Research Article

Lanthanide Coordination Polymer Nanosheet Aggregates: Solvothermal Synthesis and Downconversion Luminescence

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A lanthanide coordination polymers (CPs) nanostructure (**1**) has been synthesized via a facile template-free solvothermal strategy using DMF as solvent and 2-methyl benzoic acid (2-MeBAH) as ligands. The products are characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), elemental analyses (EA), and downward luminescence. Product **1** built from Tb³⁺ and 2-MeBAH has one-dimensional structure which is connected by trinuclear second building units (SBUs). Downward luminescence shows that sample **1** exhibits characteristic transitions of the Tb³⁺ ion at 489, 544, 583, and 621 nm, and the strongest peak is at 544 nm ascribed to the transition of ⁵D₄ → ⁷F₅ of Tb³⁺.

1. Introduction

Lanthanide coordination polymer (CP) is an important class of organic-inorganic hybrid materials formed by the coordination of lanthanide ions with organic linkers. They have shown a number of promising applications; these applications are ascribed to the best properties of organic and inorganic components and decrease their drawbacks by a synergic effect [1]. In order to get functional lanthanide materials, appropriate synthetic strategies are critical [2, 3]. Compared with first-row transition metal ions, lanthanide ions usually display high coordination number and variable coordination geometries, and they will make lanthanide ions become excellent spacers in assembling fascinating coordination polymers [4]. As a subset of such materials, lanthanide CPs continue to attract an escalating attention, owing to their unique optical, electronic, and magnetic properties [5–7]. In addition, nanosheet materials have been of continuous research interests in material science, because of their unique properties in the areas of catalysis, drug delivery, and biosensors. Herein, our group has successfully prepared terbium-based CP nanosheet aggregates, with downward green-light emission while excited by violet light.

In modern chemistry and materials science, synthesis of uniform nanosheet materials with controllable size and well-defined morphologies remains a research focus due to their superior properties of large specific area, low effective density, and good permeation [8]. Thereby, hollow spherical materials constructed by the nanosheet possess widespread potential applications in various fields, including catalysts, adsorbents, photonic devices, sensors, drug-delivery carriers, disease diagnosis agents, waste removal, and chemical reactors [9]. In recent years, a variety of synthetic routes have been developed for the preparation of hollow spheres [10, 11] such as solvothermal method, hydrothermal method, precipitation method, spray pyrolysis method, and template-assisted method. Generally, the solvothermal method is used widely, because the solvent controlling effect is versatile.

As well known, lanthanide coordination polymers have been widely applied in luminescent devices [12, 13]. However, compared with other morphologies of sphere, nanorod, and nanotube, the nanosheet of rare earth coordination polymers which are constructed into aggregates of hollow spheres morphologies has received much attention. Apart from possessing a collection of advantages, such as low weight and saving materials and costs, hollow sphere optical materials

FIGURE 1: SEM images of sample 1.

also display better luminescent properties than other solid materials.

So far, there have been many researches of organic hollow sphere structures fabrication reported. However, there have been few inorganic nanostructures constructed by the nanosheet [8]. In this paper, we report a general one-pot low-cost solvothermal method for preparation of Tb^{3+} -based CP nanosheet and construction into aggregates of hollow microspheres (**1**), using Tb^{3+} as metal center and 2-methyl benzoic acid (2-MeBAH) as ligand. The formation of nanosheet and spherical hollow structures is unusual since no templates or surfactant is intentionally used during the synthetic process. The downward luminescence of **1** was investigated in detail.

2. Experimental Section

Tb_4O_7 was bought from Ganzhou Keminrui Rare Earth Company (Ganzhou, China). 2-MeBAH was purchased from Aladdin Company (Shanghai, China) and used as received. $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving Tb_4O_7 (99.9%) with concentrated HCl_3 and then evaporated at 100°C until the crystal film formed. Other reagents were from Guangzhou Chemical Reagent Factory (AR, Guangzhou, China) and used without further purification.

In a typical process, Tb^{3+} -based CP nanosheet and its aggregates of hollow microspheres were prepared as follows: an aqueous solution of 2-MeBAH (0.1 g in 25 mL) was added with a 0.1 M NaOH solution to adjust the ligand solution at $\text{pH} = 6$, in a stoichiometric amount to yield the sodium salt in situ. The resulting solution was added dropwise to a 10 mL 0.1 g TbCl_3 DMF solution (100°C). All the ligand solution was added to the salt solution in an hour and resulted in a white precipitate. The solid was separated by centrifugation, then washed with water and ethanol, and dried in vacuum desiccator for several days.

