

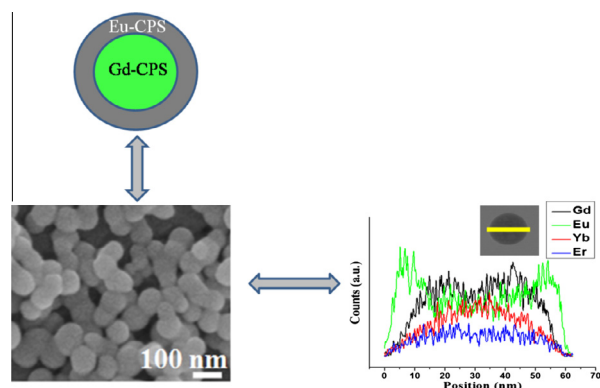
Regular Article

Coordination polymer core/shell structures: Preparation and up/down-conversion luminescence

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GRAPHICAL ABSTRACT

Coordination polymer (CP) core-shell nanoparticles with Gd-based CP (GdCP) as core and Eu-based CP (EuCP) as shell have been prepared and exhibited strong NIR-to-NIR upconversion emission and characteristic down-conversion emission.



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ABSTRACT

Coordination polymer (CP) core-shell nanoparticles with Gd-based CP (GdCP) as core and Eu-based CP (EuCP) as shell have been successfully prepared. Allantoin was employed as the organic building block without the assistance of any template. The composition, size and structure of the core-shell nanospheres were well characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX), powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TG). Results show that the resultant cores are uniform nanospheres with diameter of approximately 45 nm, while the diameters of the core-shell nanospheres are increased to approximately 60 nm. The core-shell products show enhanced luminescence efficiency than the core under 980 nm laser excitation and decreased down-conversion luminescence when excited at 394 nm.

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1. Introduction

Coordination polymers (CPs), including metal-organic framework (MOFs) made of metal nodes and organic building blocks are valuable materials due to their unique properties and

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the resulting useful applications ranging from catalysis, gas storage, separation, to optics [1–5]. The manipulation of organic building blocks and metal ions is a vital approach to adjust their properties [6]. Lanthanides are widely used in the construction of CPs because most trivalent lanthanide ions can show characteristic coordination preferences, exceptional magnetic properties and unique optical properties arising from $4f^n$ electronic configuration and transitions [7,8]. The lanthanide coordination polymers (LnCPs) with fascinating architectures and potential applications mainly focused on luminescence sensors, magnets, catalysis, and materials science [9,10]. As an important part of CPs, a wide scope of LnCPs have been prepared and their extensive applications have been widely investigated [11,12]. Recently, interests have been diverted to nanoscale CPs with the intriguing prospect to obtain defined morphologies and properties [13]. Compared with bulk CPs, nanoscale CPs exhibit new possible applications in the field of drug delivery, ion exchange, multimodal bioimaging, and so on [14–16].

Lanthanide doped upconversion CPs have attracted widespread attention due to their superior functional properties as well as technological application [17,18]. Most of the previously reported in the literature that upconversion luminescence show strong visible emission, mainly from blue (470 nm), green (551 nm) to red (660 nm), and there are few reports on emitting NIR fluorescence emission such as 832 nm [19]. Large numbers of the nanoparticles show NIR (980 nm)-to-visible (blue, green, red) upconversion photoluminescent, which limits their capability of *in vivo* imaging due to the high scattering of visible light and low penetration depth in biological tissues [20,21]. Therefore, considering the bioimaging applications of upconversion nanoparticles (UCNPs), the NIR-to-NIR upconversion luminescent are preferable for both the excitation and emission wavelengths in the region of NIR, not only shows deep penetration *in vivo* applications but also low autofluorescence background noise [22–24].

Currently, the core/shell particles stimulates tremendous interest owing to a variety of the collective functionalities of the core and the shell as well as their various potentialities in many application fields such as targeted drug delivery, multimodal bioimaging, photodynamic therapy and toxin decorporation [25–27]. CP nanomaterials have extended the scope of the utilizations through core-shell engineering [28]. The CP-on-CP Core-shell nanostructures provide a convenient platform for integrating multiple functionalities into single nanoparticles. The current synthetic method can be extended to the selected-control preparation of various CP core/shell nanostructures that show different compositions, size and shape with tunable fluorescence properties [29]. Herein, we report a facile template-free synthetic strategy to prepare nanoscale lanthanide-based CP core-shell nanospheres with Yb^{3+} , Er^{3+} doped Gd-CP as core and Eu-CP as shell. Interestingly, these core/shell structures exhibited up/down-conversion luminescence and showed excellent NIR-to-NIR upconversion emission.

