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Effect of 2-mercaptoethanol as capping agent on ZnS nanoparticles: structural and optical characterization

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Abstract

In this work, we report the effect of a capping agent on the structural and optical properties of nanocrystalline ZnS particles, which have been synthesized by co-precipitation method. The structural properties of ZnS nanoparticles have been characterized by X-ray diffraction (XRD) analysis. The XRD patterns show a hexagonal structure in the nanoparticles. The mean crystallite size calculated from the XRD patterns has been found to be in the range of 1.80 to 2.45 nm with the increase in molar concentration of the capping agent. Absorption spectra have been obtained using a UV-vis spectrophotometer to find the optical direct band gap. We also found that optical band gap (E_g) increases with the increase in molar concentration of the capping agent. This behavior is related to size quantization effect due to the small size of the particles.

Keywords: ZnS nanoparticles, Chemical co-precipitation method, Capping agent, Optical band gap

Background

Semiconductor nanocrystals represent a class of materials that have hybrid molecular and bulk properties. They have attracted much attention over the past few years because of their novel properties which originate from quantum confinement effect [1-4]. Quantum confinement effect modifies the electronic structure of the nanocrystals when the sizes of the nanoparticles are comparable to that of the Bohr excitonic radius of those materials. When the particle radius falls below the excitonic Bohr radius, the band gap energy is widened, leading to a blueshift in the band gap, emission spectra, etc. On the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size (surface effects). In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size. Therefore, the decay of an exciton at the surface states will influence the qualities of the material for an optoelectronic device. These size-dependent optical properties have many potential applications in

the areas of solar energy conversion, light-emitting devices, chemical/biological sensors, and photocatalysis [5-9].

Wide band gap II-VI semiconductors are expected to be the novel materials for the optoelectronic devices. ZnS, which is an important member of this family, has been extensively investigated as it has numerous applications to its credit. ZnS has been used widely as an important phosphor for photoluminescence, electroluminescence, and cathodoluminescence devices due to its better chemical stability compared to other chalcogenides such as ZnSe. In optoelectronics, it finds use as light-emitting diode, reflector, dielectric filter, and window material. The synthesis of ZnS remains a topic of interest for researchers, as new synthetic routes are being explored to get a single phase material via an economically and technically viable method. In the present paper, chemical method has been used to synthesize the ZnS nanoparticles. In the present paper, ZnS nanoparticles are synthesized by using mercaptoethanol as capping agent. This paper is organized as follows: The structural and optical properties of synthesized nanoparticles are presented in the 'Results and discussion' section in detail, followed by a 'Conclusion' section. In the 'Methods' section, we give a description of materials and synthesis method of ZnS nanoparticles with different molar concentrations of the capping agent.

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Results and discussion

Structural characterization

The X-ray diffraction (XRD) patterns of the prepared ZnS nanoparticles with different molar concentrations of the capping agent (HOCH₂CH₂SH) are shown in Figure 1. All of the crystalline Bragg peaks in the XRD pattern ((111), (220), and (311) planes) are in good agreement with the diffraction data of a hexagonal structure with cell parameters $a = 3.800 \text{ \AA}$ and $c = 6.230 \text{ \AA}$ from the JCPDS card. Furthermore, the peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystals with a very small size.

The peak broadening at a lower angle is more meaningful for the calculation of particle size. The mean crystallite size (D) of nanoparticles was also estimated using the Scherrer formula (Scherrer 1918) using (111) reflection from the XRD pattern as follows:

$$D = \frac{0.9\lambda}{B\cos\theta}, \quad (1)$$

where λ , B , and θ are the X-ray wavelength of the radiation used ($K_{\alpha}(\text{Cu}) = 0.154056 \text{ nm}$), the full width at half maximum of the diffraction peak, and the Bragg diffraction angle, respectively.

The values of mean crystallite size obtained from XRD for different molar concentrations of the capping agent are listed in Table 1.

