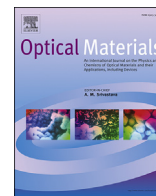




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Rapid microwave synthesis and photoluminescence properties of rare earth-based coordination polymer core-shell particles

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ABSTRACT

Coordination polymer (CP) core-shell particles, with Eu-based CP as the core and La-based CP as the shell, were prepared using a facile microwave heating method. Pyridine-2, 5-dicarboxylic acid (PDA) was selected as the organic building blo, and DMF was used as the solvent. SEM and TEM images show that the resultant cores are nanospheres with diameters of 200–400 nm. Products with different shell thickness were prepared. The luminescence properties of the core-shell structures were studied and the influence of the La-based CP shell on the photoluminescence properties of the core were investigated. The fluorescence intensity and lifetime of the Eu-based CP core were varied with the addition of shell thickness. Both of them increases at first and then decreases with the increase of shell thickness.

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1. Introduction

There has been a growing interest in core-shell structured micro/nano particles due to their enhanced electrical, magnetic, optical, and catalytic properties [1–5]. Sometimes, the properties of these particles can be obviously different from either the core or the shell materials. Furthermore, by varying the ratios of the constituting materials of the core and the shell, the properties of the particles can be tuned [6]. Core-shell structures usually can be divided into the following groups: inorganic/organic, inorganic/inorganic, organic/organic and organic/inorganic [1]. Many core-shell structures with different compositions and properties have been prepared, and several potential applications have been explored. However, majority of the studies have been limited to either inorganic/organic or inorganic/inorganic core/shell particles [1].

CP or metal–organic framework (MOF) is a very important class of inorganic-organic hybrid compounds, and has been used in diverse fields [7–10]. In the past decade, there has been a intensive interest in the preparation of CP micro/nanoparticles [11–14], and

our group has also devoted some effort on it [15,16]. Some core/shell structures with CP as the shell have been recently prepared. For example, CP-coated mesoporous silica nanoparticles were fabricated and used for pH-responsive drug delivery [17]. Sugikawa et al. prepared Au nanorod with CP crystalline shell and used it as suspension-based SERS sensor [18]. However, very limited successful example of CP-on-CP core-shell particles were found in the literature. For instance, heterocompositional hybrid CP particles were obtained by precise manipulation of the isotropic and/or anisotropic nanoscale growth of various CPs [19]. Core-shell MOF particles comprising of a porous bio-MOF-11/14 mixed core and less porous bio-MOF-14 were prepared, and the effect of the shell on the N₂ and CO₂ adsorption behavior was demonstrated [20]. MOF@MOF core-shell particles can be produced by a seeded growth technique [21]. Rare earth-based CP nanostructures are widely used as luminescent materials, catalysts, magnets, fuel cells, UV shielding and other functional materials, owing to their unique optical, electronic and magnetic properties. Meanwhile, their optical properties of the luminescence materials, such as luminescent intensity, fluorescence lifetime and so on, can be changed through coating layer, size, thickness or composition of core-shell structure, which was a synergistic effect of the multi-components materials [22]. To the best of our knowledge, preparation of rare earth CP-on-CP core-shell particles has not been reported.

Core-shell particles can be fabricated by several methods. The

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representative and typical chemical synthesis methods can be divided into five main categories: solution method, sonochemical method, hydrothermal method, ethylene glycol-assisted method, and sol-gel method [3]. Microwave-assisted reaction has demonstrated powerful benefits by greatly reducing the experimental time and potential for large-scale industrial production [23]. Our group has successfully prepared water-soluble YF_3 and $\text{YF}_3:\text{Ln}^{3+}$ nanocrystals by microwave-assisted synthesis [24]. Some core-shell particles have been prepared by microwave heating route [25,26]. However, preparation of CP-on-CP core-shell particles by microwave heating method has not been reported. In this study, core-shell structured particles, with Eu-based CP as the core and La-based CP as the shell, have been fabricated using a facile template-free microwave method. The photoluminescence properties of the core/shell particles were also measured and investigated.