2. Experimental section

2.1. Synthesis of the GdCP: Yb^{3+} , Er^{3+} core

In this paper, erbium and ytterbium-codoped gadolinium CP nanospheres have been prepared by a facile hydrothermal method. In a typical experiment, 0.3 mmol allantoin was added into a 50 mL Teflon-lined stainless steel autoclave. After that, 0.4 mL 0.2 M Gd (NO_3)₃ aqueous solution, 0.75 mL 0.02 M aqueous solution of Yb (NO_3)₃ and 0.25 mL 0.02 M Er (NO_3)₃ aqueous solution were added to the above Teflon-lined stainless steel autoclave. Then, 25 mL distilled water was added to the above solution under vigorous magnetic stirring at room temperature and the stirring was

continued for 20 min. The autoclave was sealed and heated at 160 for 2 h. The products were centrifuged and washed with distilled water three times.

2.2. Preparation of the GdCP: Yb^{3+} , Er^{3+} @ EuCP core/shell particles

The GdCP: Yb^{3+} , Er^{3+} @ EuCP were synthesized by a solvothermal method. In a typical process, 0.3 mmol allantoin and 3 mL hot distilled water were added into a 50 mL Teflon-lined stainless steel autoclave under strong magnetic stirring. After that, 0.5 mL 0.2 M Eu (NO_3)₃ aqueous solution and the above-made GdCP: Yb^{3+} , Er^{3+} nanospheres were added to the above solution. Then, 25 mL of dimethyl formamide (DMF) was added to the above solution. After 20 min stirring, the autoclave was sealed and heated at 160 °C for 2 h, the products were centrifuged and washed with distilled water three times before drying at 60 for 8 h.

2.3. Characterization

SEM images were obtained using a JEOL JSM-6330F instrument. TEM images and EDX analysis were performed with JEM-2100F (Tokyo, Japan) microscope at an accelerating voltage of 200 kV and equipped with ZrO/W(1 0 0) Schottky electron emitter. PXRD patterns were performed on a Rigaku X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). TG analysis was obtained with a TA-50 thermal analyzer. IR spectra were recorded on a Perkin-Elmer SP one FT-IR spectrometer in a KBr pellet, which was ranged from 4000 to 400 cm^{-1} at room temperature. The photoluminescence (PL) excitation, emission spectra were recorded on an FLS-980 (Edinburgh Instruments, England) at room temperature and upconversion emission spectra were carried out under 980 nm excitation light.

3. Results and discussion

3.1. Morphology, size and structure of the typical product

SEM images of the as-prepared core and the core/shell nanospheres are shown in Fig. 1. The SEM images (Fig. 1c) demonstrates that the core is composed of uniform nanosphere with average size of 45 nm. Fig. 1b revealed that the mean size of core-shell particles was increased to about 60 nm, which was larger than that of the core. The TEM images (Fig. 2) are in accordance with the SEM images. In addition, the EDX spectrum profile-scanning data of GdCP and GdCP@EuCP (Fig. 3a and b) confirmed their formation of core-shell structures. According to the Fig. 3b (right), it can be clearly observed that europium atoms were dominant at the edge of the nanosphere, and gadolinium atoms were abundant at the center of the nanoparticles, which was a typical tendency of the CP core/shell structures [26,30]. From the Fig. 3a and b, it clearly demonstrated the thicknesses of the EuCP layers were about 7.5 nm, which was accordance with the SEM observation and indicating that the core/shell nanospheres had been prepared successfully.

Powder X-ray diffraction (PXRD) of the core/shell nanospheres (Fig. 4) clearly revealed that they are amorphous and not crystalline. The FT-IR spectra of the core/shell nanospheres (Fig. 5) showed that the organic building blocks of allantoin were coordinated to metal ions. The broad band at 3438 cm^{-1} is assigned to water molecules. The peak at 1660 cm^{-1} is corresponding to C=O stretching vibration and the peak at 1511 cm^{-1} can be attributed to amide bend vibration [31]. Additionally, the absorption peaks at 1404 cm^{-1} and 1087 cm^{-1} are associated with C–N stretching vibration and N–H swing vibration [32]. TG curves of the core-shell nanospheres show that the thermal decomposition of this product is a

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