



Note

A generally synthetic route to semiconducting metal sulfide nanocrystals by using corresponding metal powder and cysteine as metallic and sulfuric sources, respectively

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ABSTRACT

The economical and large-scale preparations of metallic sulfides nanocrystals (NCs) would determine their practical industrial application. In this contribution, a series of sulfides NCs such as ZnS, CdS, PbS, Cu_xS, MnS and Bi₂S₃, have been harvested by thermolysis of a single source metal cysteinate obtained conveniently from the reaction between metal powder and cysteine in aqueous environment and constant atmosphere in glassware. The characterizations including TEM, XRD, UV–Vis, FT-IR, TG-DSC, EDX and BET confirmed that the as-synthesized products are from the decomposition of metal cysteinate, of nanoscale in size, and of mesoporous materials. The generation, low cost and benign environment made this route technologically and scientifically interesting for the preparation of metallic sulfides NCs.

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1. Introduction

In the past few decades, the large-scale and low-cost synthesis of inorganic semiconducting nanocrystals (NCs), therewith their peculiar properties in the electronics, optics and magnetics fields, have received increasing interest over the globe for their mass production [1]. Among them, representative metal chalcogenide NCs have been most extensively studied due to their quantum confinement characteristics and their dimensional matching with biological molecules [2,3]. The sulfide NCs, particularly, have been applied to many technological areas such as biological labeling and diagnostics, light-emitting diodes, electroluminescent devices, photovoltaic devices, lasers and single-electron transistors [4]. The practical applications of the sulfide NCs would have to be based on the premise that their preparations could be performed controllably, economically and on large scale. Vapor deposition methods are effective for the preparations of low-dimensional metal sulfide nanostructures when the good crystallized products deposited on substrates are concerned, but subject to yield limitation due to rigid experimental conditions [5–7]. Meantime wet chemical synthesis approaches are of fundamental interest and practical advantages in terms of the scalable synthesis of the nanostructured sulfide powder. So far, most metal sulfides NCs powders have been

prepared generally by various solution-phase synthetic schemes from the reactions of aqueous metal salt with thiourea, sulfur, thioacetamide, sodium thiosulfate or alkanethiol [6,8–13]. Due to the weak affinity of these sulfur sources to metal ions, these reactions were usually completed under the necessary help of some organic amines (poisonous and expensive) to act as chelating agent or surfactants [14,15], which would make the operation procedure complicated, and bring in inconveniences to the large-scale preparation of the metal sulfide NCs. This phenomenon gave us an inspiration that a reagent containing sulfur and amine sources would be an ideal precursor for solving the problem above. As known, cysteine is an inexpensive, simple, and environmentally benign thiol-containing amino acid, having a strong affinity to metal ions to form metal cysteinate [16]. Actually, some research groups have used this kind of amino acid and metallic salts to fabricate the corresponding metallic sulfides nanostructures with milligram yield in stainless teflon-lined autoclave, but these small-scale operations are of potential explosion due to high temperature and high pressures, not easy to expand to mass production [17–19]. Although the solvothermal reaction [20,21] or decomposition of single sulfur-containing organometallic molecule [22,23] were used to prepare sulfides nanostructures, these routes are not worthwhile of popularization due to the virulent reactants and high expense. Additionally, some uncontrollable and complicated methods like inverse microemulsion and sonochemical were also tried occasionally to synthesize the needed metallic sulfides nanostructures [24,25]. Hence developing a large-scale and facile synthesis avenue

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to metal sulfide NCs would be an important topic from an industrial perspective. In this contribution, we have developed a simple, efficient, reproducible and general synthetic route to fabricate a series of metal sulfides NCs. Because the cheap metallic powders and nontoxic L-cysteine were used as reaction precursors to react in aqueous environment and constant atmosphere in glassware, this simple and general route would be of significance for the industrial preparations of metallic sulfides NCs powder.

2. Experimental

Briefly, a certain amount of metallic powder, the cheapest metal precursor, and some cysteine were added in water and stirred at constant atmosphere in round flask for 24 h at 50–70 °C to get the corresponding metal cysteinate (defined as L–M later unless otherwise noted) suspensions. Then the top suspensions were poured out and washed with distilled water and ethanol, and followed with dryness in oven. Afterwards the dried L–M were decomposed at a certain temperature in Ar flow for rupturing the C–S bonds in L–M [26,27], and finally the desired metal sulfides NCs were harvested. A little powder was dispersed in ethanol 50% water under ultrasonic condition, and a droplet of suspension was dripped onto copper grids coated with ultrathin carbon film. Thus the sample was ready for the latter observation of electron microscopy. The products were characterized by low- and high-resolution transmission electron microscopy (TEM: JEOL-JEM-1005, HRTEM: JEM-40001X) equipped with energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD; Philips X'pert Pro diffractometer), ultraviolet–visible (UV–Vis) diffuse reflectance spectra (VARIAN Cary-5000 UV/Vis/NIR spectrophotometer), Fourier transform infrared (FT-IR) spectra (Nicolet Magna 560 FTIR spectrometer at a resolution of 2 cm⁻¹), Brunauer–Emmett–Teller (BET) surface area (Micromeritics ASAP 2020) and thermogravimetry-differential scanning calorimetry (TG-DSC) (STA-499C thermal analyzer, Netzsch).

