

Size Controlling of ZnS Quantum Dots Synthesized by Ultrasonic-assisted Chemical Precipitation

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Abstract: ZnS quantum dots (QDs) are prepared by ultrasonic-assisted chemical precipitation method with the presence of different concentration Trisodium citrate (TSC). The TSC molecules play very important role in inhibiting the growth of the ZnS particles. The mean size of the ZnS crystals which is estimated from the X-ray diffractions decreases from 1.7 nm to 1.4 nm when the added amount of the TSC increases. The lattice constant of the particles decreases from 5.40 Å to 5.38 Å and the band gap of the material increases from 3.92 eV to 4.74 eV. The particles are well dispersive in aqueous solution and emit blue light at around 430 nm while being excited by 320 nm ultraviolet light, which guarantees good attitude for further biological applications.

Keywords: ZnS, size controlling, ultrasonic, precipitation

1. Introduction

Metal sulfide colloids which could conjugate easily with thiol groups (-SH) containing organic molecules [1,2] are discussed as bio-compatible materials for biomedicine applications. Among these materials, zinc sulfide - based semiconductors (ZnS, metal doped ZnS) are deeply investigated because of their comfortable optical properties [2-5]. The band gap of the bulk zinc sulfide is 3.68 eV [3] and the Bohr radius is approximately 2.5 nm [4]. When the size of the material in at least one dimension is smaller than the Bohr radius, some properties of metal doped ZnS are different in comparison with the bulk material [4,5]. The phenomenon is named as quantum confinement effect. In order to reach as small size ZnS nanoparticles (ZnS QDs) as the quantum confinement effect occurs, the particles are synthesized using 2-mercaptoethanol as surface activator [5] or using different volume ratios of the reacting reagents in co-precipitation method [6]. Despite that the properties of the ZnS particles are deeply studied [2-5], there are still less experimental researches discussing about their confinement effect at small sizes below 2 nm.

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In this study, we use ultrasonic wave as a physical active agent to create small sizes of ZnS particles by precipitation method. The sizes of the particles are modified by adding different amounts of trisodium citrate (TSC). The role of the TSC is discussed as growth inhibitor. As well, the quantum confinement effect is discussed in detail by comparing the estimated crystal sizes with lattice constant and optical band gap of the as-prepared ZnS particles.

2. Experiment and method

All the reagents - zinc acetate ($\text{Zn}(\text{Ac})_2$), sodium sulfide (Na_2S), Trisodium citrate (TSC) - are of analytical grade purchased from MERCK, Germany. Before use, distilled water is bubbled by flowing Ar in order to discard all the remained oxygen.

The particles are prepared by ultrasonic-assisted precipitation method. In detail, 4mL of 0.25 M $\text{Zn}(\text{Ac})_2$ and different amounts of TSC 2.5 M (1 mL, 2 mL, 4 mL, 6 mL, 10 mL and 20 mL) are dissolved into a three-neck flask. Distilled water is filled up to 100 mL and NaOH 0.5 M is used to adjust the pH to 9.0. Next step, 50 mL of 0.02 Na_2S is drop-wisely added to the flask while approximately 200 W ultrasonic is applied. The reaction time is 2h at 0°C and white precipitate forms which contains ZnS QDs nanoparticles.

After washing the products several times with 50% ethanol in distilled water, their X-ray diffractions (XRD), morphology, UV-vis absorption and photoluminescence (PL) spectra are investigated respectively by Broker X-ray Diffractometer, JEOL Transmission Electron Microscope, Shimadzu UV-2405 UV-Vis Spectrometer and Fruolog 3 Photoluminescence Spectrometer at Center for Materials Science, Faculty of Physics, VNU Hanoi University of Science.