Optical characterization

The absorption spectra of the different samples are shown in Figure 2. The absorption edge is observed in the range of 324 to 270 nm, which is blueshifted compared to bulk ZnS. As the molar concentration of the capping agent increases, the absorption edge shifts to a lower wavelength compared to ZnS (A). This blueshift of the absorption edges for different-sized nanocrystals is related to the size decrease of particles and is attributed to the quantum confinement limit reaching of nanoparticles. The quantum confinement effect is expected for semiconducting nanoparticles, and

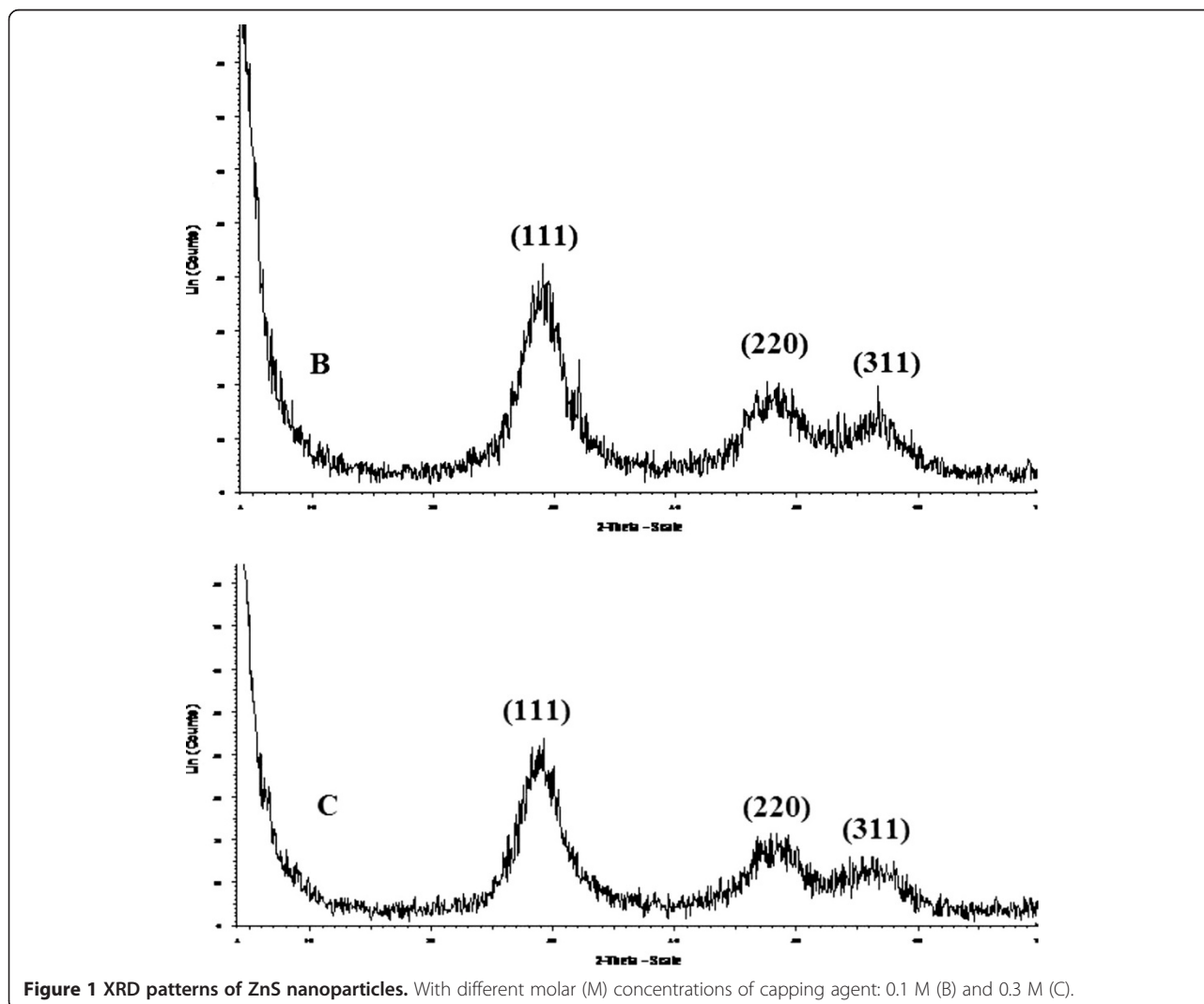


Figure 1 XRD patterns of ZnS nanoparticles. With different molar (M) concentrations of capping agent: 0.1 M (B) and 0.3 M (C).