3. Results and discussion

For the synthesis of ZnS NCs, 1.5 g of Zn powder (200 mesh) and 3.0 g of cysteine were added into 200 ml of distilled water in a round flask equipped with a reflux device, and vigorously stirred for 24 h under constant atmosphere, then the top suspensions in flask were poured out and washed several times by distilled water and ethanol, then dried 2 h at 70 °C, thereafter the white colored powder of L–Zn was collected. After the simple thermolysis of the L–Zn at 350 °C in Ar, 2.12 g of brown colored powders was obtained with a yield of 94.6% when calculated with the used Zn powder. From TEM images (Fig. 1a and b), the as-prepared brown powders are composed of very small NCs forming aggregates. The selected area electron diffraction (SAED) pattern (inset in Fig. 1a) presents a set of bleak diffraction circles indicating the polycrystal feature, which could be indexed to the hexagonal ZnS. The size of all NCs was affirmed from the HRTEM image (Fig. 1c). The typical NCs have the size of 3–5 nm in diameter, and the lattice spacing of 2.24 Å between the adjacent fringes corresponds to the *d*-spacing of (1 0 2) planes of the hexagonal ZnS. XRD pattern (Fig. 1d) of the product further shows its crystal structure is hexagonal ZnS (ICDD-PDF #792204). The broadening peaks indicated that the crystal sizes are on the nanoscale, as confirmed by the TEM observations. From the broadening peak width of ZnS (0 0 2) X-ray spectral peaks using the Scherrer formula $D = K\lambda/\beta(\cos \theta)$ [28], the even size of the NCs is 3.2 nm and in close accordance with the observed size in HRTEM. From the empirical relationship between the even size of ZnS NCs and the onset of UV absorption, the average size of ZnS particles was estimated to be about 4.2 nm,

also consistent with the HRTEM observation (Fig. S1). Herein the facile and large-scale synthesis of wurtzite ZnS NCs in aqueous solution is very interesting because that, ZnS NCs prepared by wet chemistry usually have the cubic zinc blende structure which is a stable phase at low temperatures [8,10] while wurtzite phase is stable in the cases of preparations of hexagonal ZnS NCs whether at the high temperature or in the solvothermal reaction systems [14,15,29]. Hence our ability to synthesize a high temperature stable phase at very low temperatures and in aqueous condition, offers the exciting prospect of economically facile route for applications of wurtzite ZnS NCs. Very recently, Yang reported that, when the diameter of ZnS NCs is smaller than 7 nm, the wurtzite ZnS become thermodynamically stable over cubic phase. This calculation further supported the very small size of as-prepared ZnS NCs in this synthesis [30].

The reaction process of ZnS NCs growth was explored. The cysteine reacted with metallic Zn particulates to form L–Zn under the help of dissolved oxygen in aqueous solution [31]. If the reaction system was conducted in a sealed glass flask filled with deaerated water, Zn powder did not show any changeable. The functional groups of –SH, –NH₂ and –COOH in cysteine clung to Zn atoms to form metal cysteinate. After thermolysis, the rupture of C–S bonds in cysteinate salt resulted in the generation of ZnS NCs [32]. However the remanet of amorphous carbon embedded ZnS NCs and thus changed the product's essential color by brown. Hence ZnS NCs showed an aggregate. The total growth process of ZnS NCs was revealed by some convincing examinations such as XRD, FT-IR and TG-DSC (Fig. S2), which was also shown by Xie's research group [18,19].

The route reported here is also applicable to other metallic sulfide NCs. By the similar reaction procedure, the CdS and PbS nanopowders have been obtained with the yield of 91.2% and 85.7% after the thermolysis of L–Cd and L–Pb at 300 °C and 250 °C, respectively. Their morphologies and structures were shown in Figs. 2 and 3. The synthesized CdS and PbS NCs are black. Fig. 2a shows an aggregate composed of numerous very small NCs. HRTEM image (Fig. 2c) confirms that the typical NCs have the size of ~5 nm in diameter, and the lattice spacing of 3.4 Å between the adjacent fringes corresponds to the *d*-spacing of (0 0 2) planes of the hexagonal CdS. XRD pattern (Fig. 2d) of the product could further show its crystal structure is hexagonal CdS (PDF #800006), while the broadening peaks indicated several nanometer-sized CdS NCs. Accordingly, Fig. 3 revealed that, the PbS NCs are of cubes with edge length of ca. 18 nm, and the PbS nanocubes are single crystal with cubic structure (PDF #050592) and nearly monodisperse in ethanol. Herein the aggregated CdS NCs were as small as ZnS NCs, thereby easily embedded in the remained amorphous carbon; while the PbS NCs were much larger than ZnS or CdS NCs, and were hardly anchored onto the amorphous carbon, thus showing monodispersed in water solution.

Besides the successful preparations of ZnS, CdS and PbS NCs by this route, we applied this idea to synthesize others metallic sulfides NCs. In result, a series of sulfides NCs including Cu₂S, MnS and Bi₂S₃ NCs has been successfully obtained (Fig. S3). These samples exemplified such an ingenious synthetic route is general and promising for preparing metallic sulfide NCs. However, when using some easily passivated metals such as Ti, Al, Cr, Mo and so on, we failed to prepare the corresponding metallic sulfides, since these metals are preferentially self-passivated in water thereby cannot be easily eroded by the dissolved cysteine and O₂ in water.

Some typical samples' element analysis by energy-dispersive X-ray analysis confirmed the products obtained are composed of sulfur and corresponding metal elements with a certain atomic stoichiometric of 1:1 for ZnS, CdS and PbS NCs. Interestingly, some Cu_xS NCs with varying stoichiometric [33] could be also prepared by this novel route through changing the mass ratio of cysteine

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