2. Experimental

2.1. Preparation of the core/shell particles

In a typical experiment (sample 1), the Eu-based CP core was prepared as follows (see Scheme 1): 8 mL N, N-dimethylformamide (DMF) solution containing 0.05 mmol $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 8 mL DMF solution containing 0.05 mmol pyridine-2, 5-dicarboxylic acid (PDA) were added into a 100 mL round bottom flask. The mixture was stirred for 20 min at room temperature, and then heated in a microwave oven for 15 min in a refluxing apparatus at 150 W and 2450 MHz. After that, 8 mL DMF solution containing 0.05 mmol $\text{La}(\text{NO}_3)_3$ and 8 mL DMF solution containing 0.05 mmol PDA were poured into the same flask immediately when the reaction mixture was still hot. After stirring, the reaction mixture was placed under microwave irradiation for another 15 min at 150 W and 2450 MHz. Subsequently, the precipitate was cooled to room temperature, washed several times with ethanol, and dried at 60 °C in vacuum for 6 h. Core/shell particles with different shell thickness were prepared by similar procedure (Table 1), just by varying the amount of $\text{La}(\text{NO}_3)_3$ and PDA in the second stage.

2.2. Characterization

SEM and energy dispersive X-ray (EDX) analysis were performed with a field-emission scanning electron microscope (JEOL JSM-6700F, 15 kV), equipped with an EDX detector. TEM was

Table 1

Samples and corresponding experiment parameters.

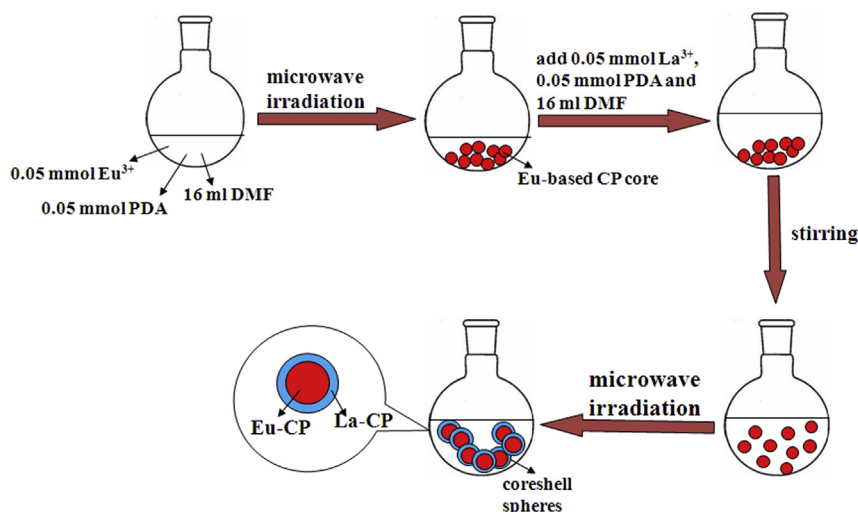
No.	Reaction Time (min)	$n(\text{La}^{3+})$ (mmol)	$n(\text{BTTA})$ (mmol)
0	0	0	0
1	15	0.05	0.05
2	15	0.1	0.1
3	15	0.15	0.15
4	15	0.2	0.2
5	15	0.25	0.25
6	15	0.3	0.3

performed with a Hitachi (Tokyo, Japan) H-800 transmission electron microscope at an accelerating voltage of 200 kV. XRD patterns were performed on a Rigaku X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Infrared (IR) spectra were taken on a Perkin-Elmer SP one FT-IR spectrometer in a KBr pellet, which was scanned from 4000 to 400 cm^{-1} at room temperature. The TG and DTG curves were performed on a Diamond TG/DTA simultaneous thermal analyzer. Elemental analysis was performed with a Euro-Vector EA3000 elemental analyzer, and inductive coupled plasma (ICP) atomic emission spectrometric analysis (POEMS, TJA). The photoluminescence (PL) spectra were recorded on an FLS-980 (Edinburgh Instruments, England) at room temperature.

3. Results and discussion

SEM and TEM images of the core (sample 0) and the core-shell products (sample 1) were shown in Fig. 1. Fig. 1a showed that the core was composed of uniform microspheres, with diameters ranging from 200 to 400 nm. Enlarged image (Fig. 1b) showed that the surface of the core was rough, with some cracked holes. According to the SEM images in Fig. 1d and e, the mean diameter of the core-shell particles was about 550 nm, much larger than that of the core. TEM images confirmed the SEM results (Fig. 1c and f). Careful observation showed a crudely-formed yolk-shell particle (white arrow in Fig. 1e), which further confirmed that core-shell particles could be formed in our experiment.

XRD, IR, TG-DTA, EDX and element analysis were used to determine the structure and composition of sample 1. XRD results showed that the product was not well crystallized, and the exact composition could not be indexed to any known compounds in the JCPDS reference database (Fig. 2a). Many CPs at nanoscale were found to be amorphous, indicating that the RE^{3+} in the products



Scheme 1. Schematic illustration of the preparation of the core-shell particles.

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