Powder X-ray diffraction (PXRD) was carried out using a Rigaku X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) was performed on a Hitachi S-3400. Elemental analysis (EA, C and H) was performed on an EA3000 elemental analyzer. Downconversion luminescence spectrum was recorded on an FLS 980 (Edinburgh Instruments, UK) at room temperature.

3. Results and Discussion

SEM was utilized to characterize the morphology and structure of as-prepared samples. As presented in Figure 1(a), it can be seen that sample **1** consists of well aggregated

FIGURE 2: PXRD of simulated and bulk sample **1**. FIGURE 3: The 1D structure of **1** constructed by trinuclear SBUs.

nanosheet, and the aggregated nanosheet forms uniform ball-like structure (Figure 1(b)). Enlargement of the ball-like structure shows that the aggregate units of nanosheets are uniform, with a smooth surface and a narrow size distribution in 50–70 nm (Figure 1(c)).

PXRD of bulk sample **1** in Figure 2 shows evident diffraction peaks, which means that **1** is a crystalline material. Further investigation found that the diffraction peaks compete well with the data (CCDC: 634372) reported by Busskamp et al. [14]. The reported result is a lanthanum complex, and in our result, **1** may be a terbium complex; this indicates that **1** is isostructural to the reported data [14]. Thus, it can be deduced that nanomaterial **1** has the chemical formula of $\text{Tb}_3(2\text{-MeBAH})_9(\text{DMF})_3$. It has one-dimensional polymer structure (Figure 3), and the one-dimensional structure is connected by the trinuclear second building unit (SBU, Figure 4); the 1D structure is connected by hydrogen bond and van der Waals (VDW) forth to form 3D structure.

FIGURE 4: The SBU structure of material **1**.

The elemental analysis of **1** reveals that C is 51.17% and H is 4.151%, which is consistent with the calculated results

FIGURE 5: The SEM of different weight ratio of Tb^{3+} to ligand: (a) $\text{Tb}^{3+}/\text{ligand} = 1:3$; (b) $\text{Tb}^{3+}/\text{ligand} = 3:1$.

FIGURE 6: Downconversion luminescence spectrum of **1**.

well (C, 50.94; H, 4.220). This further confirms that bulk nanomaterial really has structure as depicted in Figures 3 and 4 and has the molecular formula of $\text{Tb}_3(2\text{-MeBAH})_9(\text{DMF})_3$.

In order to reveal the factors influencing the formation and morphology of the hollow spheres of **1**, controlled experiments were carefully performed [15]. As shown by the SEM images in Figure 5, when the weight ratio of Tb^{3+} to ligand is 1:3, it is found that almost all the products are microrods, and when the weight ratio is 3:1, the product is ruleless ball-like structure.

Due to the unique properties of rare earth elements, the downward luminescent property of sample **1** was determined at the excitation wavelength of 320 nm under ambient temperature. Sample **1** exhibits characteristic transitions of the Tb^{3+} ion at 489, 544, 583, and 621 nm, corresponding to the transitions of $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$, respectively (Figure 6) [16–19]. The strongest peak is ascribed to the transition of $^5\text{D}_4 \rightarrow ^7\text{F}_5$ [4, 20–22]. The ligand is at the excited $^1\pi\pi^*$ state after the simultaneous absorption of one photon and then transfers to the excited $^3\pi\pi^*$ state through intersystem crossing (ISC), after that, the

energy transfer (ET) to $^5\text{D}_4$ state of Tb^{3+} , and luminescence is generated by the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3) transitions.

4. Conclusions

Lanthanide CPs nanosheet aggregates have been synthesized via a facile template-free solvothermal strategy using DMF as a solvent and 2-MeBAH as ligand. The products were characterized by PXRD, SEM, EA, and downward luminescence. The downward luminescence of product **1** built from Tb^{3+} and 2-MeBAH has one-dimensional structure connected by trinuclear SBU. Downward luminescence shows that sample **1** exhibits characteristic transitions of $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$ and 3) for Tb^{3+} at 489, 544, 583, and 621 nm, respectively, and the strongest peak is at 544 nm ascribed to the transition of $^5\text{D}_4 \rightarrow ^7\text{F}_5$.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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