A Simple Large-scale Synthesis of Well-defined Silver Sulfide Semiconductor Nanoparticles with Adjustable Sizes

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A one-pot method characterized by thermolysis of a novel kind of single-source precursor was proposed to generate size-tunable monodisperse $Ag_2S(r)$ semiconductor nanoparticles in large scale.

A driving force behind the development of new chemical methods for preparing size-selected nanocrystalline compounds is the potential for "tuning" electronic properties of individual nanocrystals and arrays assembled using nanocrystals.[1] It is well known that the low-temperature phase of bulk silver sulfide ($Ag_2S(r)$ or acanthite) is an important kind of semiconductor and R-Ag_2S nanoparticles represent an interesting class of semiconductor nanoparticles with unique properties.[2] However, the attempts to synthesize monodispersed Ag_2S nanoparticles have been for the most part very difficult owing to the fact that the Ag_2S clusters show a strong tendency to aggregate into bulk.[2,3] The solutions are the largely reported reverse micelles techniques, by which Ag_2S nanocrystallites of a size 2.3–7.6 nm with relative narrow size distribution can be prepared.[4] A more convenient approach is the recently reported two-phase synthesis route using silver thiolate polymers.[1] However, more efficient method to produce highly uniform Ag_2S nanocrystallites with ajustable size should be developed to enable the in-depth study and application of these fascinating materials.

A new direction for the preparation of nanomaterial being pursued is the use of single-source precursors, by which the reproducibility of size dispersity, facility of preparation process, and synthetic scale were largely surmounted.[5] Examples are the preparation of CdS, ZnS, ZnSe, CdSe, and Ag_2S nanoparticles from pyrolyzable single-source molecular precursors such as metal dithio- and diselenocarbamate complexes.[6] However, new precursors should be explored to facilitate the synthetic process, enlarge the synthetic scale and improve the quality of the production.

In the present communication, a novel lyothermal route was used to achieve the large-scale synthesis of highly monodispersed $Ag_2S(r)$ lyophobic nanoparticles with adjustable sizes. The method is characterized by using the readily available complexes of silver(I) *O*,*O*′-dialkyldithiophosphate (abbreviated as AgC_nDTP)[7] with the universal molecular formula to be expressed as $Ag[S_2P(OR)_2]$ ($R = C_nH_{2n+1}$, $n = 5$–20 and in this report $n = 8$, 12, and 16), as a single-source precursor. These compounds are stable under ambient conditions, but melt rapidly when heated in Ar atmosphere to give a colorless precursor liquid, which was gradually decomposed to produce, at a yield higher than 84% according to silver, the dark brown product contains highly monodispersed hydrophobic nanoparticles of $Ag_2S(r)$. The particle size can be well "tuned" by altering the value of "*n*" or reaction temperature. This synthetic process is simple (only one agent is required), reproducible, scalable (up to the kilograms scale in laboratory), and obviously a more efficient approach toward "size-tunable" well-defined Ag_2S nanoparticles.

A representative TEM image shown in Figure 1a confirms that the resulting product is nanosized particulates of a narrow size distribution, with the mean diameter of 14.3 ± 0.7 nm. The powder X-ray diffraction (XRD) and selective-area electron diffraction (ED) patterns (Figure 2) are characterized by broad peaks and diffusion rings, respectively, which are typical for small crystallites. The indexing of the lattice parameters of the XRD and SAED patterns conforms to acanthites phase, which indicates that the core of the nanoparticles must be $Ag_2S(r)$.

The ligand of the precursor, long chain dialkyldithiophosphate (DTP), has been reported to be a good capping agent for metal sulfide nanoparticles because it can tightly and chemically adsorb on metal sulfide surface to form a protective monolayer.[7,8] Therefore, it is unsurprising that the synthetic nanoparticles are hydrophobic and show less tendency to aggregate, owing to the presence of organic moiety around the Ag_2S core. This is further confirmed by the IR and ^1H NMR analysis of the fully purified product sample to avoid the effect of isolated organic impurities. Namely, the IR[9] and ^1H NMR[10] spectra of the synthetic nanoparticles are similar to those of the ligand (dialkyldithiophosphoric acid) in their precursor, which indicates that DTP does exist around the nanoparticles. We deduce that during the preparation process, combining with the cracking of the precursor to form Ag_2S, portion of the ligand might eliminated form the complex and simultaneously attached on the growing nuclei.

