Zinc Sulfide Nanocrystals in Paraffin Liquid Open to Air: Preparation, Structure, and Mechanism

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We describe a new, green, and cheap route to the preparation of zinc sulfide nanocrystals at moderate temperature open to air in noncoordinating solvent paraffin liquid. The as-prepared ZnS nanocrystals with average size 4.7 nm presented particular UV–vis absorption. Cubic crystal lattice structures with good crystallization are characterized. A mechanism of ZnS nanocrystals formed in paraffin liquid as well as other similar solvent is demonstrated.

Semiconductor nanoparticles have been identified as materials with potential in a wide range of technological applications owing to their size-dependent optical and electronic properties. Among these semiconductor materials, zinc sulfide is typical wide band gap semiconductor with bulk band gap of 3.66 eV at room temperature, which is interesting emitting material in the blue to the ultraviolet range. The wide band gap of ZnS also makes it an ideal choice as an inorganic passivation shell for a variety of semiconductor core/shell and even core/shell/shell nanocrystals in order to improve the stability and emission properties of the semiconductor core nanocrystals with a relatively narrow band gap, such as CdSe/ZnS,[1] ZnSe/ZnS,[2] CdSe/CdS/ZnS,[3,4] and CdSe/ZnSe/ZnS.[4,5] This semiconductor nanocrystal is also an attractive host for the formation of doped nanocrystals, such as ZnS:Mn^{2+},[6] ZnS:Cu^{2+}.[7] For these reasons, preparation of high quality ZnS nanocrystals with a minimum of exertion is still an attractive subject although much effort has been made to evolve efficient routes for high-quality monodispersed quantum dots.[8] Additionally, little knowledge has been obtained for the mechanism of the formation of the ZnS nanocrystals. In particular, to the best of our knowledge, no chemical reaction equations in organometallic synthetic schemes[9] and its alternatives[10] have been proposed, although those routes have been proven to be the most popular.

In this study, ultrasmall ZnS nanocrystals were prepared in sole solvent paraffin liquid with zinc oxide, sulphur, and oleic acid in the air. Paraffin liquid and oleic acid are much cheaper and greener than TOP (trioctylphophine), TOPO (trioctylphosphine oxide), and ODE (octadecene), which generally used as solvents or capping ligands in organometallic synthetic schemes[9] and its alternatives.[10]

Typically, 1 mmol of S pellet was dissolved in 10 mL of paraffin liquid when carefully heated to 120 °C and cooled down to rt. Then, 1 mmol of ZnO, 5 mL of oleic acid (OA), and 20 mL of paraffin liquid were mixed and stabilized at 200 °C to generate a light yellowish but homogeneous solution. Finally, the S-source solution was swiftly injected into Zn-source solution to form ZnS nanocrystals.

Figure 1a shows the UV–vis absorption spectra of 20-min-reaction crude solution, which is characterized by a main absorption peak at 266 nm with a shoulder at 280 nm. By the process of size-selective precipitation,[9] the particle size distribution could be narrowed significantly. One, two, and three cycles of such process on the aforementioned solution were performed by using anhydrous methanol/toluene as nonsolvent/solvent. The corresponding spectra are collected in Figures 1b–1d. One can see that the spectra from b to d are dramatically sharpening relative to the initial solution and reveal the red shift from 266 to 270 nm, in which enriched with relatively larger crystals. This phenomenon is exploited in further narrowing the particle size distribution. The removal of a supernatant subset of particles from the initial size distribution narrows the size distribution of precipitate.[9] By systematically varying the reaction time, the initial reagent concentrations and the initial temperature, it was possible to finely and easily tune the size of nanocrystal.[14]

TEM images confirm that the ZnS nanocrystals are nearly spherical with the average size of 4.7 nm.[14] Figure 2 displays the representative HRTEM images of the as-prepared ZnS nanocrystals as well as SAED pattern. The SAED pattern (inset) can be indexed as the (111), (200), and (220) lattice planes (inside-out) in correspondence to the cubic phase, which also indicate the good crystallization. However, it should be noted

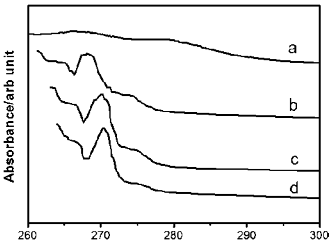

Figure 1. Example of the size-selective precipitation on the absorption spectra of as-prepared ZnS nanocrystals before (a) and after (b) one, (c) two, and (d) three cycles.

