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# Novel 3D flower-like $TiO_2:Eu^{3+}$ hierarchitectures: Hydrothermal synthesis and luminescent properties

Hongguang Zhang [a], Ye Sheng [a], Xiuqing Zhou [a], Yanhua Song [a], Zhan Shi [b], Xuechun Xu [c], Haifeng Zou [a,*]

[a] College of Chemistry, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China
[c] College of Earth Science, Jilin University, Changchun 130012, PR China

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ABSTRACT

Self-assembled 3D flower-like $TiO_2:Eu^{3+}$ microspheres have been synthesized by a simple hydrothermal method and crystallized by subsequent heat treatments at elevated temperatures. The as-prepared samples are loose and porous with flower-like structure, and the subunits are irregularly shaped nanosheets. A possible growth mechanism is proposed for the 3D flower-like $TiO_2:Eu^{3+}$ microspheres, and it was found that the synergistic effect of citric acid ($H_3Cit$), ethanediamine (En) and hydrofluoric acid (HF) is of crucial importance for the controllable fabrication of $TiO_2:Eu^{3+}$ flower-like hierarchical structures. Furthermore, the calcined flower-like $TiO_2:Eu^{3+}$ hierarchical microspheres exhibit excellent red emission corresponding to the $^5D_0$–$^7F_2$ transition of the $Eu^{3+}$ ions under UV light excitation.



## 1. Introduction

Over the past decades, three-dimensional (3D) hierarchical architectures have attracted considerable attention due to their unique properties resulting from the nanobuilding blocks and their potential applications in photoelectric devices [1], catalysts [2,3], lithium-ion batteries [4] and sensors [5,6]. The simplest synthetic route to 3D architectures is probably self-assembly, in which ordered aggregates are formed in a spontaneous process [7]. Thus, many recent efforts have been focused on the hierarchical assembly of 1D and 2D nanoscale building blocks, such as nanowires [8], nanorods [9], and nanosheets [10], into ordered complex hierarchical architectures, which are expected to have novel collective optical, magnetic, and electronic properties. Currently, numerous methods, such as the low-temperature aqueous solution route [11,12], precipitation process [13], sonochemical method [14], and hydrothermal technology [15–17], have been developed to fabricate various hierarchical superstructures. Among them, the hydrothermal method shows special advantages for the synthesis of a variety of hierarchical architectures owing to the mild synthesis conditions, potential for scale-up, economic factors, simplicity, and ease of operation.

Recently, much research attention has been paid to the field of rare earth doped luminescent materials since they have many potential applications in optical telecommunication, lasers, biochemical probes, and medical diagnostics based on the electronic, optical, and chemical characteristics arising from the 4f electrons [18]. Among variety of rare earth doped matrix materials, $TiO_2$ is suggested to be a promising host lattice for the luminescence of various optically active lanthanide ions because of its low cost, high transparency in the visible-light region, and good thermal, chemical, and mechanical properties [19]. To date, many rare earth doped $TiO_2$ with various morphologies have been synthesized via a hydrothermal route. For example, Jianbao Li et al. have prepared $Eu^{3+}$ doped $TiO_2$ nanotubes via a hydrothermal method [20]. Z.V. Saponjic and co-workers have reported the fabrication of $Eu^{3+}$ doped $TiO_2$ nanocrystals and prolate nanospheroids by the hydrothermal processing [21]. The $TiO_2:Eu^{3+}$ submicrospheres have been prepared by our group through a simple hydrothermal method [22]. However, to the best of our knowledge, few studies have been reported on the synthesis and the luminescence properties of the 3D $TiO_2:Eu^{3+}$ hierarchical architectures. Therefore, it is strongly desirable to develop a general and simple method for fabricating the 3D $TiO_2:Eu^{3+}$ hierarchical architectures.

Here, we present a simple hydrothermal route for the synthesis of the 3D flower-like $TiO_2:Eu^{3+}$ microstructures in high yield. The morphologies of the $TiO_2:Eu^{3+}$ hierarchical architectures can be controlled by adding the $H_3Cit$, En and HF. In addition, the formation process and luminescence properties of the 3D flower-like $TiO_2:Eu^{3+}$ microstructures have been investigated in detail.

## 2. Experimental section

### 2.1. Materials

$Eu(NO_3)_3$ aqueous solution was obtained by dissolving $Eu_2O_3$ (99.99%) in dilute $HNO_3$ solution under heating with ceaseless agitation.

* Corresponding author. Tel./fax: +86 431 85155275.
*E-mail address:* zouhf@jlu.edu.cn (H. Zou).

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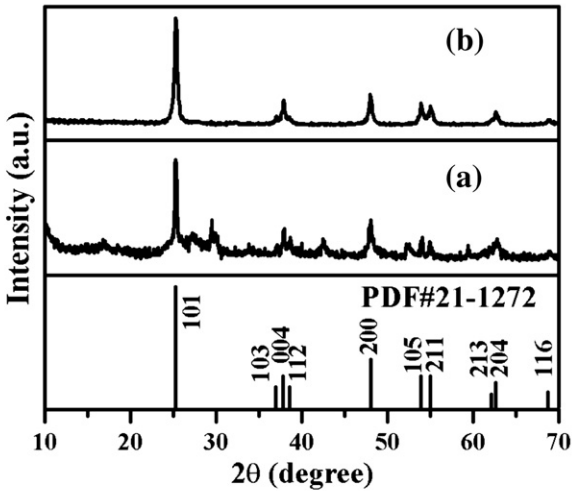


**Fig. 1.** XRD patterns of the samples (a) before calcination and (b) after calcination.

All other chemicals were analytical-grade reagents and used as received without further purification. Deionized water was used for all treatment processes.

