



# Preparation and characterization of ultrafine zinc sulfide particles of quantum confinement

Ming Wu, Wanzhen Gu, Wenzhao Li, Xiangwei Zhu, Fudong Wang, <sup>世世</sup> Shiting Zhao

*Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS), P.O. Box 110, Dalian 116023, People's Republic of China*

Received 15 February 1994; in final form 25 April 1994

## Abstract

We describe the preparation and characterization of highly monodispersed, stabilized and size-fixed ZnS Q-particles. In these samples, small ZnS particles were well accommodated by  $\beta$ -cyclodextrin cavities. The included ZnS particle size was determined to be 9.7–12.2 Å by scanning tunnel microscope, which is consistent with the inner diameter of the cyclodextrin cavity. The microcrystalline structure was identified to be of sphalerite-type by X-ray diffraction. A very sharp and blue-shift exciton peak of optical absorption was observed at the 245–250 nm band and was well accounted for by a recent theoretical model based on a tight-binding approximation.

## 1. Introduction

Excellent reviews have recently been published on the unique photochemical and photophysical behaviors of various Q-particles (materials of extremely small particle size showing quantum size effect, often known as quantum dots and quantum well) [1–4], which are being intensively studied. With a view to facilitate practical use and theoretical approaches, however, one inevitably encounters a very intractable problem, that is, how to make macroscopic amounts of stabilized and characterized Q-particles [4]. Accordingly, one not only needs to achieve significantly more narrow size distribution but also to have precise control over the surface chemistry of these Q-particles. Great efforts have been made in these respects [3,4]. A promising approach is the use of the host/guest inclusion as a nanoscale lithographic tool to create stabilized and characterized Q-particles, for example, the self-assembly of Q-particles in the angstrom-sized channels and cages of a molecular sieve or zeolite host framework [5]. In this

Letter, we wish to briefly report a new synthetic approach in which stabilized, monodispersed and size-fixed zinc sulfide Q-particles, accommodated by  $\beta$ -cyclodextrin (BCD) cavities (i.e. in the form of the inclusion complex: ZnS/BCD), were prepared. Their microstructures and photophysical properties were investigated by scanning tunnel microscope (STM), powder X-ray diffraction (XRD) and optical absorption spectroscopies, and their quantum size effects were also discussed in terms of current theoretical models. The unusual photochemical catalysis of these included ZnS Q-particles will be reported in subsequent papers.

## 2. Experimental

Rapid precipitation technique<sup>1</sup>, a much used method for colloidal preparation of small particles, was adapted and extended to a rather high jet speed

<sup>1</sup> Commentary articles: Refs. [3,6].

(up to  $3.5 \text{ m s}^{-1}$  linear speed) with a pneumatic pump to which two syringes were attached.

The preparation of zinc sulfide Q-particles (ZnS/BCD) was achieved, first by fast injecting and turbulent mixing of two deaerated solutions containing  $\text{ZnSO}_4$  with BCD (SIGMA Chem. Co.) in one syringe and  $\text{Na}_2\text{S}$  in the other <sup>2</sup>, and then, the resulting translucent solution, under  $\text{N}_2$  atmosphere, was further processed by a temperature treatment <sup>3</sup> (e.g., changing solution temperature first from 30 to  $60^\circ\text{C}$  and then back to  $30^\circ\text{C}$ , keeping the three temperatures a couple of hours for each). The initial concentrations of all components were  $\approx 10^{-2} \text{ M}$ . The sample solution was still translucent and was essentially transparent when diluting to  $\approx 10^{-4} \text{ M}$ .

Solid samples were obtained by rotary evaporation at  $60^\circ\text{C}$ .

For STM analysis, a drop of the solution was air-dried onto a clean single crystal face of graphite plate. The experiments were conducted by using a Scanning tunnelscope 2400 apparatus (Denmark). XRD measurements were performed with a Rikagu D/max-rb powder diffractometer (Japan). Copper  $K\alpha$  radiation (average  $\lambda = 1.542 \text{ \AA}$ ) was used. Solid samples were completely dried in a desiccator prior to XRD measurement. Optical absorption and emission spectra were measured with a MPF-4 spectrophotometer (Japan).