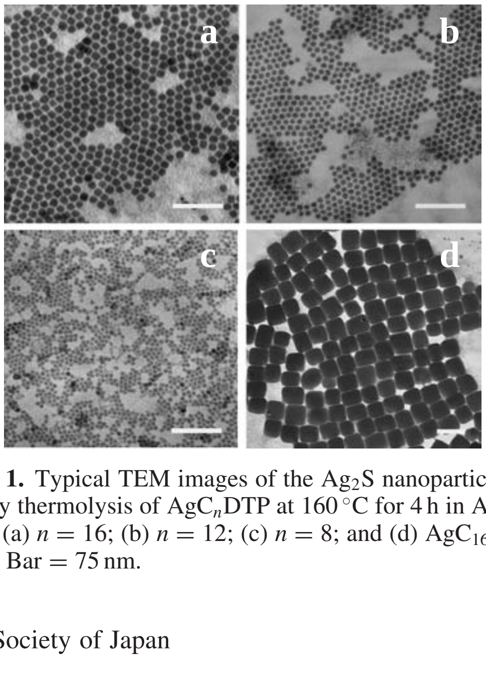

Figure 1. Typical TEM images of the Ag_2S nanoparticles prepared by thermolysis of AgC_nDTP at 160 °C for 4 h in Ar atmosphere. (a) $n = 16$; (b) $n = 12$; (c) $n = 8$; and (d) $AgC_{16}DTP$ at 180 °C. Bar = 75 nm.

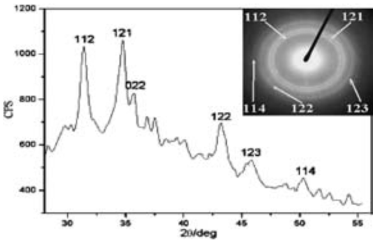

Figure 2. XRD and ED (top-right inset) patterns of the nanoparticles prepared by thermolysis of $AgC_{16}DTP$ at 160 °C for 4 h.

The precursors with various substituted alkyl chains can be used in this synthetic route; however, the chain length should be at least five in order to obtain well-capped nanoparticles. The most obvious effect of the alkyl chain length we noticed is on the final grain size. Under the same experimental conditions, the mean diameter of the nanoparticles synthesized from AgC_nDTP ($n = 8$, 12, and 16) is 6.0 ± 0.9, 9.5 ± 0.6, and 14.3 ± 0.7 nm calculated from their TEM images in Figures 1a, 1b, and 1c, respectively. The diameter values indicate that a long chain length corresponds to a large grain size. This observation is in accordance with what has been reported "lengthier ligands stabilize larger particles."[11] The proper reaction temperature is determined to be 150–170 °C by parallel experiments with which the reaction speed is moderate and the quality and yield of the target nanoparticles are high. Reaction temperature in this range shows no obvious effect on the final grain size of the target nanoparticles. However, thermolysis of the precursors above 180 °C will lead to a partial destruction of the ligand and sufficient growth of the nuclei, thus result in a few large cubic Ag_2S particles (Figure 1d) with less hydrophobic nature. In virtue of these findings, we can finely adjust the final grain size of the product by changing the substituted alkyl chain length of the precursor or the reaction temperature to some extent.

The synthesized particles have strong tendency to form self-assembled superlattice similar to other monodispersed lyophobic nanoclusters, which is in good accordance with their narrow size distribution. It is feasible to obtain one layer, two layers, and multilayers (Figures 1 and 3) close-packed superlattice of the synthetic nanoparticles on TEM carbon grid simply by dropping their hexane solution of different concentrations. With a view to the increasing interests in nanostructure construction which are critically important to chemical, optical, magnetic, and electronic nanodevices,[2b] the nanoparticulate materials made by the present facile synthetic route and the successive assembly procedure provide good candidate systems for the fabricating of novel superstructure as well as the probing of their properties and applications.

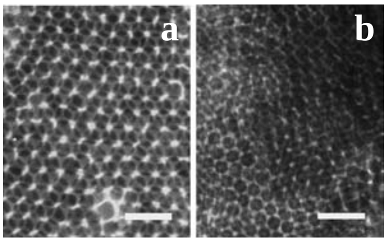

Figure 3. TEM images of the bilayer (a) and multilayer (b) self-assembled Ag_2S nanoparticles from $AgC_{16}DTP$ on the TEM copper grid by dropping ≈0.1 g/L and ≈1 g/L as-prepared Ag_2S nanoparticle/hexane solution thereon. Bar = 50 nm.

To conclude, monodispersed Ag_2S nanoparticles with adjustable size were conveniently synthesized via a facile lyothermal route. The use of a novel single-source precursor, silver(I) dialkyldithiophosphate, provides a convenient reactive intermediate for the growth of Ag_2S nanoparticulate materials with given grain size in large quantities under relatively mild conditions, which will greatly stimulate the application of this fascinating material in materials science and artificially engineered nanosized particles with novel properties.

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References and Notes

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9 The IR for the corresponding ligand *O*,*O*′-dihexadecyldithiophosphoric acid: 2953s (CH_3), 2922s (CH_2), 2852s (CH_2), 2400–2600 (νS–H), 1464s (CH_3), 1378s (CH_3), 995s (OPO), 662s (νP=S), 533w (νP–S) cm^{-1}; those for the purified Ag_2S nanoparticles from $AgC_{16}DTP$: 2954s, 2919s, 2849s, 1620s, 1465s, 1378s, 983s, 633s, 548w cm^{-1}.

10 The ^1H NMR (400 MHz, CDCl3, 25 °C, TMS) for the purified Ag_2S nanoparticles: δ 0.87 (6H, CH_3), 1.29 (60H, CH_2); that for the corresponding ligand: δ 0.85 (6H, CH_3), 1.30 (60H, CH_2).

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