3. Result and discussion

3.1. XRD and TEM analysis

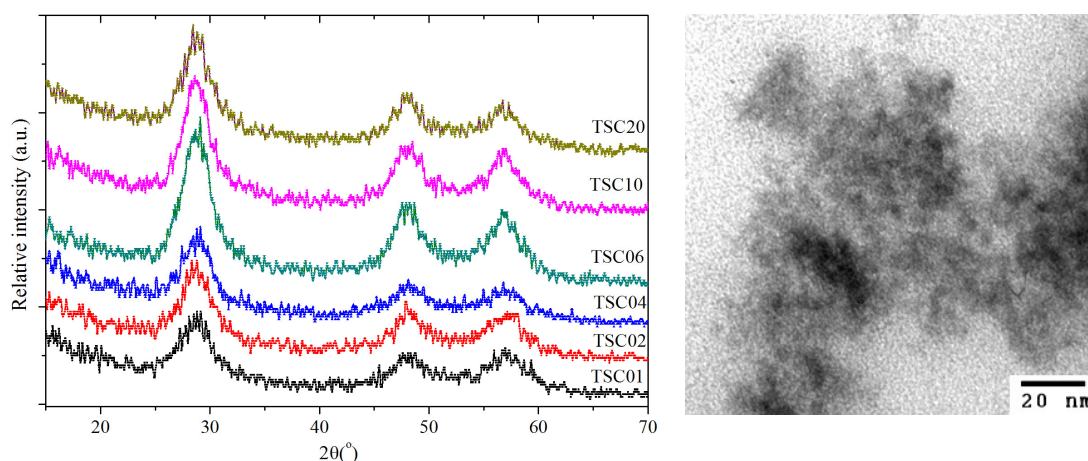


Figure 1. XRD pattern and TEM image of the ZnS nanoparticles synthesized by ultrasonic-assisted co-precipitation method.

Figure 1 shows the XRD patterns (left panel) and TEM image (right panel) of the as-prepared ZnS QDs. After being washed several times with 50% ethanol in distilled water, the particles are well dispersible in aqueous solution. The TEM image shows that the sizes of the particles are very small (about 2 nm). The XRD patterns show that the particles are well crystallized and have typical close-packed face central cubic structure of sphalerite ZnS in No. JCP2 – 05-0566. Besides, minor shifts to higher reflection angle could be recognized at the peaks when the added amount of TSC increase (Figure 1 – left).

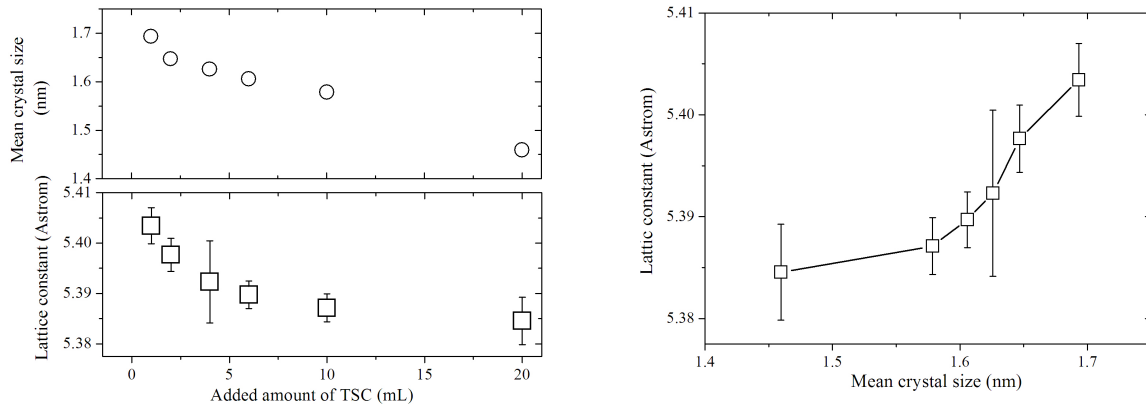


Figure 2. Dependence of the calculated mean crystal size and lattice constant of the ZnS nanoparticles on the added amount of TSC (left panel) and their relation (right panel).

Gaussian fitting simulation is applied to calculate the peak positions and the full width at half maximum (FWHM) of the (311) peak at around $2\theta = 56^\circ$. From these values, lattice constant and mean crystal sizes of the particles are estimated by applying Bragg law and Debye-Scherrer formula. It is observed that the estimated lattice constant and mean crystal size decrease when the added amount of TSC increases (Figure 2 – left). The estimated particles' sizes increase from about 1.4(5) nm to 1.7(0) nm, which are smaller than the Bohr radius [4]. We suggest that the TSC molecules create a negative charge media surrounding the ZnS nucleus right after their formulation, which inhibits their growth during the precipitation reaction. The more TSC molecules in solution could result smaller particles. Mean while, the lattice constant of the particles decreases from 5.40(2) Å to 5.38(5) Å when the TSC amount increases (Figure 2- left, bottom). When the size of the particles decreases down to quantum size – smaller than 2.5 nm, the interaction between the atoms is suggested to become stronger. This indicates the smaller distance between the atoms. As consequence, the lattice constant of the materials decreases (Figure 2 – right).

