produce small CdS nanoparticles¹⁶.

CONCLUSION

The sample used or SEM observations were prepared by transferring the particles that at first was dispersed in the ethanol to the SEM stage. After allowing the evaporation of ethanol from the stage, the particles on the stage were coated with a thin layer of gold. UV-VIS absorption spectrum.

A simple method for preparation of CdS nanoparticles by using a chemical reaction has been described. The XRD pattern of CdS nanoparticles showed the materials to be of the nanometric size regime with a predominantly cubic phase. It was shown that the sizes of nanoparticles are 30-40 nm. The CdS nanoparticles showed blue shift in their UV-VIS absorption band edge. Synthesis of porous quantum-size cadmium sulfide membranes: photoluminescence phase shift and demodulation measurements

The PL spectrum of CdS nanoparticles showed a fluorescence band with a maximum at about 315 nm.

REFERENCES

1. A. Henglein, *Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles* // *Chem. Rev.*, **89** (1989) p. 1861-1873.
2. A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima, M. Ichikawa, *Novel Templating Synthesis of Necklace-Shaped Mono- and Bimetallic Nanowires in Hybrid Organic-Inorganic Mesoporous Material* // *J. Amer. Chem. Soc.*, **123** (2001) p. 3373-3374.
3. B. Petit, M. P. Pilleni, *Synthesis of Cadmium Sulfide in Situ in Reverse Micelles and in Hydrocarbon Gels* // *J. Phys. Chem.*, **92** (1988) p. 2282-2286.
4. A. P. Alivisatos, *Semiconductor Clusters, Nanocrystals, and Quantum Dots* // *Science*, **271** (1996) p. 933-937.
5. V. L. Kolvin, M. C. Schlamp, A. P. Alivisatos, *Light Emitting Diodes Made from Cadmium Selenide Nanocrystals and a Semiconducting Polymer* // *Nature*, **370** (1994) p. 354-357.
6. D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos, *A single-Electron Transistor Made from a Cadmium Selenide Nanocrystal* // *Nature*, **389** (1997) p. 699-701.
7. R. S. Mane, C. D. Lokhande, *Chemical Deposition Method for Metal Chalcogenide Thin Films* // *Mater. Chem. Phys.*, **65** (2000) p 1-31.

8. G. Henshaw, I. P. Oarkin, G. Shaw, Convenient, Low-Energy Synthesis of Metal Sulfides and Selenides; PbE, Ag₂E, ZnE, CdE (E = S, Se) // *Chem. Commun.*, **27** (1996) p. 1095-1096.
9. Y. Wada, H. Kuramoto, J. Anand, T. Tikamura, T. Sakata, H. Mori, S. Yanagida, Microwaveassisted Size Control of CdS Nanocrystallites // *J. Mater. Chem.* **11** (2001) p. 1936-1940.
10. T. Torimoto, H. Kontani, Y. Shibutani, S. Kuwabata, T. Sakata, H. Mori, H. Yoneyama // *J. Phys. Chem.*, **105**, 6838 (2001).
11. A. Guinier, X-ray Diffraction. Freeman, San Francisco, CA (1963).
12. L. Sapanhel, M.A. Anderson, // *J. Amer. Chem. Soc.*, **112** (1990) p. 2278-2284.
13. W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, Y. Qian, Preparation and Characterization of CdS Nanoparticles by Ultrasonic Irradiation // *Inorg. Chem. Commun.*, **4** (2001) p. 208-210.
14. X. Ge, Y. Ni, H. Liu, Q. Ye, Z. Zhang, γ -Irradiation Preparation of Cadmium Selenide Nanoparticles in Ethylenediamine System // *Mater. Res. Bull.*, **36** (2001) p. 1609-1613.
15. X. Guo-yue, W. Han, C. Chuan-Wei, Synthesis of Single Crystalline CdS Nanowires with Polyethylene Glycol 400 as Inducing Template // *Nonferrous Met. Soc., China*, **16** (2006) p. 105-109.