Table 1 Mean crystallite size and optical band gap variation of ZnS nanoparticles

Sample	Molar concentration of capping agent	Mean crystallite size (nm)	Optical band gap E_g (eV)
ZnS (A)	0.0	2.45	3.83
ZnS (B)	0.1	2.38	4.27
ZnS (C)	0.3	2.22	4.49
ZnS (D)	0.5	1.80	4.59

the absorption edge will be shifted to a higher energy when the particle size decreases [10,11].

The obtained direct optical band gap values for different samples are shown in Table 1. It is necessary to mention that the optical direct band gap values of the ZnS nanoparticles were determined using Tauc's relation [12,13]:

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^{1/2}, \quad (2)$$

where $h\nu$, α_0 , and E_g are the photon energy, a constant, and optical band gap of the nanoparticles, respectively. Absorption coefficient (α) of the powders at different wavelengths can be calculated from the absorption spectra. Finally, the values of E_g were determined using extrapolations of the linear regions of the plot of $(\alpha h\nu)^2$ versus $h\nu$.

As seen in Table 1, the values of optical band gap ' E_g ' increase with the increase in molar concentration of the capping agent, and therefore, the decrease in particle size as mentioned earlier is due to the quantum confinement effect. Also, the variation of optical band gap with particle size is shown in Figure 3. As illustrated in Figure 3, the optical band gap values of nanoparticles have changed from 3.83 to 4.59 eV by decreasing the particle sizes. The increase in band gap with increase in molar concentration of the capping agent is attributed to size quantization effect due to the small size of the particles [14].

These semiconductor nanocrystals were then subjected to transmission electron microscopy (TEM; JEOL JEM3010, JEOL Ltd., Tokyo, Japan) for characterization. Figure 4

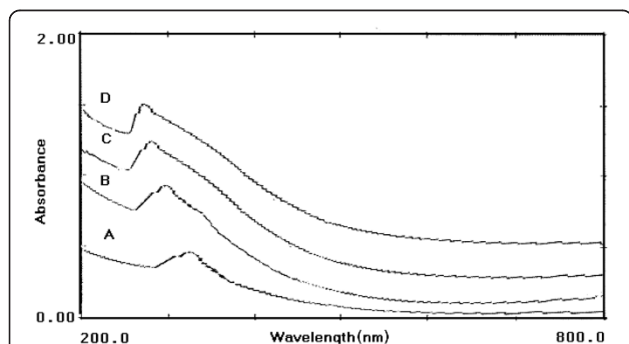


Figure 2 Absorption spectra of different samples of ZnS nanoparticles. 0 M (A), 0.1 M (B), 0.3 M (C), and 0.5 M (D).

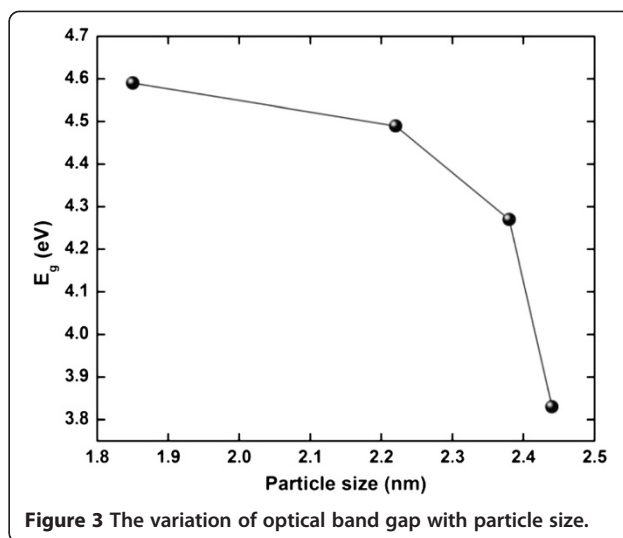


Figure 3 The variation of optical band gap with particle size.

shows the TEM image of ME-capped ZnS semiconductor nanocrystals.

