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Article

Simultaneous structure and luminescence property control of barium carbonate nanocrystals through small amount of lanthanide doping

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ABSTRACT

Rare earth doping has been widely applied in many functional nanomaterials with desirable properties and functions, which would have a significant effect on the growth process of the materials. However, the controlling strategy is limited into high concentration of lanthanide doping, which produces concentration quenching of the lanthanide ion luminescence with an increase in the Ln^{3+} concentration, resulting in lowering the fluorescence quantum yield of lanthanide ion. Herein, for the first time, we demonstrate simultaneous control of the structures and luminescence properties of BaCO_3 nanocrystals via a small amount of Tb^{3+} doping strategy. In fact, Tb^{3+} would partially occupy Ba^{2+} sites, resulting in the changes to the structures of the BaCO_3 nanocrystals, which is primarily determined by charge modulation, including the contributions from the surfaces of crystal nuclei and building blocks. These structurally modified nanocrystals exhibit tunable luminescence properties, thus emerging as potential candidates for photonic devices such as light-emitting diodes and color displays.

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1. Introduction

Lanthanide (Ln^{3+}) doped nanocrystals [1,2], as conventional functional materials, have excellent emission properties resulting from their unique intra 4f transitions [3], which enable their wide-spread application in optics, biolabels, color displays and light-emitting diode [4–8]. In general, the luminescence properties of Ln^{3+} doped nanocrystals could be affected not only by their composition but also by the morphology, dimension and size, thus necessitating the need to synthesize nanocrystals with the desired structures [9,10]. At present, the high concentration Ln^{3+} doping methods [11–13] were used for achieving greater control over the structures of the Ln^{3+} -doped nanocrystals. Nevertheless, the method produces concentration quenching of lanthanide ion luminescence with the increase of Ln^{3+} concentration, which lowers the fluorescence quantum yield of the lanthanide ion. Therefore, to avoid the concentration quenching of lanthanide ion luminescence, it is imperative to synthesize nanocrystals with various structures via a small amount of Ln^{3+} ion doping strategy with clear formation

mechanism, which is critical to expand the properties of these important materials.

The f-f transition of lanthanide ions has a small oscillator strength (10^{-6}) [14], leading to low excitation efficiencies. Therefore, Ln^{3+} ions require sensitization of the host materials, which can greatly affect the luminescence properties of Ln^{3+} ions. Many efforts have been undertaken to develop novel host materials [15–17] for the purpose of improving the optical performance, such as fluorides, phosphates and carbonates. Among these, carbonates, especially barium carbonates, have attracted tremendous attention as doping hosts because of their high solubility for lanthanide ions [18], which can suppress non-radiative loss and thus improve the luminescence properties of the doping ions. Trivalent lanthanide ions substituting for divalent alkaline earth ions can bring the changes in the surface charge density of the host materials through charge modulation [12,13], which requires the extra counter anions to establish charge balance or charge compensation, thus inducing a transient electric dipole with the negative pole pointing outward. The negative pole should be remarkably enlarged by the introduction of more negative charges, which can provide the possibility that small amount of lanthanide doping can efficiently affect the growth process of the host materials because of the repulsive force of charge.

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Herein, for the first time, we demonstrate a facile and feasible route to control the structures of barium carbonate with tunable luminescence properties via a small amount of Tb³⁺ doping. First, dumbbell-like BaCO₃ nanocrystals assembled by nanowires were synthesized through a series of time-dependent hydrothermal processes, with urea and citrate as the carbonate source and chelating agent, respectively. The obtained nanocrystals produced tunable luminescence emissions, thus emerging as promising host candidates for lanthanide ion doping. A small amount of Tb³⁺ ions was selected to add into the system to form BaCO₃:x% Tb nanocrystals with totally different shape and size compared with pure BaCO₃, which may result from the strong effects of Tb³⁺ doping on the crystal growth rates via charge modulation. Tb³⁺, which mainly occupied the Ba²⁺ sites in the BaCO₃ host lattice, showed four characteristic emission peaks at 491, 546, 586 and 622 nm because of efficient energy transfer from the BaCO₃ lattice with the optimum concentrations of 3 mol% Tb³⁺. The synthesis strategy should give a useful enlightenment for controlling the structures and luminescence properties of nanocrystals through a small amount of lanthanide ion doping, which can facilitate the development of novel optical materials for photonic devices.

2. Experimental

2.1. Materials synthesis

Barium chloride, sodium citrate, urea and Tb(NO₃)₃·xH₂O were purchased from Alfa Aesar and used without further purification. In a typical experiment, 5 mL of barium chloride (0.3 mol/L) aqueous solution was added to 5 mL of aqueous solution containing 0.6 M of sodium citrate. The resulting solution, turning turbid because of the formation of barium citrate complexes, was kept under vigorous stirring for 30 min. Then, 5 mL urea aqueous solution (1.2 mol/L) was added. After stirring for another 40 min, the solution was transferred into a 20 mL sealed Teflon autoclave, which was heated at 200 °C for different time in an electric oven. After cooling the autoclave to room temperature, the precipitate was separated by three centrifuge-wash cycles, and dried overnight under air at 80 °C. Tb³⁺-doped BaCO₃ samples were obtained under the same conditions by adding a fraction of Tb(NO₃)₃ to the barium chloride solution with designed molar ratios.