### 3. Results and discussions

Experimental results confirmed that the resulting sample particles are stable in water, though they tend to be only moderate water soluble. They could not be removed from the solution by centrifugal treatment (up to 4000 rpm). They could be obtained in powders by rotary evaporation and redissolved to yield a transparent solution again, the absorption spectrum

<sup>2</sup> By transient optical spectroscopy, we have found that the UV absorption feature changes with the jet speed. The higher the speed (i.e. the higher the mixing rate of the precipitants), the steeper the absorption threshold and the more blue-shift of the exciton peak, indicating a more narrow particle size distribution [7,8].

<sup>3</sup> Such temperature treatment is commonly used in synthesis of inclusion complexes so as to improve the quality, increase the product yield, of the complexes.

of which was practically identical to that prior to drying and redissolving treatment.

#### 3.1. STM and TEM

Fig. 1 shows a dark field STM image ( $48.5 \times 48.5 \text{ \AA}^2$ ), from which the individual and spherical ZnS particles can be seen. Since the highest point of STM scanning-tip was  $38 \text{ \AA}$  when the image was taken, the diameters are certainly no more than  $38 \text{ \AA}$  for all these particles. It cannot be excluded, in this case, that some of them piled up together which led the tip to lift up to that point. In the figure, one of these particles is marked with a circle. According to the deduction of STM analysis, The height of the particle (from the top of it to the graphite substrate) is  $9.7 \text{ \AA}$ , the diameter of the circle is  $12.2 \text{ \AA}$ . Since STM image will be smeared when the tip closes to boundaries of particles, actual particle size is somewhat smaller than that from STM. Furthermore, it is felt important to note that the 'empty' BCD molecules, i.e. with no ZnS particles filled in, were not observed in our STM investigations under the comparable measurement condition.

We also carried out TEM experiments. However, TEM imaging contrast ratio is poor for the particles, principally in that CD molecule is a light element. The particle size from TEM was  $\approx 1 \text{ nm}$  and the size dis-

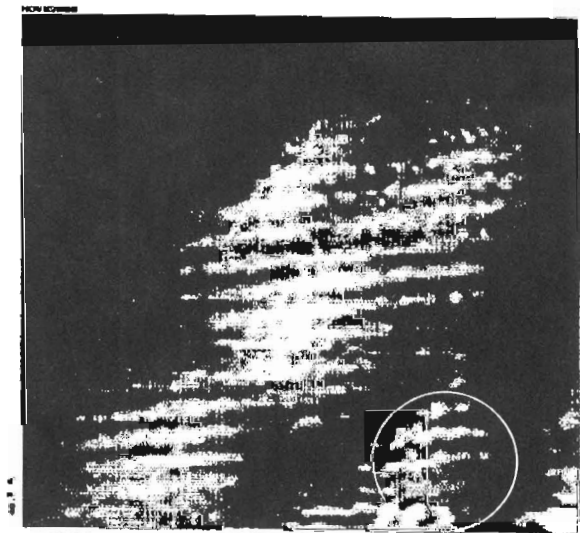


Fig. 1. Dark field image of STM for the inclusion complex ZnS/BCD. The diameter of the particle marked with a circle is  $9.7\text{--}12.2 \text{ \AA}$  based on the STM analysis.

tribution was essentially the same. Also we noted that some of these particles stuck together and formed 1 nm width long chains, perhaps because of the condition of sample preparation for TEM, i.e. the evaporation of the solvent.

STM and TEM experimental results led the authors to envisage that extremely small ZnS particles are included by BCD cavities and the diameter of which is consistent with that of BCD cavity (note: a recently published value is 9 Å [9]). If such is not the case, these particles would surely grow into larger size through aggregation and show a relatively wide particle size distribution.