3.2. UV-vis absorption

Typical UV-vis absorption spectra of the ZnS QDs containing solutions are shown in Figure 3 – left. The solutions show less light absorbability at visible and near-infrared region and have higher absorption at UV region, which agrees with earlier published results [2,3,5]. Since, ZnS are discussed as direct band gap materials [2,3], the relation between the absorbance coefficient α and the incident photon energy $h\nu$ is shown in the following formula:

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

where A is a constant and E_g is band gap of the material. The E_g values could be estimated from the $(\alpha h\nu)^{1/2}$ versus the incident photon energy $h\nu$ [2], which are shown in Figure 3 – right. It is observed that the band gap of the material increases from 3.92 eV to 4.74 eV when the added TSC amount increases from 1 mL to 20 mL (Figure 4 – left).

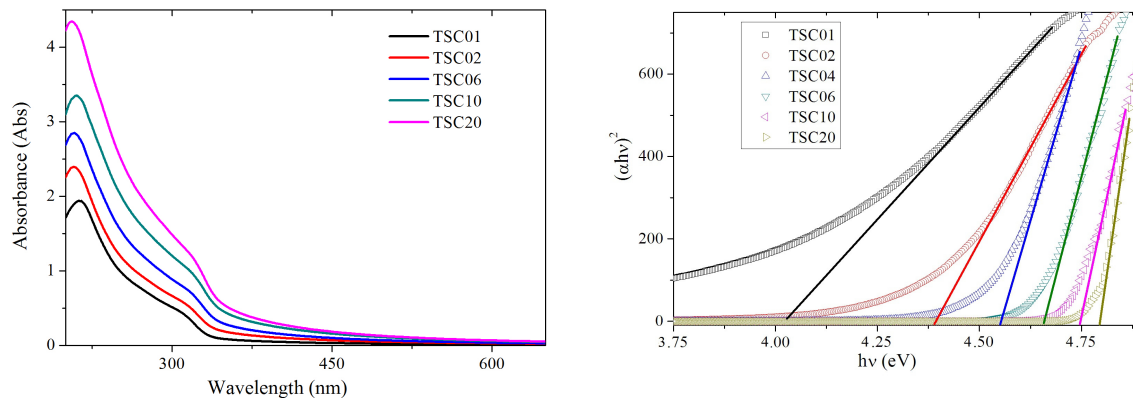


Figure 3. Light absorption property of the ZnS nanoparticles synthesized with different amount of added TSC (left panel) and their band gap calculation (right panel).

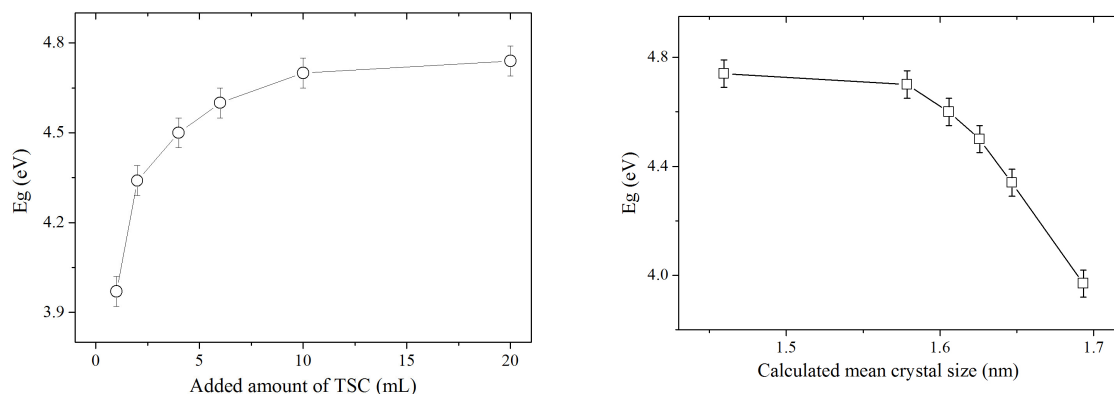


Figure 4. Dependence of the calculated band gap on added TSC amount (left panel) and their relation with the calculated mean crystal size (right panel).

In comparison to that the band gap of ZnS bulk material is 3.68 eV [3], the band gaps of the as-prepared ZnS QDs are much larger, which demonstrates strong quantum confinement effect of ZnS material. The same effect is occurred in other groups' studies. Tran Thi Quynh Hoa's group observes 4.06 eV of ZnS/Mn band gap with the calculated mean crystal size of the particles is 2.1₆ nm [2]. Bijoy Barman's group obtains ZnS QDs at 2.8 nm and the band gap of the particles is 4.06 eV [3]. Therefore, the wide band gaps obtained in this study could correspond to the very small sizes of the particles, which are estimated from the XRD diffractions. In further estimation, the mean crystal size of the ZnS QDs can be calculated using the effective mass approximation (EMA) relation in SI system [2,3,7]:

$$Eg = Eg_{bulk} + \frac{\hbar\pi^2}{2r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1}{4\pi\epsilon_0} \frac{1.8e}{\epsilon r} \tag{2}$$

where Eg , Eg_{bulk} are particles' and bulk material's band gaps, \hbar is reduced Planck constant, m_e^* and m_h^* are effective mass of electron and hole, ϵ is dielectric constant of bulk ZnS materials and ϵ_0 is the electric permittivity of free space. For ZnS $m_e^* = 0.34 m_0$, $m_h^* = 0.23 m_0$, $\epsilon = 8.76$ and m_0 is electron mass [2,3]. The crystal sizes of the ZnS QDs synthesized with different amount of added TSC are determined by the above mentioned (2) equation and are shown in table 1.