Relation particle size with chemical reaction rate

Chemical reaction rate directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process. First, the influence on nucleation is obvious: nucleation is faster when the chemical reaction is faster. Second, growth will be strongly influenced by the nuclei number which already formed at a given time. A great number of nucleation favor a fast autocatalytic growth, giving rise to a large number of small particles. Chemical reaction controls this kind of growth, in which the autocatalytic growth is faster when the chemical reaction is faster. However, in nanoparticle formation, there is another contribution to the growth molecules on the surface of a small particle which will tend to diffuse through the solution and add to the surface of a larger particle (growth by ripening). A slow chemical reaction

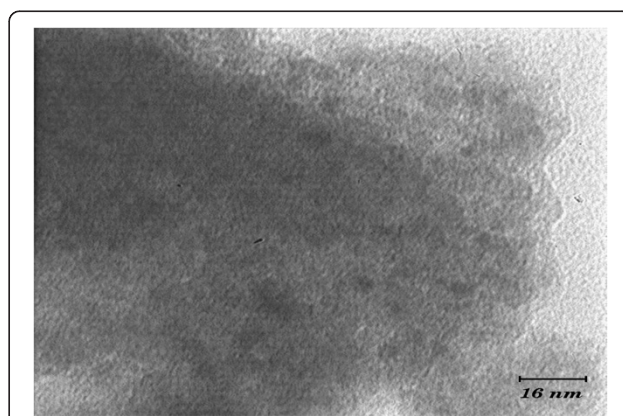


Figure 4 TEM image of ME-capped ZnS semiconductor nanocrystals (0.1 M (B)).

favors continuous nuclei, keeping always a certain number of nuclei in the system. As a result, growth by ripening can take place during the whole process. This fact explains the bigger particle size obtained from a slow reaction. One can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. A high number of nuclei are still forming at this stage when the reaction is slow at the same time; some particles have already grown to the final value of size. This means that in this case (slow reaction rate), nucleation and growth take place simultaneously. This overlapping of nucleation and growth processes, which is more pronounced as the chemical reaction is slower, leads to larger nanoparticle sizes [15].

Rate of reaction depends on the molar concentration of the reactant solution and increases with the increase in molar concentration of the reactant solution. In the present study, the molar concentration of the capping agent varies from 0 to 0.5 M; the reaction rate is highest for the 0.5 M solution, and hence, the particle size obtained is smallest for the 0.5 M solution as compared to other materials in the series, which is in consistent with the above made argument.

Conclusions

It is possible to produce different-sized ZnS nanoparticles using a simple chemical method using different molar

concentrations of the capping agent. XRD and optical band gap data have been obtained to confirm the nanosize of these materials. It is also observed that the particle size depends on the molar concentration of the capping agent. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. As the particle size depends on the molar concentration of the doping agent, a decrease in the size of particle is observed with the increase of molar concentration of the capping agent. The mean crystallite size range of particles was between 1.85 and 2.44 nm, depending on molar concentration of the capping agent. The optical band gap values of ZnS nanoparticles have changed from 3.83 to 4.59 eV by increasing the molar concentration of the capping agent. These values exhibit a blueshift in E_g which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles.

Considering these results, the chemical co-precipitation method using 2-mercaptoethanol as a capping agent is very efficient for the preparation of ZnS nanoparticles in order to control the particle size and also for modern optoelectronic technology and other industrial applications.

Methods

Materials

Zinc chloride ($ZnCl_2$) and sodium sulfide (Na_2S) as starting materials, 2-mercaptoethanol ($HOCH_2CH_2SH$) as