### *2.2. Synthesis of the 3D $TiO_2$:$Eu^{3+}$ microspheres*

Monodisperse 3D $TiO_2$:$Eu^{3+}$ microspheres were synthesized by a facile hydrothermal method. Firstly, 1 mmol of $Ti(SO_4)_2$ was dissolved into 12.8 mL of deionized water. Then, 3 mmol of $H_3Cit$ ($C_6H_8O_7 \cdot H_2O$), 8 ml of ethanediamine ($C_2H_8N_2$), 0.2 mL of $Eu(NO_3)_3$ (0.1 mol/L), 10 mL of $C_2H_5OH$, and 1.2 mL of HF were added into the above solution in turn. (Caution! HF is hazardous and very strong corrosive. Goggles and gloves must be worn during the operation.) The resulting mixture solutions were stirred for 30 min, the clear and transparent solution was transferred into a Teflon stainless steel autoclave with a capacity of 50 mL. Finally, the autoclave was maintained at 180 °C for 8 h. After cooling to room temperature naturally, the precipitates were collected and washed with deionized water and absolute ethanol several times. The products were dried at 60 °C for 12 h in air. The as-prepared samples were then annealed at 500 °C in air for 3 h.

### *2.3. Characterization*

The crystalline structure of the samples was evaluated by X-ray diffraction (XRD) analyses, carried out on a XRD-6000 X-Ray diffractometer from Shimadzu with Cu Kα radiation ($\lambda = 0.15405$ nm). The morphology of the samples was inspected using a field-emission scanning electron microscope (S-4800, Hitachi). Transmission electron microscope (TEM) patterns were obtained by a FEI Tecnai $G^2$ S-Twin transmission electron microscope with a field emission gun operating at 200 kV. Photoluminescence (PL) excitation and emission spectra were recorded with a Jobin Yvon FluoroMax-4 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

## 3. Results and discussion

### *3.1. Crystal structure*

The phase structures and purities of the as-synthesized samples before and after calcination were investigated by XRD analysis and the results are shown in Fig. 1. From Fig. 1a, it can be seen that peaks of the samples are relatively weak, indicating the weak crystallinity of

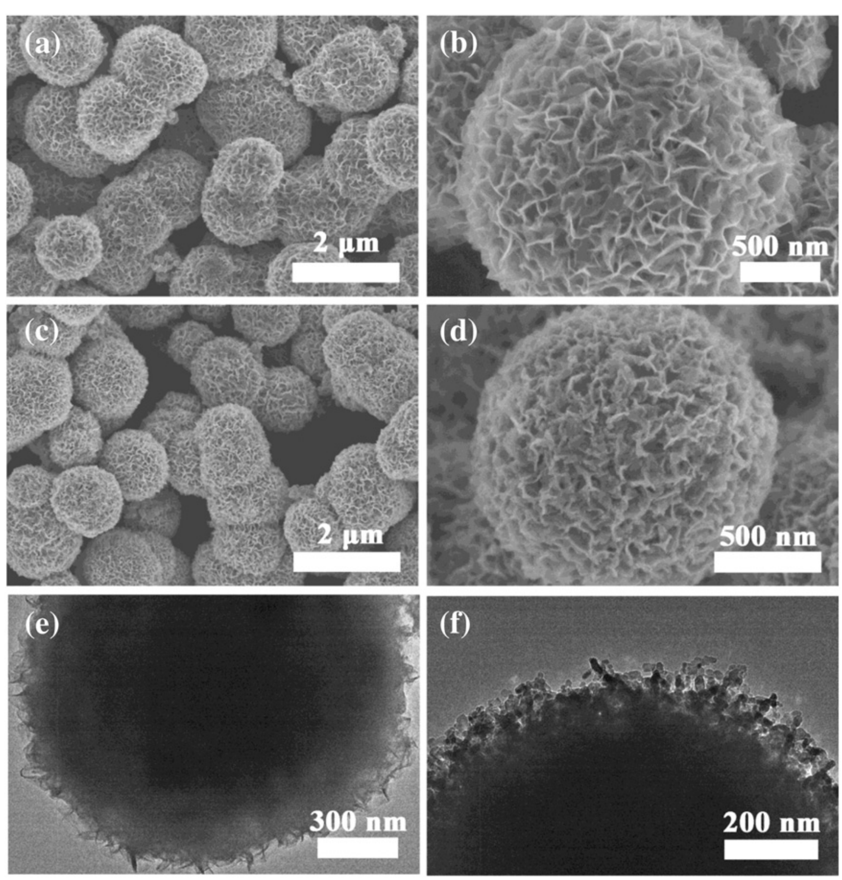


**Fig. 2.** (a, b) SEM and (e) TEM images of the $TiO_2$:$Eu^{3+}$ microspheres before calcination; (c, d) SEM and (f) TEM images of the $TiO_2$:$Eu^{3+}$ microspheres after calcination.