### 3.2. XRD

XRD patterns of crystalline  $\beta$ -cyclodextrin (BCD), spectroscopically pure zinc sulfide powder (ZnS), the prepared powder sample (ZnS/BCD) and a mechanical mixture (ZnS+BCD) with an equimolar amount of each are given in Fig. 2. It is clear that the intensity maxima of ZnS+BCD correspond to those of ZnS and BCD, whereas, for the sample ZnS/BCD, the maxima corresponding to ZnS and BCD crystallites are significantly reduced (note: the curve for ZnS/BCD in the figure is twofoldly amplified), implying that a true complex (i.e. ZnS inclusion complex) was formed. Still, the ZnS/BCD shows very broad and flat peaks associated with the macrocryst-

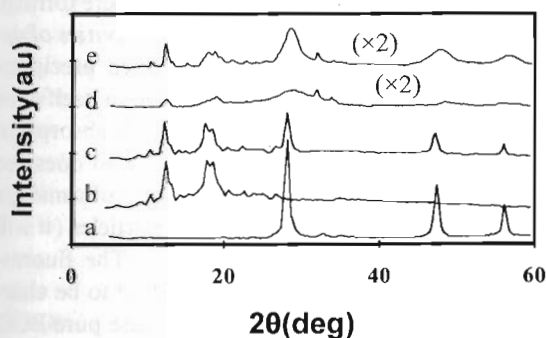


Fig. 2. X-ray diffraction diagram. From curve a to curve e, it represents ZnS powder (spectroscopically pure, sphalerite ZnS), pure  $\beta$ -cyclodextrin (BCD), a mechanical mixture (ZnS+BCD) with an equimolar amount of each to the complex ZnS/BCD, the complex (ZnS/BCD), and a complex with an excess amount of  $S^{2-}$  used in the preparation (ZnS/BCD· $S^{2-}$ ), respectively. The intensity scale was twofoldly amplified for ZnS/BCD and ZnS/BCD· $S^{2-}$ .

talline structure of cubic  $\beta$ -ZnS powders (sphalerite) which have a set of Miller indices at  $2\theta$  value of 28.5 (111), 47.8 (220) and 56.6 (311), respectively<sup>4</sup>. This relatively amorphous character of the XRD pattern provided information of the existence of extremely small ZnS particles and the absence of the long-range periodicity like their macrocrystalline particles.

Quantitative interpretation of the ZnS particle size from XRD is difficult since the corresponding peak is too flat to measure its peak width. Interestingly, the not-very-broadened peaks with these Miller indices appeared in the XRD spectrum for another stable 'inclusion complex' sample in which high excess concentration of sulfide anion ( $S^{2-}$ ) was introduced in the preparation, as can be seen in the figure (ZnS/BCD· $S^{2-}$ ). In this case, the particle size is possibly evaluated by Scherrer's equation. The calculation value is about 4 nm. Such phenomenon is strange, yet true<sup>5</sup>. It has already been known that both 'channel' and 'cage' structures are possible for inclusion complexes depending on the size and the ionic or molecular character of the substrate [11]. Therefore, one may reasonably conjecture that the broadening of the peaks in this case might be the consequence of a change in the apparent particle size due to a larger amount of 'channel' or 'cage' structure being formed, in which excess sulfide anions play a role of linkage between the ZnS/BCD complexes. This phenomenon was also found in our spectroscopic investigations which will be discussed below.

Information acquired from XRD examinations shows that ZnS particles in the sample ZnS/BCD is extremely small and fundamentally dispersed by the solvent-like BCD molecules on the nanoscale dimension. Thereby, the conjecture that the ZnS/BCD inclusion complex was obtained is reasonable. XRD results also suggested that neither extensive aggregation nor escape from BCD cavity for these included ZnS particles occurred during the removal of water in the course of sample preparation.