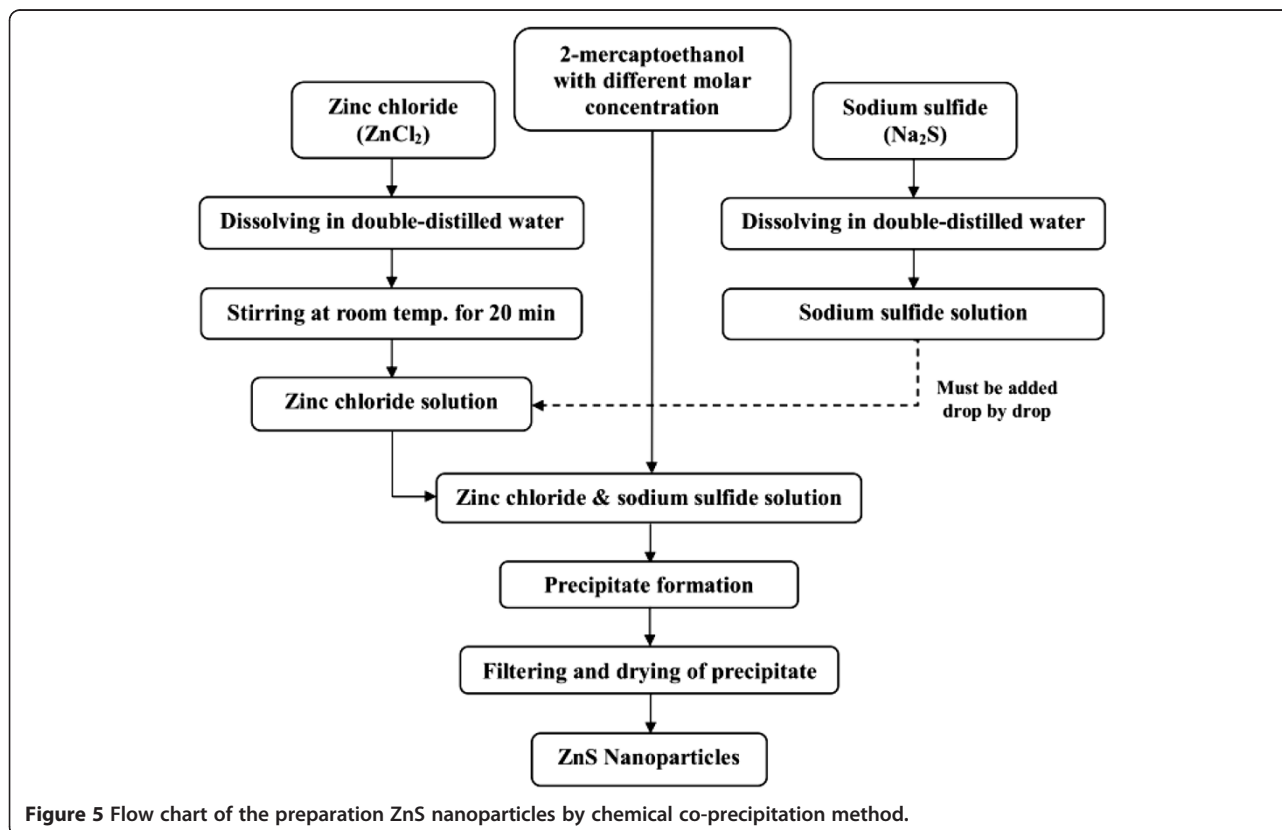


Figure 5 Flow chart of the preparation ZnS nanoparticles by chemical co-precipitation method.

a capping agent for the control particle size, and double-distilled water as dispersing solvent were used to prepare ZnS nanoparticles.

Synthesis of ZnS nanoparticles by co-precipitation method

The ZnS nanoparticles were synthesized using the chemical co-precipitation method as follows. First, ZnCl_2 was dissolved in double-distilled water (0.1 M), and then, the obtained molar solution was stirred for 20 min at room temperature to achieve complete dissolution. Sodium sulfide (Na_2S) was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first, sodium sulfide solution was added drop by drop to the zinc chloride solution, and then, an appropriate amount of 2-mercaptoethanol as a capping agent was added to the reaction medium to control the particle size of ZnS. As a result of this, the white precipitate of the ZnS nanoparticles is formed slowly in the solution. In the final step, the obtained precipitate was filtered and dried at room temperature to remove both water and organic capping and other byproducts which formed during the reaction process. After sufficient drying, the precipitate was crushed to fine powder with the use of mortar and pestle. It is mentioned that the synthesis was done by passing nitrogen gas.

