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Research paper

A two-phase synthesis of metal sulfide-gold nanocomposites

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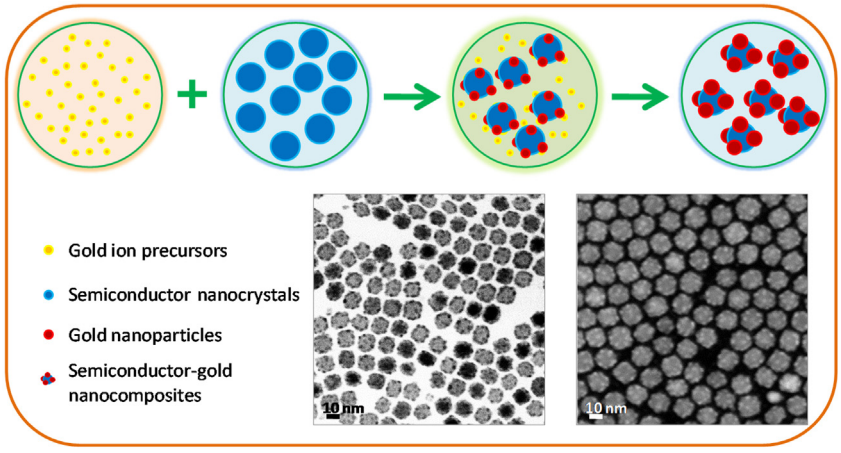
HIGHLIGHTS

- A two-phase method is used to create metal sulfide-gold nanocomposites.
- The strategy does not need the phase transfer of Au ions.
- The strategy relies on the catalysis of semiconductor for the reduction of Au ions.
- The strategy is more facile for the synthesis of metal sulfide-gold nanocomposites.

GRAPHICAL ABSTRACT



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ABSTRACT

The integration of chemically distinct materials within a single nanostructure is an effective way to increase their functionality for given applications. Herein, we report a two-phase method with remarkable simplicity and universality for the synthesis of nanocomposites consisting of metal sulfide semiconductors and gold (Au) metal. The metal sulfide nanocrystals dispersed in toluene are firstly mixed with an aqueous solution of Au ion precursors, e.g. gold(III) chloride ($HAuCl_4$), and then upon vigorous agitation, the Au ions contacted with semiconductor nanocrystals at the interfaces between organic and aqueous phases are reduced into Au atoms, which are subsequently nucleate and grow on the surface of metal sulfide nanocrystals, resulting in the formation of composite nanostructures with semiconductor and Au at different domains. This strategy reasonably makes use of the catalytic property of semiconductor nanocrystals for the reduction of Au ion precursors at room temperature, and from engineering aspect, its facile feature might have provided a promising method with ease of control for the production of metal sulfide-Au nanocomposites.

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1. Introduction

The research interest for the fabrication of composite nanomaterials consisting of semiconductor and noble metals has been increasing in recent years [1–5]. The composite nanostructures integrate chemically distinct materials at their different domains to yield a unique hybrid system with synergistic effects for engineering applications, e.g. photocatalysis [6–15], electrocatalysis [16–21], photovoltaics [22], sensing [23], thermal-insulating coating [24], and antimicrobial [25], etc. To date, gold (Au)-based nanocomposites, which are constructed by depositing Au on the surface of various substrate nanocrystals, are the topics being studied most sufficiently [26–40]. For example, Ying and coworkers synthesized three different types of semiconductor–Au nanocomposites (CdS–Au, CdSe–Au and PbS–Au) for catalyzing the three-component coupling reaction of benzaldehyde, piperidine and phenylacetylene in water. Through electronic coupling between semiconductor and Au domains, PbS–Au nanocomposites provided superior catalytic activity, offering the desired propargylic amine product in isolated yields of up to 95% [41]. Recently, Li group reported a one-pot approach to synthesize polypeptide-gold nanocomposites for *in vitro* gene transfection [42]. They found that the positively charged polypeptide-conjugated gold nanoparticles are effective gene delivery vectors. A gradual and prolonged intracellular uptake and transfection could be achieved, and transfection activity is maintained for almost two weeks without compromising the cell viability.

The common strategy for creating semiconductor-Au nanocomposites usually starts with the mixing of Au ions and preformed semiconductor nanocrystals in a nonpolar solvent, e.g. toluene, hexane, or dichloromethane, and then a weak reducing agent, e.g. dodecylamine (DDA), is used to reduce the Au ions into atoms, which nucleate and grow on the surface of semiconductor nanocrystals. However, a phase transfer process of Au ions is often needed in the above-mentioned strategy since Au ions cannot be dissolved directly in nonpolar organic solvents. The transfer process of Au ions would inevitably complicate the synthesis of semiconductor-Au nanocomposites by introducing additional transfer agents, e.g. tetraoctylammonium bromide (TOAB) in Brust-Schiffrin method [43] and dodecyldimethylammonium bromide (DDAB) in the approach developed by Banin and coworkers [26].