<sup>4</sup> We noticed in the literature that a gradual  $2\theta$  shift for small CdS particles would occur as the particle size decreases [10]. However, this phenomenon was not observed in our XRD investigations.

<sup>5</sup> Correlation has been made between the  $Zn^{2+}/S^{2-}$  ratio and XRD pattern, UV absorption, fluorescent emission and photocatalytic  $H_2$  evolution. A paper on it is in preparation.

### 3.3. Optical absorption and emission

Optical spectroscopy has been a helpful method to investigate semiconductor particles of nanometer size. In terms of the current theories, absorption peak of semiconductor Q-particles will appear pronounced as the particle size decreases, the peak is assigned to an exciton energy level, its position depends on the average size of particles in solution and its shape [7] is related to the particle size distribution. Alivisatos et al. reported that a 1% variation in particle size must be achieved to observe discrete excitonic features in the absorption spectra [8]. As for small ZnS particles (often in colloidal solution), a great deal of investigations on their spectroscopic behavior have been done [12,13]. Among them, Rossetti et al. reported  $\approx 20 \text{ \AA}$  ZnS particles in methanol solution, the UV absorption of which showed a clearer exciton peak at about 280 nm [13]. Here, we show the absorption and fluorescence spectra of the saturated ZnS/BCD solution in Fig. 3 (curve a and curve b). For comparison, Fig. 4 shows the absorption spectra of (a) the saturated ZnS inclusion solution without undergoing the temperature treatment (ZnS//BCD, for convenience), (b)  $\approx 10^{-3} \text{ M}$  fresh colloidal solution (mixed by manual operation of two syringes), (c) spectroscopically pure ZnS powder and (d) the saturated ZnS/BCD $\cdot\text{S}^{2-}$  solution.

For ZnS/BCD (Fig. 3a), one may find that there

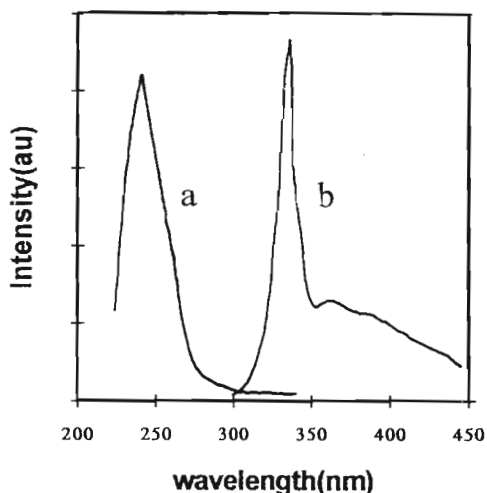


Fig. 3. Absorption and fluorescence spectra of saturated ZnS/BCD solution. (a) absorption spectrum; (b) fluorescence spectrum ( $E_{\lambda}=260 \text{ nm}$ ).

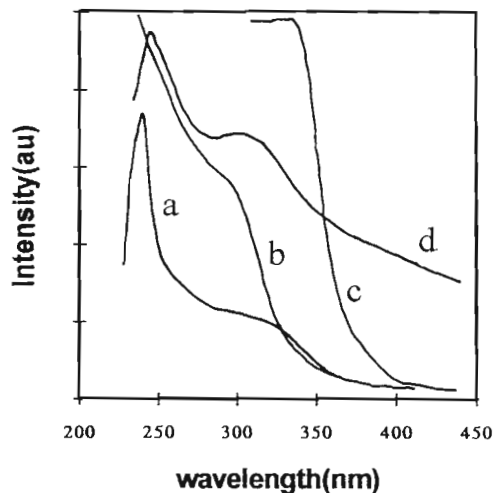


Fig. 4. Absorption spectra of different type ZnS samples. From curve a to curve d, it represents the saturated ZnS//BCD solution (without undergoing the temperature treatment),  $\approx 10^{-3} \text{ M}$  fresh colloidal ZnS solution, spectroscopically pure ZnS powder and the saturated ZnS/BCD $\cdot\text{S}^{2-}$  solution (an excess amount of  $\text{S}^{2-}$  used), respectively.