Table 1. Mean crystal sizes of the ZnS QDs synthesized with different amount of added TSC estimated by Debye- Scherrer formula and by effective mass approximation (EMA) relation [7].

Added TSC amount	Mean crystal size (nm)	
	Calculated by Debye-Scherrer	Calculated by EMA relation
1 mL	$1.6_9 \pm 0.3_6$	3.4_3
2 mL	$1.6_5 \pm 0.3_1$	2.2_7
4 mL	$1.6_3 \pm 0.7_1$	2.0_2
6 mL	$1.6_1 \pm 0.2_4$	1.8_9
10 mL	$1.5_8 \pm 0.2_6$	1.7_9
20 mL	$1.4_6 \pm 0.3_8$	1.7_5

The mean crystal sizes estimated by Debye-Scherrer formula are also illustrated. There is about 0.1 nm differences between two methods – by Debye-Scherrer formula and by EMA relation. It could be the consequence of the Gaussian fitting from XRD, which generates bigger standard errors (shown in Table 1). However, the two estimation methods show that the mean crystal sizes of as-prepared ZnS QDs are very small. As the knowledge of the authors, these ZnS QDs are the smallest ZnS particles ever synthesized by precipitation method.

3.3. Photoluminescence

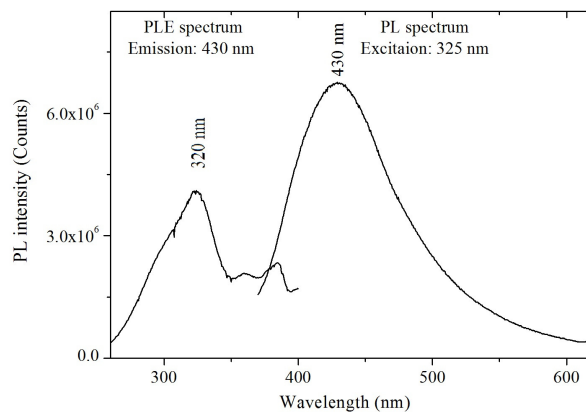


Figure 5. Photoluminescence spectra of the ZnS quantum dots synthesized by ultrasonic- assisted co-precipitation method.

Photoluminescence (PL) and excitation photoluminescence (PLE) spectra of the ZnS QDs containing solution are demonstrated in Figure 5. Under the excitation of ultraviolet (UV) light at 320 nm, the QDs containing solution emits blue light, of which the PL spectrum has a peak at 430 nm (2.88 eV). This peak could be assigned to the radiation of the QDs when electrons move from defect level to valence band [2,8]. The PLE spectrum has relative high peak at 320 nm (~3.89 eV) which is close to the near-band-edge absorption [2]. The peak indicates that under the excitation light at 320 nm the ZnS QDs attribute the most intensive blue emission. The properties that the particles are as small as the bio-molecules, well dispersive in aqueous solution and emit intensive blue luminescence indicates that the ZnS QDs would be a comfortable materials for biological applications.

Conclusion

Small size ZnS quantum-dots are successfully synthesized by ultrasonic-assisted co-precipitation method with the presence of trisodium citrate (TSC) at different concentration. As the turbulent current generator, ultrasonic wave indicates the creation of small size ZnS particles in solution. Besides, TSC molecules play as surface activators, which inhibit the growth of the crystal size under ultrasonical precipitation condition. The increasing of added TSC amount decreases the crystal size of the as-prepared ZnS quantum dots. The size of the particles is smaller than 2 nm. At this size the particles clearly show the evidences of quantum confinement effect. The lattice constant decreases from 5.40(2) Å to 5.38(5) Å and the band gap increases from 4.97 eV to 5.79 eV, when the mean crystal size decreases from 1.7(0) nm to 1.4(5) nm. The particles are well dispersive in aqueous solution; their sizes are at the range of biological molecules' size and they emit blue light at 430 nm with high intensity when being excited at 325 nm, which is promising potential applicability for bio-medicine and/or bio-imaging.

Acknowledgement

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