For the study of the effect of the capping agent on structural and optical properties of ZnS nanoparticles, different samples of nanoparticles have been obtained by changing the molar concentration of the capping agent, namely ZnS (A), ZnS (B), ZnS (C) and ZnS (D), as the amount of molar concentration of the capping agent used in the preparation is 0, 0.1, 0.3 and 0.5 M, respectively. The synthesis process of ZnS nanoparticles by the co-precipitation method is summarized in a flow chart shown in Figure 5.

Powder characterization

The XRD patterns of ZnS nanoparticles were recorded using a Bruker system (Bruker Optik GmbH, Ettlingen, Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm) with 2θ ranging from 5° to 70° . The optical absorption spectra of nanoparticles were measured using a USB-2000 UV-vis spectrophotometer (Ocean Optics, Inc., Dunedin, FL, USA). Therefore, the obtained nanopowders have been suspended in glycerol using a magnetic stirrer, and their optical absorption spectra have been recorded at room temperature over the range of 200 to 800 nm to determine the optical band gap values.

Competing interests

The author has no competing interests.

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References

1. Rossetti, R, Ellison, JL, Gibson, JM, Brus, LE: Size effects in the excited electronic states of small colloidal CdS crystallites. *J. Chem Phys.* **80**, 4464 (1984)
2. Sang, W, Qian, Y, Min, J, Li, D, Wang, L, Shi, W, Liu, Y: Microstructural and optical properties of ZnS:Cu nanocrystals prepared by an ion complex transformation method. *Solid State Commun.* **121**, 475–478 (2002)
3. Prabhu, RR, Abdul Khadar, M: Characterization of chemically synthesized CdS nanoparticles. *Pramana- J. Phys.* **5**, 801 (2005)
4. Wageh, S, Ling, ZS, Xu-Rong, X: Growth and optical properties of colloidal ZnS nanoparticles. *J. Cryst. Growth* **255**, 332–337 (2003)
5. Rajeswar, K, Tacconi, NR, Chenthamarakshan, CR: Semiconductor-based composite materials: preparation, properties, and performance. *Chem. Mater.* **13**, 2765 (2001)
6. Alivisatos, AP: Semiconductor clusters, nanocrystals, and quantum dots. *Science* **271**, 933–937 (1996)
7. Anderson, MA, Gorer, S, Penner, RM: A hybrid electrochemical/chemical synthesis of supported, luminescent cadmium sulfide nanocrystals. *J. Phys. Chem. B* **101**, 5895 (1997)
8. Henshaw, G, Parkin, IP, Shaw, G: Convenient low-energy synthesis of metal sulfides and selenides; PbE , Ag_2E , ZnE , CdE ($\text{E} = \text{S}, \text{Se}$). *Chem. Commun.* **10**, 1095–1096 (1996)
9. Hirai, T, Bando, Y, Komasa, I: Immobilization of CdS nanoparticles formed in reverse micelles onto alumina particles and their photocatalytic properties. *J. Phys. Chem. B* **106**, 8967–8970 (2002)
10. Zhu, H, Yang, D, Yu, G, Zhang, H, Yao, K: A simple hydrothermal route for synthesizing SnO_2 quantum dots. *Nanotechnology* **17**, 2386 (2006)
11. Sarhaddi, R, Shahtahmasebi, N, Rezaee Rokn-Abadi, M, Bagheri-Mohagheghi, MM: Effect of post-annealing temperature on nano-structure and energy band gap of indium tin oxide (ITO) nano-particles synthesized by polymerizing-complexing sol-gel method. *Physica E* **43**, 452–457 (2010)
12. Tauc, J: *Optical Properties of Solids*. Academic Press, New York (1966)
13. Liu, CM, Zu, XT, Wei, QM, Wang, LM: Fabrication and characterization of wire-like SnO_2 . *J. Phys. D: Appl. Phys.* **39**, 2494 (2006)
14. Amaranatha Reddy, D, Divya, A, Murali, G, Vijayalakshmi, RP, Reddy, BK: Synthesis and optical properties of Cr doped ZnS nanoparticles capped by 2-mercaptoethanol. *Physica B* **406**, 1944–1949 (2011)
15. de Dios, M, Barroso, F, Tojo, C, Blanco, MC, Lopez-Quintela, MA: Effects of the reaction rate on the size control of nanoparticles synthesized in microemulsions. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **83**, 270 (2005)

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