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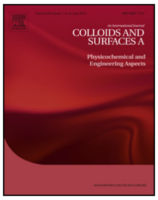

Metallurgical leaching of metal powder for facile and generalized synthesis of metal sulfide nanocrystals

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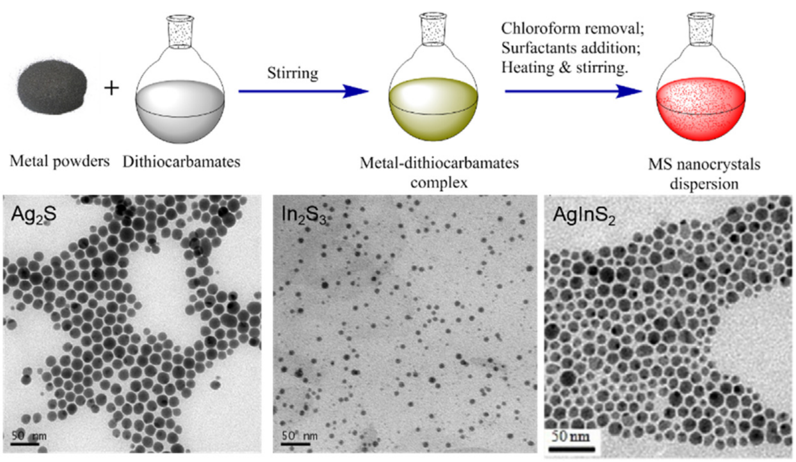
HIGHLIGHTS

- A general and facile strategy for preparing metal sulfide nanocrystals was reported based on metallurgical leaching of metal powders.
- In_2S_3, Ag_2S, and $AgInS_2$ nanocrystals can be synthesized just mixture of Ag, In, and dithiocarbamate in stoichiometric molar ratio.
- The size, shape, and chemical composition of the nanomaterials can be easily controlled, and the metal sulfides exhibit novel optical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of high-quality metal sulfide semiconductor nanocrystals through a facile and general metallurgical processes. Metal powders employed as readily available chemicals were metallurgically leached with dithiocarbamate in chloroform solution to form in situ the metal dithiocarbamate complex precursor, which was directly heated under appropriate experimental conditions to produce a variety of metal sulfide nanocrystals. Based on this, 11.8, and 21.5 nm uniform spherical Ag_2S and 34.5 nm cubic Ag_2S nanocrystals were synthesized. Binary In_2S_3 nanocrystals with 9.1 nm were obtained from the reaction of indium and dithiocarbamate. Furthermore, ternary $AgInS_2$ nanocrystals were prepared from a reaction mixture of Ag, In, and dithiocarbamate in stoichiometric molar ratio. Using this method, the size, shape, and chemical composition of the nanomaterials can be easily controlled, and these as-synthesized metal sulfides exhibit novel optical properties. This facile methodology for the synthesis of metal sulfides can be generally expanded to fabricate other nanocrystals, and the readily available metal elements may provide an alternative approach for the industrial synthesis of nanomaterials.

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1. Introduction

Metal sulfide nanocrystals have been widely investigated for many applications, such as biological labeling, medical diagnostics, light-emitting diodes, photovoltaic devices, and electroluminescent devices, due to their unique size-dependent optical, electronic, and chemical properties [1,2]. Thus, the development of facile and general synthetic approaches that yield metal chalcogenides with precise control over size, shape, and chemical composition, is highly desirable from fundamental studies to practical industrial applications [3,4]. Over the past decades, great efforts have been made on the development of approaches for the synthesis of metal chalcogenide nanoparticles [5]. Hyeon et al. developed a general and facile approach for the synthesis of metal chalcogenide nanocrystals through the thermal reaction of metal chloride and sulfur in oleylamine and the thermolysis of metal oleate complexes in alkanethiol [6,7]. In addition, Li et al. prepared a series of chalcogenide nanocrystals using metal nitrates and sulfur or selenium powder as precursors [8]. Furthermore, single-source precursor thermolysis has become one of the most relevant approaches because of its simplicity and the ability to control the nanoparticle morphology [9,10]. As dithiocarbamate is quite unstable, metal complexes incorporating dithiocarbamate ligands are becoming widely adopted as single-source precursors for the synthesis of metal chalcogenide nanocrystals [11–13]. Wang et al. have reported their endeavors on the synthesis of binary and ternary metal sulfide semiconductor nanocrystals with precise control of size, shape, and chemical composition through thermal decomposition of metal diethyldithiocarbamates [14,15]. However, the above approaches have some demerits in their use that may preclude their employment in commercial-scale, solution-based synthesis [16]. For instance, dithiocarbamate salts must be synthesized and complexed with different transition metals; the resultant product must then be isolated and purified before use in the synthesis of metal sulfide nanocrystals [10,17].