2.2. Characterization

The BaCO₃:x% Tb nanocrystals were characterized with SEM (Hitachi S-4800) and XRD (Philips X'pert PRO), respectively. The luminescence emission spectra were measured with fluorescent spectroscopy (HITACHI F-4500). The luminescence decay curves were obtained from fluorescence lifetime spectrometer (Edinburgh-FLSP920 and HAMAMATSU C11367). The photoluminescence microscopy images were recorded using a photoluminescence microscope after exciting the samples with the blue band (400–450 nm) of the mercury lamp. All spectroscopic measurements were implemented at room temperature.

3. Results and discussion

Barium carbonate nanocrystals were synthesized via a facile hydrothermal procedure. During the synthesis process, Ba²⁺ ions and CO₃²⁻ ions can participate in a typical preparation to afford BaCO₃ nanocrystals with CO(NH₂)₂ as the carbonate resource and Na₃Cit as the strong chelating agent. In order to investigate the structural evolution of the nanocrystals, a series of time-dependent hydrothermal processes were carried out. When reaction time was 15 min, we obtained the nanowires-shaped struc-

tures with lengths up to 10–20 μm and diameters of 200–300 nm as shown in Fig. 1a. Along with the reaction time was increased to 2 h, the nanowires were converted into uniform slender dumbbell-like structures with a length of 12 μm, a fantail diameter of about 3 μm and a middle diameter of about 2 μm (Fig. 1b). The high magnification SEM image (inset of Fig. 1b) shows that the slender dumbbell-like structure is assembled by numerous nanowires. With a further increase in the reaction time, the dumbbell-like shape of the nanocrystals remains not to be a significant change, but the length increases from 12 to 25 μm, the middle diameter from 2 to 4 μm and the fantail diameter from 3–10 μm for reaction time at 2–12 h (Fig. 1b–d).

The XRD analysis was carried out to investigate the crystal structures from nanowires to dumbbell-like nanocrystals, which indicates that all nanocrystals are indexed as the orthorhombic phase of BaCO₃ nanocrystals (JCPDS No. 71-2394) (Fig. 1e). No extra diffraction peaks emerged, indicating that pure BaCO₃ nanocrystals were obtained. Under 340 nm excitation, the emission spectra of BaCO₃ with different reaction times were measured for studying the luminescence properties. The emission spectra showed the blue emissions due to energy band-gap engineering [19] ranging from 400 to 650 nm with maximum point at 405 and 429 nm, in which the nanocrystals at the reaction time of 12 h exhibit excellent blue luminescence emissions (Fig. 1f). Therefore, the following experimental reaction time for subsequent experiments was fixed at 12 h.

As we know, BaCO₃ nanocrystals [20,21], as important optoelectronic materials, might be promising host candidates for lanthanide ion doping based on the blue luminescence emission. The crystal structure of BaCO₃ is subordinate to the orthorhombic phase and *Pmcn* space group (Fig. 2a), with the Ba²⁺ sites selectively occupied by Ln³⁺ ions, resulting in significant charge modulation to accommodate the structural change [13]. The divalent Ba²⁺ ions are occupied by trivalent Ln³⁺ sites in the lattice, which can produce a transient electric dipole with negative pole pointing outward [13] that slow the diffusions of CO₃²⁻ from the solution to the crystals. Here, Tb³⁺ ions were selected as doping ions to modify the shape and size of BaCO₃ nanocrystals. In order to avoid the concentration quenching of Tb³⁺, BaCO₃:x% Tb nanocrystals were obtained via doping Tb³⁺ ions at small amount of concentrations (1 mol%–5 mol%).

When 1 mol% Tb³⁺ ions were added into the system, the peanut-like barium carbonate nanocrystals were formed with a length of 22 μm and width of 12 μm (Fig. 2b), where the morphology of BaCO₃:1% Tb is totally different from that of the dumbbell-like BaCO₃, indicating doping 1 mol% Tb³⁺ can obviously modify the shape of BaCO₃ nanocrystals (Fig. 1d). With an increase in the Tb³⁺ concentration to 3 mol%, it is striking that the nanocrystals are converted into sunflower-plate-like structures with the diameters decreasing into 7 μm (Fig. 2c). When the concentration of Tb³⁺ was further increased to 5 mol%, the resultant products were flower-shaped structures with the diameter of 4 μm (Fig. 2d). Insets of Fig. 2b–d reveal that these nanocrystals are assembled by the nanomaterials building blocks, such as nanowires and sheets. All the diffraction peaks were found to be in good agreement with the reported in JCPDS No. 71-2394, suggesting that the pure orthorhombic phase of BaCO₃:x% Tb nanocrystals was obtained (Fig. S1 online). The doped Tb³⁺ ions do not cause any significant crystal phase changes in the host materials, although even a small amount of Tb³⁺ doping directly affects the final shape and size of the nanocrystals.

On the basis of the above observations, the possible effect of a small amount of Tb³⁺ doping on the shape and size of the BaCO₃:x% Tb nanocrystals is schematically illustrated in Fig. 3. First, sodium citrate could react with Ba²⁺ ions to form citrate complexes [22], which greatly decreases the free Ba²⁺ ions concentration. The

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