

Tunable optical properties of ZnS nanoparticles

M. Moussaoui¹, R. Saoudi^{*1}, A. V. Tishchenko¹, and F. Chassagneux²

¹*Université de Lyon, Université Jean Monnet, Laboratoire Hubert Curien CNRS UMR5516, 18 Rue du Professeur Benoît Lauras, 42000, Saint-Etienne, France.*

²*Université de Lyon, Laboratoire Multimatériaux et Interfaces UMR5615, 43 Bd du 11 novembre 1918, 69622, Lyon France.*

In this study, we synthesized ZnS nanopowders with size ranging from 2 to 200 nm by a simple, low-cost, and mass production chemical method. The nanoparticles were characterised by X-ray powder diffraction (XRD), Atomic force microscopy (AFM), Transmission electron microscopy (TEM), and UV–VIS absorption spectroscopy. From the optical response of ZnS nanoparticles, we estimate the band gap and dielectric permittivity.

INTRODUCTION

When semiconductor particles are reduced in scale to nanometer dimensions, their physical properties differ noticeably from those of the corresponding bulk material and depend on the size and the morphology of the studied structures [1, 2]. The extremely small size of these nanoparticles (NPs) result in quantum confinement of the photogenerated electron-hole pair. When the radius of the particle approaches the Bohr radius of the exciton, the quantum size effect becomes apparent: the energy gap increases with decreasing grain size, which leads to a blueshift of the optical absorption edge with respect to the bulk material [3]. In order to exploit these size-tunable properties, many works have been devoted to the development of simple methods for synthesizing semiconductor particles of various sizes in a controllable manner [4]. Zinc sulfide (ZnS) is an important direct wide-band-gap ($E_g = 3.6$ eV at 300 K) semiconductor, which is considered important for applications such as ultraviolet-light-emitting diodes, electroluminescent devices, flat-panel displays, sensors, and injection lasers [5].

In this contribution, ZnS nanoparticles with size ranging from 2 to 200 nm were prepared from an easy and economic chemical method. The synthesis of ZnS NPs was based on the reaction of zinc acetate and thioacetamide. The resulting mixture was heat treated at different temperatures. After the reaction was completed, the resulting product was collected by centrifuging to select a size distribution. The NPs were characterised by X-ray powder diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), and UV–VIS absorption spectroscopy.

To investigate the optimal reaction condition for the fabrication of ZnS NPs, series of experiments have been carried out by changing the experimental parameters. We have observed that the ZnS nanopowder size distribution depends on duration and temperature elaboration.

* Corresponding author: Rachida Saoudi (saoudi@univ-st-etienne.fr)

The XRD pattern of the ZnS NP elaborated at 100°C - 1H is shown in Fig. 1. The spectrum exhibits that ZnS is in pure cubic phase. The three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes, respectively. An average crystallite size of about 3 nm was estimated according to the line width analysis of the (111) diffraction peak based on the Scherrer formula [6].

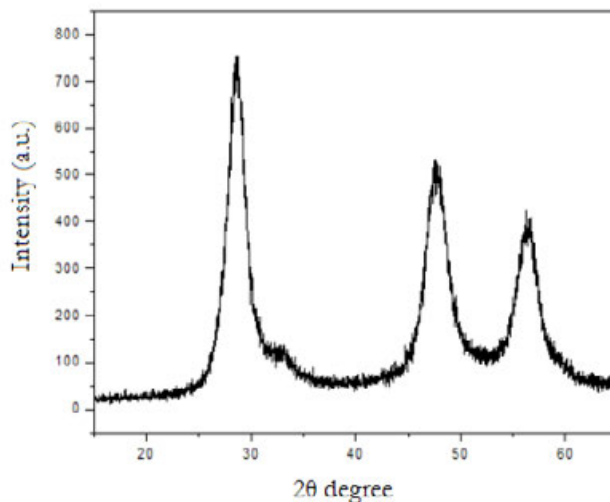


Figure 1. X-ray diffraction pattern of ZnS nanoparticles.

From the AFM picture (Fig. 2) we observe, for the selected scan area, that the ZnS nanoparticles are almost spherical and have diameter ranging from 20 to 100 nm. Fig.3 shows the TEM image of the prepared nanopowders. It can be seen that the majority of the nanoparticles has the average size less than 10 nm and a spherical shape.

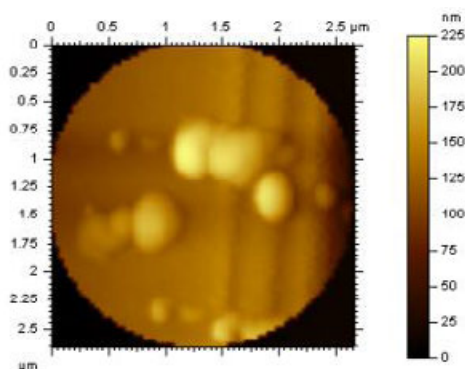


Figure 2. AFM image of the prepared ZnS nanoparticles.