exists a markedly blue-shift and sharp exciton absorption peak at 245–250 nm (5.0–5.1 eV), the onset of which is  $\approx 275 \text{ nm}$ . The peak shifts roughly 65 nm compared to colloidal ZnS particles (Fig. 4b) and 100 nm compared to ZnS powder (Fig. 4c). Clearly, such a higher energy absorption threshold with such an obviously resolved spectral feature indicates that a large amount of extremely small and monodisperse ZnS particles of quantum confinement were formed, which were dispersed and included by cavities of cyclodextrin molecules during the arrested precipitation. Of particular note is that inclusion in itself does not exert any noticeable influence on UV absorption spectra of most of guest molecules and so does the case. The UV spectrum does reflect the information dominantly from these included ZnS particles (it will be further discussed in Section 3.4). The fluorescence emission (Fig. 3b) was identified to be characteristic for the Q-ZnS particles because pure BCD molecules do not fluoresce under the comparable measurement condition.

A ZnS//BCD solution often exposes an absorption tail along the absorption threshold (Fig. 4) which, however, would be curtailed if the solution undergoes the aforementioned temperature treatment. The effectiveness of the treatment can be

understood by the following consideration. Generally speaking, water molecules inside BCD cavities are to be expelled and guest molecules outside BCD molecules (adsorption would be possible) are about to thread themselves in the cavities during the inclusion process. For the energy reason, a proper temperature treatment should promote the process to be easier to happen. As for this reason, in this case, ZnS species outside the cavities should be less (desorption may occur if adsorption exists) and the particle size distribution should be narrow after the temperature treatment. Our experiments confirmed the importance of the temperature treatment. On the other hand, however, situation is different if excess sulfide anions are introduced in the preparation. In the case of ZnS/BCD·S<sup>2-</sup>, a broad absorption peak at  $\approx 310$  nm ( $\approx 4.0$  eV) still appeared after the temperature treatment (Fig. 4d). It may be that the formation of the sulfide-linked 'channel' or 'cage' structure, as discussed above in the XRD results, closed the opening to BCD cavities.

### 3.4. IR

In order to study intrinsic properties of Q-particles, it is imperative to separate strong interactions which may exist between the Q-particles and various surrounding media from true quantum size effect. The inclusion system of ZnS/BCD reported herein appears to provide an example in which such is the case. It was found in our IR experiments that the vibrational frequencies of the ZnS/BCD complex were fundamentally the same as those for the ZnS+BCD mixture, except that the vibrational intensity characteristic for ZnS ( $300\text{ cm}^{-1}$ ) was considerably enhanced and among the various functional groups in ZnS/BCD, the intensity for the C–OH groups of the glucose unit ( $1075\text{ cm}^{-1}$ ) in BCD molecules was somewhat weakened in comparison with those of ZnS+BCD. IR results showed that no significant interactions and damages were found to take place when ZnS particle and BCD molecules were associated with each other and hence the included ZnS particles were chemically intrinsic. The formation of the inclusion complex can be accounted for in terms of van der Waals and dispersion forces. Among them, the hydrophobic interaction is thought to be much involved since the inner surface of BCD cavity is more

hydrophobic and the apolar cage is thus an environment favorable for the accommodation of the hydrophobic ZnS species.

### 3.5. Tight-binding approximation

As the inclusion process is chemically independent and as the inclusion is of little influence on spectral feature in our case, the quantum size effect of the included Q-particles would thus be truly reflected by their optical absorption behaviors. The correlation between the small particle size and the exciton peak position could be made by models based on an effective-mass approximation [14–17] and a recent tight-binding approximation [18]. The former gives a clear understanding of the blue-shifting of the optical absorption threshold, while the latter was found to be able to make a better description of band structure [10]. For the 1 nm included ZnS particles (ZnS/BCD, in Fig. 3a) and the 4 nm larger particles (ZnS/BCD·S<sup>2-</sup>, in Fig. 4d), using  $m_e^* = 0.42$ ,  $m_h^* = 0.61$  and  $\epsilon = 5.2$  [14,18] respectively for the effective electron and hole mass and the dielectric constant, the tight-binding calculation gives the exciton energy level of 5.2 and 3.9 eV, respectively. They are quite satisfactory as compared with our experimental data (5.0–5.1 eV for ZnS/BCD,  $\approx 4.0$  eV for ZnS/BCD·S<sup>2-</sup>).