Different metal salts are widely employed in the fabrication of various nanocrystals; however, we are aware of scarce studies that have examined the metal element as a reagent from the perspective of nanocrystals preparation. Metal elements usually have the advantages of being convenient availability, low cost, and high security guarantees, which may provide an alternative approach for nanomaterial synthesis. Feng et al. reported that a series of sulfides nanocrystals have been harvested by thermolysis of a single source metal cysteinate obtained conveniently from the reaction between metal powder and cysteine in aqueous environment [18]. Metallurgical cyanide leaching of gold is widely known to be a metallurgical technique for extracting gold element from low-grade ore by converting the gold to a water-soluble coordination complex [19]. It is the most commonly used process for gold extraction [20]. Analogous to the metallurgical cyanide, dithiocarbamate is another metal collector in mineral flotation and is commonly used in the flotation of metal chalcogenide and noble metal-bearing ores [21,22]. Here, dithiocarbamate is chosen as the coordination reagent for metallurgical leaching of a variety of metal powders. To facilitate the metallurgical leaching of metal powder with dithiocarbamate salts, chloroform organic solvent was employed as the reaction media. Then, the in situ formation of the reactive dithiocarbamate metal salt allowed us to directly prepare a variety of metal sulfides using a reproducible and convenient protocol. This is a general, facile, and cost-saving method for the direct preparation of a large variety of metal sulfide nanocrystals from metal powders of interest. The size, shape, and chemical composition of metal sulfide nanocrystals could be well-controlled by changing the thermolytic reaction conditions. Furthermore, the use of cheap and readily available metal powders as reactants makes it possible for these nanocrystals to be produced in large quantities, which is important for industrial applications.

2. Materials and methods

2.1. Materials

Silver metal powder (Ag, 100 mesh, 99.95%) and Indium metal powder (In, 99.9%) were obtained from J&K. Oleic acid (OA, 90%), sodium diethyldithiocarbamate trihydrate (Na(DTC)) were purchased from Sigma-Aldrich. Octadecylamine (ODA, 90%) and octadecene (ODE, 90%) were obtained from Acros. Ethanol and chloroform were from Sinopharm. All chemicals were used as received without further purification.

2.2. Metallurgical leaching of metal powders with dithiocarbamate

In a typical synthesis, 0.1 mmol of Ag and 0.1 mmol Na(DTC) were firstly mixed in 5 ml of chloroform. After vigorous stirring for 3 h, Ag powder was completely dissolved, resulting in a yellowish-brown solution of 0.1 mmol silver dithiocarbamate salt (Ag(DTC)). Similar procedures were used to prepare indium dithiocarbamate salt ($In(DTC)_3$), while the corresponding metal powders were adopted as the react reagents, and the molar ratio of metal powder and Na(DTC) was consistent with their own reaction stoichiometry.

2.3. Preparation of metal sulfide nanocrystals

A typical procedure for preparation of Ag_2S nanocrystals was described as follows. A given amount of Ag(DTC) (0.1 mmol) solution was rotary evaporated to remove the chloroform solvent. 10 mmol of OA, 10 mmol of ODA, as well as 20 mmol of ODE solvent were added at room temperature. Then, the slurry was heated to 60 °C to remove the possible volatile substances with vigorous magnetic stirring under vacuum for several minutes in a temperature-controlled electromantle, and thus to form a light yellow solution. The solution was further heated to a temperature of 140 °C at a heating rate of 15 °C/min and kept for 30 min under N_2 atmosphere. After cooling to a room temperature, the nanocrystals were precipitated by adding an excess amount of the absolute chloroform into the reacted solution, followed by washing with methanol and the as-formed nanocrystals were easily redispersed in chloroform. Preparation of In_2S_3 nanocrystal was performed with similar procedures, except that the $In(DTC)_3$ precursor was heated to 240 °C for thermolytic synthesis of nanocrystals. As for $AgInS_2$ nanocrystals, identical Ag(DTC) and $In(DTC)_3$ were mixed and the precursors were heated to 180 °C for thermolytic synthesis.

2.4. Characterization

Transmission electron microscopy (TEM) and energy dispersive spectrograph (EDS) were performed on Tecnai G2 F20 S-Twin transmission electron microscopy equipped with an X-ray energy dispersive spectrometer. TEM samples were prepared by dropping 1–2 droplets of the sample solution onto a carbon-coated Cu grid. Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). Absorption spectra were recorded on a UV–vis 1601 Shimadzu spectrophotometer. Steady-state fluorescence measurements were performed on Hitachi F7000 fluorescence spectrophotometer or PTI Quantimaster QM-4 spectrofluorometer equipped with near infrared spectroscopy. FTIR spectra of KBr powder-pressed pellets were recorded on Bruker Tensor 27 spectrophotometer scanning from 4000 to 400 cm^{-1}. Thermo