In the present work, we report a two-phase approach with remarkable simplicity, universality, and high-yield for the synthesis of nanocomposites consisting of semiconducting metal sulfides and Au metal, which is based on the catalytic property of semiconductor nanocrysals for the reduction of Au ions at room temperature. In this strategy, instead of phase transfer of Au ions from water to an organic solvent, the aqueous solution of gold(III) chloride ($HAuCl_4$) is mixed directly with metal sulfide nanocrystals dispersed in toluene. Then under vigorous agitation, the Au ions contacted with semiconductor nanocrystals at the interfaces between organic and aqueous phases are reduced into Au atoms, which are subsequently nucleate and grow on the surface of semiconductor nanocrystals for the formation of nanocomposites with metal sulfides and Au at different domains. The remarkable simplicity may render this strategy will be potentially promising to produce metal sulfide-Au nanocomposites for given engineering applications.

2. Experimental section

2.1. Reagents

Cadmium chloride ($CdCl_2$, ≥99%), copper(II) chloride ($CuCl_2$, 99%), lead(II) nitrate ($Pb(NO_3)_2$, ≥99%), silver nitrate ($AgNO_3$, ≥99%), gold(III) chloride trihydrate ($HAuCl_3{\cdot}3H_2O$), dodecylamine (DDA, 98%), oleylamine (OLA, 70%, technical grade), and element sulfur (S, ≥99.5%) from Beijing Chemical Works, methanol (99%) and toluene (99.5%) from Aladdin Reagents were used as received.

2.2. Synthesis of metal sulfide nanocrystals

Metal sulfide nanocrystals including silver sulfide (Ag_2S), cadmium sulfide (CdS), copper sulfide (CuS), and lead sulfide (PbS) were synthesized using the approaches established before with slight modifications [44–47]. In detail, 1 mmol of $AgNO_3$, $CdCl_2$, $CuCl_2$ or $Pb(NO_3)_2$ was added into 20 mL of oleylamine in a three-necked flask equipped with a condenser and a stir bar. The solution was heated and kept at an elevated temperature (100 °C for $AgNO_3$, 150 °C for $CuCl_2$, 180 °C for $CdCl_2$, and 210 °C for $Pb(NO_3)_2$, respectively) under flowing N_2 until the complete dissolution of the metal precursors. Separately, an oleylamine-sulfur solution was prepared by dissolving 2 mmol of sulfur into 5 mL of oleylamine at 90 °C, which was then injected into the oleylamine solutions of metal precursors. The reaction mixtures were continuously maintained at elevated temperature (100 °C for $AgNO_3$, 150 °C for $CuCl_2$, 180 °C for $CdCl_2$, and 210 °C for $Pb(NO_3)_2$, respectively) for 1 h for the formation of Ag_2S, CdS, CuS, and PbS nanocrystals, which were then precipitated with methanol, collected by centrifugation, and re-dispersed into 20 mL of toluene.

2.3. Synthesis of metal sulfide-Au nanocomposites

Typically, to 10 mL of the semiconducting metal sulfide (Ag_2S, CdS, CuS, or PbS) organosol in toluene, 2 mL of DDA was added as reducing agent, followed by mixing with 10 mL of aqueous $HAuCl_4$ solution (25 mM). Then the mixture was vigorously agitated at room temperature for 1 h to achieve the deposition of Au on the surface of metal sulfide nanocrystals. After reaction, the organic layers containing semiconductor-Au nanocomposites were collected after complete separation of two phases.

2.4. Particle characterizations

The transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning TEM (STEM) characterizations were carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. For the microscopic measurements, a drop of the organosol was loaded onto a 3-mm carbon-coated copper grid, followed by drying in vacuum at room temperature. The average diameters and the standard deviations of the particles were calculated from a few randomly chosen areas in the TEM image containing approximately 100 nanoparticles each. An energy dispersive X-ray spectroscopy (EDX) analyzer attached to the TEM operated in STEM mode was used to analyze the chemical components in the composite samples. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max–3 B diffractometer, using Cu K_α radiation ($\lambda = 0.154056$ nm). Samples for XRD were concentrated from the toluene solution of nanocomposites to 0.5 mL using flowing N_2. 10 mL of methanol was then added to precipitate the composite particles, which were collected by centrifugation, washed thrice with methanol, and then dried at room temperature in vacuum.

3. Results and discussion

It has been documented that semiconducting metal sulfide nanocrystals with uniform sizes could be prepared in oleylamine at metal precursor/element sulfur molar ratio of 1/2 [44–46]. Fig. 1a, e, i, and m show the TEM images of Ag_2S, CdS, CuS, and PbS nanocrystals generated by injecting sulfur into a preheated solution of $AgNO_3$, $CdCl_2$, $CuCl_2$, and $Pb(NO_3)_2$ in oleylamine at 100 °C (For $AgNO_3$), 180 °C (for $CdCl_2$), 150 °C (for $CuCl_2$), and 210 °C (for