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A general microwave-assisted two-phase strategy for nanocrystals synthesis

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ABSTRACT

A general microwave-assisted two-phase strategy (MTS) has been developed for the synthesis of monodisperse inorganic nanocrystals (NCs). A series of metal oxides, ferrite, hydroxides, and metal sulfide NCs were synthesized by using water-soluble metal salts. The obtained NCs were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The composition, size, and shape of the NCs can be tuned by the types of precursors, the concentrations of metal ions, and the species of ligands. This protocol creates a new synthetic route, which may also be further extended to synthesize other nanomaterials, including alloy, noble metal, rare-earth fluorescent, etc.

1. Introduction

The synthesis of nanocrystals (NCs) has been intensively pursued, not only for their fundamental scientific interest, but also for their many technological applications [1]. A success synthetic route to prepare homologous size series of monodisperse NCs is indispensable for uncovering and mapping size-dependent properties of materials [2]. The well-defined NCs samples in this intermediate, nanometer size regime between molecular species and bulk solid, exhibit very interesting size-dependent optical, electrical, magnetic, and chemical properties [3]. For many future applications, such as catalysis, magnetic data storage, solar cells, lithium ion batteries, and medicine, the synthesis of uniform-sized NCs is of key importance [4–10]. The preparation of nearly monodisperse NCs is essential to study the novel properties inherent to homogeneous nanoscale structures [11]. Solution phase syntheses and size-selective separation methods to prepare monodisperse NCs have been developed [12,13]. Accordingly, the designed synthesis of NCs with controllability of their size and shape is essential.

To obtain monodisperse semiconductor NCs, in 1993, Murray et al. explored a novel hot-injection method [14,15]. However, this route always requires expensive and toxic reagents including alkylphosphites, alkylphosphates, pyridines, alkylamines, and furans. In 2004, Hyeon reported on the ultra-large-scale synthesis of monodisperse nanocrystals by using inexpensive and non-toxic metal salts as reactants [16]. Nevertheless, the preparation process requires harsh conditions, such as high temperatures (~320 °C) and protective atmosphere (N_2 or Ar). In 2005, Li developed a general liquid–solid–solution (LSS) strategy for the synthesis of NCs [17]. But the method still needs to be improved in view of the uniformity and reproducibility. Subsequently, phase-transfer technique was also developed by several groups [18,19]. Yang and co-workers introduced a phase-transfer protocol to synthesis of NCs by using dodecylamine as ligand [20]. The above methods have greatly enriched the synthesis of monodisperse NCs; however, it is still necessary to develop a facile, fast, and non-toxic route to prepare monodisperse NCs.

In this paper, we developed a general microwave-assisted two-phase strategy (MTS) for the synthesis of inorganic NCs with uniform size and shape. The procedure is facile, rapid, and environmentally benign. Inorganic NCs with different chemical compositions, sizes and shapes can be synthesized using the inexpensive metal salts. Metal oxides (Fe_2O_3, Fe_3O_4, Co_3O_4, CuO, SnO), ferrite ($CoFe_2O_4$), hydroxides [$Mg(OH)_2$, $Ni(OH)_2$], and metal sulfide (HgS) NCs of uniform size and shape have been produced by the general strategy.

2. Experimental section

2.1. Starting materials

All chemical were used as received without further purification. Iron(III) nitrate nonahydrate [$Fe(NO_3)_3{\cdot}9H_2O$, 98.5%], iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, 99.0%), iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99.0%), cobalt(II) nitrate hexahydrate [$Co(NO_3)_2{\cdot}6H_2O$, 99.0%], copper(II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, 99.0%), tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$, 98.0%), magnesium(II) nitrate

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hexahydrate [$Mg(NO_3)_2{\cdot}6H_2O$, 99.0%], nickel(II) nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$, 98.0%], mercury(II) chloride ($HgCl_2$, 99.5%), oleic acid ($C_{18}H_{35}COOH$ or OA), sodium hydroxide (NaOH, 96.0%), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 98.0%), and sulfur (S, 99.0%) were obtained from Tianjin Fuchen Chemical Reagents Co., Ltd. Sodium oleate ($C_{18}H_{35}COONa$ or NaOA, technical grade) and oleylamine ($C_{18}H_{35}NH_2$ or OAm, C_{18}: 80–90%) were purchased from Aladdin reagents company. Hexane and absolute ethanol were analytical grade and purchased from Tianjin Zhiyuan Chemical Reagents Co., Ltd.

2.2. NCs synthesis

All NCs in this work were prepared by the MTS. Detailed information on the synthesis of inorganic NCs is given below.

2.2.1. Synthesis of metal oxide NCs

For Fe_2O_3 NCs, 1.0 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ (0.40 g) and 6.0 mmol of NaOA (1.83 g) were added the solution containing 10 mL of deionized water, 20 mL of absolute ethanol, and 30 mL of hexane. The resulting mixture was held at 70 °C for 30 min with stirring. Then, the two-phase mixture was transferred into a Teflon-lined microwave reactor (Milestone ETHOS microwave system). The system was heated to 180 °C in 5 min under microwave irradiation and kept for 20 min with stirring. After cooled down to room temperature, the Fe_2O_3 naocrystals in upper organic phase were collected by centrifugation and washed with absolute ethanol. The as-obtained samples can be easily redispersed into nonpolar solvents such as hexane, toluene, and chloroform.