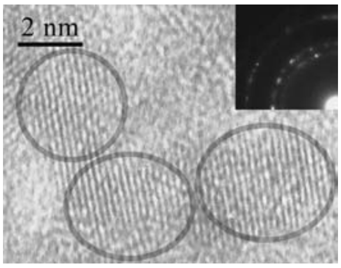

Figure 2. HRTEM image and SAED pattern (inset) of the as-prepared ZnS nanocrystals.

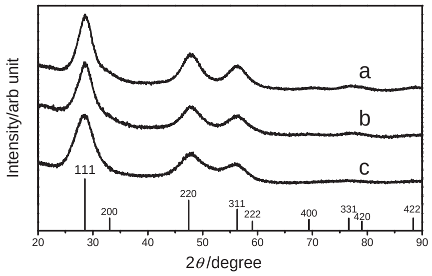

Figure 3. X-ray diffraction patterns of ZnS nanoparticles, a and b prepared by Zn-source and S-source solution, c obtained by the reaction Zn-source solution and H_2S gas.

that the conjunctional ZnS particles were also observed in our samples, which hint the growth process of small to large nanoparticles to some extent.

The powder XRD patterns of two as-prepared samples are shown in Figures 3a and 3b. As we can see, all the patterns match well with the reported bulk value of cubic ZnS (JCPDS, No. 5-0566). The peak broadening clearly indicates that very small nanocrystals are present in the samples. No peaks corresponding to impurities are detected. The consistency of two patterns implys that the experiments could be well reproducible. Interestingly, the SAED results show the (200) plane, which is not detected obviously in XRD data (probably owing to broadening and strengthening of the peak of (111) plane), although they both confirm the blende structure of ZnS exactly and consist with each other.[14]

In order to explore the mechanism of the preparation, an in-depth study between paraffin liquid and sulfur was carried out. When the S mixture was carefully heated to 260 °C, a great amount of colorless gas generated. The gas makes red alkaline phenolphthalein become colorless quickly. When the gas was conducted into Zn-source solution, the yellowish solution turned dark. The precipitate was washed to get final product. The X-ray diffraction pattern in Figure 3c shows the formation of pure ZnS nanocrystals. The energy dispersive X-ray (EDX) result shows that the precipitation is full of Zn and S. The calculated atomic ratio of Zn and S is approximately 1:1. As a result, we can verify the existence of H_2S gas and ZnS precipitation. Experiments replacing the paraffin liquid with other similar solvents such as *n*-hexadecane, oleic acid, a mixture of oleic acid and paraffin liquid with S pellet were also carried out. ZnS generated at similar conditions. To obtain further evidence, we also deduce the formation of alkene by Fourier transform infrared (FT-IR) spectroscopy. Taking *n*-hexadecane as solvent, an absorption band at $1710\,\mathrm{cm}^{-1}$ clearly appears in the spectra after heating, which is the characteristic of the C=O stretching. Because of weakness of C=O absorption peak compared with other peaks in the spectra and the easy oxidation of C=C (possibly caused by the residuary air in the reaction device or in air), this feature suggests the formation of C=C, i.e., the formation of alkene after heating. It is worth noting that the reaction between selenium and paraffin wax, which was discovered to generate H_2Se gas,[11] supports our mechanism to some extent because of the periodic comparability between sulfur and selenium. All the other featuers in the FT-IR spectra are identical to the long alkane chain.[14]

Based on above experimental results, we now can propose the mechanism of the formation of ZnS nanocrystals in our procedure:

$$\mathrm{ZnO} + \text{Oleic acid} \rightarrow \text{Zn-complex} \quad (1)$$

$$n/4\ \mathrm{S} + \mathrm{R\text{-}CH_2(CH_2)}_n\mathrm{CH_3} \rightarrow$$

$$n/4\ \mathrm{H_2S} + \mathrm{R\text{-}CH_2(CH{=}CHCH_2)}_{n/4}\mathrm{CH_3} \quad (2)$$

$$\text{Zn-complex} + \mathrm{H_2S} \rightarrow \mathrm{ZnS} \quad (3)$$

In which, step 1 demonstrates that the ZnO reacts with the oleic acid to generate Zn-complex, which is similar to the former report.[12,13] Step 2 is a process involving S pellet dissolved in paraffin liquid and a dehydrogenation reaction to generate H_2S gas. Step 3 describes that Zn-complex reacts with H_2S gas to form ZnS nanocrystals.

Choosing paraffin liquid and oleic acid as the reaction medium without expensive, toxic, and not environmentally friendly reagents significantly benefit the green and low-cost preparation of the ZnS nanocrystals both for laboratory and industry. The possible mechanism of ZnS nanocrystals formed in paraffin liquid as well as the other high boiling point solvents with long alkane chains is proposed. The new mechanism is expected to apply in other green and low-cost preparation of similar high-quality nanocrystals.

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