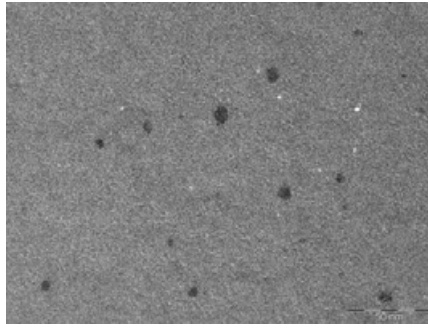


Figure 3. TEM image of the prepared ZnS nanoparticles.

UV-VIS spectra were measured in matched quartz cells of 5 mm path length in lambda 900 spectrophotometer. Fig. 3 is the UV-VIS absorption spectrum of freshly prepared ZnS NPs, which was recorded after the powder sample being dispersed in water. It shows an absorption peak at 323 nm ($E = 3.84$ eV), which is considerably blue-shifted from 340 nm ($E_g = 3.65$ eV) for bulk zinc blende ZnS because of quantum size effect [7].

The resulting estimated average diameter of the nanoparticles is 3 nm, in close agreement with the diameter measured from XRD studies.

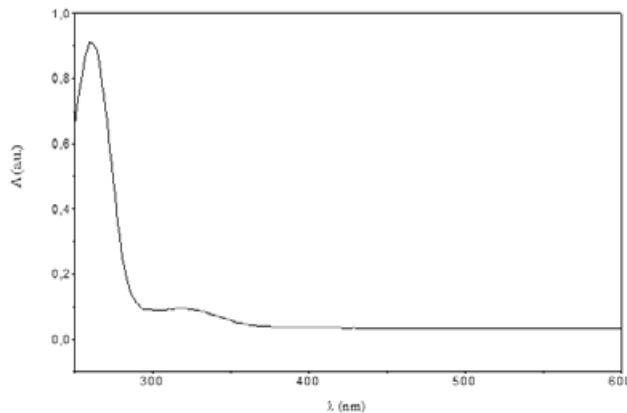


Figure 3. UV-VIS absorption spectrum of the ZnS nanoparticles.

We also studied the dependence of band gap, diameter, and dielectric permittivity of ZnS nanoparticles on treatment parameters (temperature and duration). The direct allowed optical band gap of the ZnS NPs was estimated from the Tauc plot [8] according to the following relation:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (1)$$

where α , ν , C , and E_g are the molar absorption coefficient, frequency of light, an arbitrary constant and the band gap of the nanoparticles, respectively. The obtained E_g was fairly

large (4.97 – 3.84 eV) in comparison with the bulk ZnS value (3.68 eV) corresponding to the ZnS nanoparticle diameters of 2.7 to 10 nm, respectively.

The dielectric permittivity ϵ of ZnS nanoparticles was also calculated from Wang equation [9]:

$$E_g = E + \left(\frac{\hbar^2 \pi^2}{2R^2} \right) \times \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.786e^2}{\epsilon R} \quad (2)$$

where E is the bulk band gap of ZnS (3.68 eV), m_e and m_h are the effective mass of electron and the effective mass of the hole respectively, and R the nanoparticle radius.

The obtained dielectric permittivity value falls in the range of $8.43 \cdot 10^{-11}$ to $10.19 \cdot 10^{-11} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ to within a diameter of 1.6 to 2.5 nm. From our experiments we confirm that the estimated permittivity ϵ increases with the nanoparticle diameter [7, 10].

We also measured the light scattering for different ZnS NPs concentrations in solutions. The results of these measurements permit us to determine the limits in which the optical index of ZnS water dispersed NPs can be measured precisely.

REFERENCES

- [1] A. K. Bandyopadhyay. *Nano Materials*. NewAge International (P) Ltd. Publishers (2008).
- [2] A. L. Rogach. *Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications*. Springer-Verlag/Wien (2008).
- [3] C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, Chemistry and Properties of Nanocrystals of Different Shapes. *Chem. Rev.* **105** (2005).
- [4] G. Schmid. *Nanoparticles from theory to application*. WILEY-VCH Verlag GmbH Co.KGaA (2004).
- [5] G. Cao. *Nanostructures and nanomaterials*. Imperial College Press (2004).
- [6] B.D. Cullity. *Element of X-ray Diffraction*. A.W.R.C.Inc. Massachussets (1967).
- [7] A. D. Yoffe. Semiconductor quantum dots and related systems: electronic, optical, luminescence and related properties of low dimensional systems. *Advances in Physics* **50**(1) (2001).
- [8] J.Tauc and A. Menth. States in the gap. *Journal of Non-Crystalline Solids* **569** (1972).
- [9] Y. Wang and N. Herron. Nanometer-Sized Semiconductor Clusters: Materials Synthesis, Quantum Size Effects, and Photophysical properties. *J. Phys. Chem.* **95** (1991).
- [10] V. Turco Liveri. *Controlled Synthesis of Nanoparticles in Microheterogeneous Systems*. Springer (2006).