For Fe_3O_4 NCs, the same procedure as for Fe_2O_3 except that $Fe(NO_3)_3{\cdot}9H_2O$ was replaced by $FeCl_2{\cdot}4H_2O$ (1.0 mmol, 0.20 g), $FeSO_4{\cdot}7H_2O$ (1.0 mmol, 0.28 g), or $Fe(NO_3)_3{\cdot}9H_2O$ (1.0 mmol, 0.40 g) and 1 mL of $N_2H_4{\cdot}H_2O$.

For Co_3O_4 NCs, 6.0 mmol of NaOH (0.24 g) and 2.0 mL of OA were dissolved in the solution containing 10 mL of deionized water, 20 mL of absolute ethanol, and 30 mL of hexane. Then, 1.0 mmol of $Co(NO_3)_2{\cdot}6H_2O$ (0.29 g) was added the above mixture. The follow procedure was similar to the synthesis of Fe_2O_3 NCs.

For CuO NCs, the same procedure as for Co_3O_4 except that 1.0 mmol of $CuSO_4{\cdot}5H_2O$ (0.25 g) was used.

For SnO NCs, 20.0 mmol of NaOH (0.80 g) and 20 mL of OA were dissolved in the solution containing 20 mL of deionized water, 10 mL of absolute ethanol, and 10 mL of hexane. Then, 8.0 mmol of $SnCl_2{\cdot}2H_2O$ (1.80 g) was added the above mixture. The follow procedure was similar to the synthesis of Fe_2O_3 NCs.

2.2.2. Synthesis of ferrite NCs

$CoFe_2O_4$ NCs were prepared by our versatile route. Typically, 9.0 mmol of NaOH (0.36 g) and 4 mL of OA were dissolved in the solution containing 10 mL of deionized water, 20 mL of absolute ethanol, and 30 mL of hexane. Then, 1.0 mmol of $Co(NO_3)_2{\cdot}6H_2O$ (0.29 g) and 2.0 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ (0.81 g) were added the above mixture. The follow procedure was similar to the synthesis of Fe_2O_3 NCs.

2.2.3. Synthesis of hydroxide NCs

For $Mg(OH)_2$ NCs, the same procedure as for Fe_2O_3 except that 1.0 mmol $Mg(NO_3)_2{\cdot}6H_2O$ (0.26 g) and 2.0 mmol of NaOA (0.61 g) were used and the system was heated 120 °C under microwave irradiation.

For $Ni(OH)_2$ NCs, the same procedure as for Fe_2O_3 except that 1.0 mmol of $Ni(NO_3)_2{\cdot}6H_2O$ (0.29 g) and 2.0 mmol of NaOA (0.61 g) were used. Using a similar method, $Ni(OH)_2$ NCs with different sizes and morphologies were prepared under different experimental conditions.

2.2.4. Synthesis of metal sulfide NCs

HgS NCs were prepared using a similar method. Typically, 1.0 mmol of $HgCl_2$ (0.27 g) and 2.0 mL of OAm were dissolved in the solution containing 10 mL of deionized water, 20 mL of absolute ethanol, and 30 mL of hexane. The resulting mixture was held at 70 °C for 30 min with stirring. Then, the two-phase mixture was transferred into a Teflon-lined microwave reactor containing sulfur powders (3.0 mmol, 0.10 g). The system was heated at 120 °C for 20 min with stirring. After cooled down to room temperature, the HgS naocrystals in upper organic phase were washed with absolute ethanol and dried at room temperature.

2.3. Characterization

The phase of the as-prepared samples was characterized by X-ray diffraction (XRD) using a DX-1000 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Transmission electron microscope (TEM) images of the products were obtained on a Hitachi H-600 transmission electron microscope with acceleration voltage of 100 kV.

3. Results and discussion

The synthesis was carried out by a combinative approach of phase-transfer and microwave-solvothermal. The overall synthetic procedure for inorganic NCs is depicted in Fig. 1. The first step in the process is the transport of the metal ions from the aqueous phase to the organic phase with the aid of ligands, such as NaOA or OAm. The resulted intermediate metal-oleate or metal-OAm

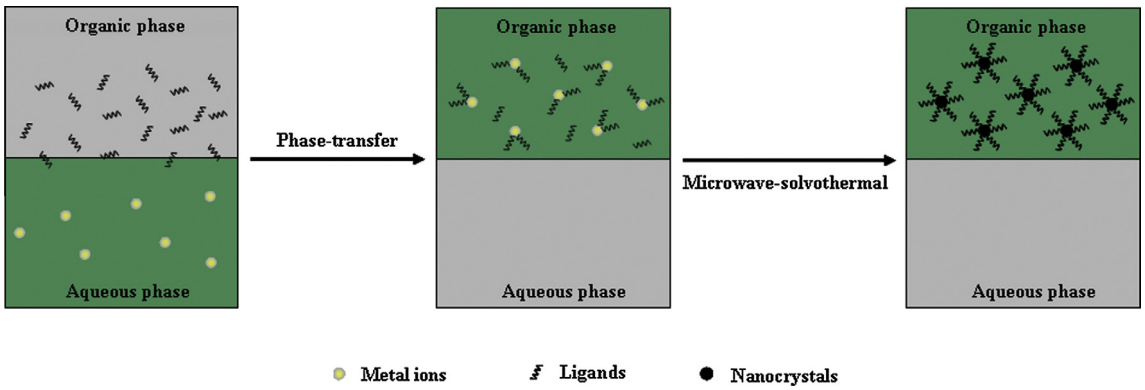

Fig. 1. The scheme of the MTS.