## 4. Conclusion

We have shown that monodispersed, size-fixed and chemically intrinsic 1 nm ZnS Q-particles can be fabricated by embedding them into  $\beta$ -cyclodextrin cavities. With respect to several advantages of the present system, including the simplicity of its design, the authors envisage that the system appears to be only one example of a rather unexplored, general class of the host/guest inclusion complexes between various cyclodextrins and various quantum dots or quantum wells.

## Acknowledgement

This work was supported by Natural Science Foundation of China (NSFC). Acknowledgement is gratefully given to Professor Hongli Wang, this Insti-

tute, for careful reading and helpful discussion of the manuscript, as well as to Professor Ruifeng Lin, Institute of Photographic Chemistry, CAS, for assistance with the STM experiments.

## References

- [1] A. Henglein, *Topics Current Chem.* 143 (1988) 115.  
[2] A. Henglein, *Chem. Rev.* 89 (1989) 1861.  
[3] H. Weller, *Angew. Chem. Intern. Ed. Engl.* 32 (1993) 41.  
[4] L.E. Brus, *Appl. Phys. A53* (1991) 465.  
[5] G.D. Stucky and J.E. MacDougall, *Science* 247 (1990) 669.  
[6] T. Sugimoto, *Surface (Japan)* 22 (1984) 177; 29 (1991) 978.  
[7] H. Weller, H.M. Schmidt, U. Koch, A. Fojtik, S. Baral, A. Henglein, W. Kunath and K. Weiss, *Chem. Phys. Letters* 124 (1986) 557.  
[8] A.P. Alivisatos, A.L. Harris, N.J. Levinos, M.L. Steigerwald and L.E. Brus, *J. Chem. Phys.* 89 (1988) 4001.  
[9] T. Furuki, F. Hosokawa, M. Sakurai, Y. Inoue and R. Chujo, *J. Am. Chem. Soc.* 115 (1993) 2903.  
[10] Y. Wang and N. Herron, *Phys. Rev. B* 42 (1990) 7253.  
[11] W. Saenger, *Angew. Chem. Intern. Ed. Engl.* 19 (1980) 344.  
[12] H. Weller, U. Koch, M. Gutierrez and A. Henglein, *Ber. Bunsenges. Physik. Chem.* 88 (1984); D.E. Dunstan, A. Hagfeldt, M. Almgren, H.O.G. Siegbahn and E. Mukhatar, *J. Phys. Chem.* 94 (1990) 6797; S. Yanagita, M. Yoshiya, T. Shiragami, C. Pac, H. Hori and H. Fujita, *J. Phys. Chem.* 94 (1990) 3104.  
[13] R. Rossetti, R. Hull, J.M. Gibson and L.E. Brus, *J. Chem. Phys.* 82 (1985) 552.  
[14] L.E. Brus, *J. Chem. Phys.* 79 (1983) 5566; 80 (1984) 4403.  
[15] Y. Kayanuma, *Solid State Commun.* 59 (1986) 405.  
[16] Y. Kayanuma, *Phys. Rev. B* 38 (1988) 9797.  
[17] S.V. Nair, S. Sinha and K.C. Rustagi, *Phys. Rev. B* 35 (1987) 4098; T. Takagaha, *Phys. Rev. B* 36 (1987) 9293.  
[18] P.E. Lippens and M. Lannoo, *Phys. Rev. B* 39 (1989) 10935.