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Uniform europium-based infinite coordination polymer submicrospheres: Fast microwave synthesis and characterization

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ABSTRACT

Uniform europium-based infinite coordination polymer (ICP) submicrospheres have been prepared via a facile and fast microwave heating method in 5 min, with pyridine-2, 5-dicarboxylic acid and europium nitrate as reagents and N, N-dimethylformamide (DMF) as solvent. The products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FTIR). Thermogravimetric (TG) and derivative thermogravimetric analysis (DTG) were also carried out. XRD results reveal that the product is amorphous. SEM and TEM results show that the submicrospheres are with diameters of 200–400 nm. Furthermore, the surface of the microspheres is smooth and the submicrospheres are solid. Strong red emission centering at 618 nm was observed in the europium-based ICP microspheres on excitation with 394 nm UV light. This method may be employed to the preparation of other coordination polymers micro/nanostructures.

Crystalline metal-organic frameworks (MOFs) are a particularly fascinating class of materials because of their interesting properties in applications such as gas storage, catalysis, drug delivery, separations, and sensing [1–5]. Like MOFs, ICP particles are assembled via coordination chemistry principle. However, ICP particles have properties that are different from their MOFs counterparts [6]. They exhibit a higher level of structural tailorability, including size- and morphology-dependent properties. Indeed, it has been demonstrated that one type of ICP particle could be readily converted into three other classes of particles through metal ion exchange without significantly changing the physical structure of the particles [7]. The ICP particles are attractive for many applications through choice of transition metal nodes and ligands. Thus far, ICP particles include amorphous and semi-crystalline coordination polymer materials, which have clearly identifiable morphology (e.g. spheres, rods or cubes) [8]. Very recently, Tb-based ICP hollow spheres have been prepared by our group [9].

Owing to their unusual coordination characteristics arising from 4f electrons, lanthanide metal–organic frameworks (Ln-MOFs) have been intensively studied [10]. In particular, MOFs based on Tb^{3+} and Eu^{3+} are fascinating because of their versatile coordination geometry, unique luminescent and magnetic properties [11]. Pyridine-2, 5-dicarboxylic acid (pydc), known as isocinchomeric acid, is one of the six isomers of pyridine dicarboxylic acid. It is mainly caused by the presence of two carboxyl groups separated by the nitrogen and carbon atom from the ring. Metal ion can be easily coordinated and supramolecular and multidimentional structures can be created [12]. According to recent reports, MOFs incorporating lanthanides and rigid pyridine dicarboxylic acid may be promising multidimensional solid materials [13]. To the best of our knowledge, the preparation and application of lanthanide-based ICP have been rarely considered.

Three different synthetic strategies for the preparation of ICP particles have been established and a lot of new coordination polymers have been prepared based on these methods, which are precipitation, microemulsion and solvothermal synthesis, respectively [6]. However, methods for controlling particle size and shape of ICP are still fairly rudimentary. Microwave-assisted reaction has demonstrated its powerful benefits for greatly reducing the experiment time and holding promise for potentially large-scale industrials productions [14,15]. It has been successfully applied with promising results as an alternative to synthesize coordination polymers which generally needs several days for their hydrothermal preparation [16]. In the past years, many known and novel MOFs structures have been produced by using microwave heating [16–19]. However, most of the previously reported MOFs prepared by microwave heating are in the microscale and their sizes are not uniform. Furthermore, the preparation of ICP particles employing microwave heating has been seldom mentioned. In this paper, uniform europium-based ICP submicrospheres were obtained with the assistance of microwave heating in a short time. In a typical experiment, 16 mL of DMF solution containing 0.1 mmol of Eu $(NO_3)_3 \cdot 6H_2O$ and 16 mL of DMF solution containing 0.3 mmol of pyridine-2, 5-dicarboxylic acid were poured into a 100 mL round bottom flask. The resulting mixture was stirred for 20 min at room temperature and then got heated in a microwave oven for 5 min. The microwave power and frequency were set at 150 W and 2450 MHz, respectively. The microwave oven used in our

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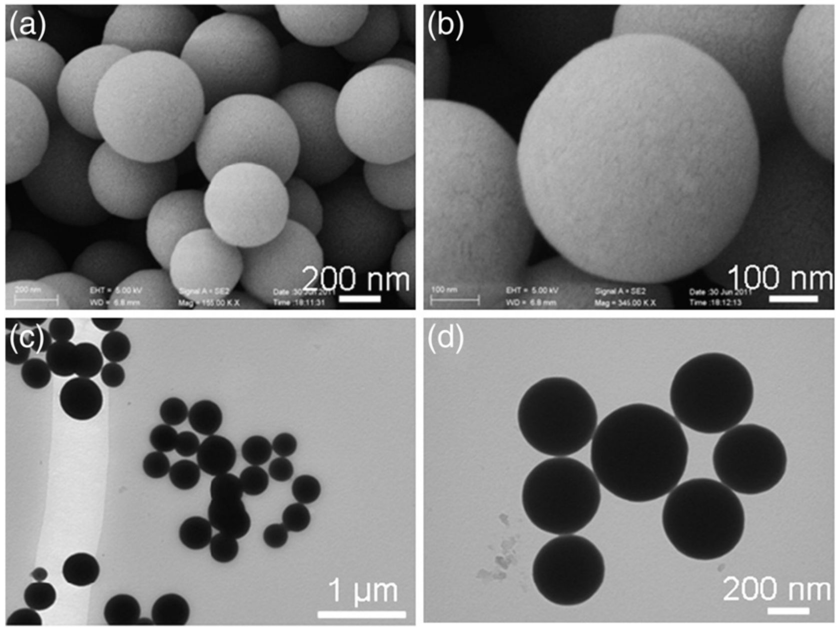

Fig. 1. SEM images (a, b) and TEM images (c, d) of the product obtained after microwave irradiation at 150 W for 5 min.

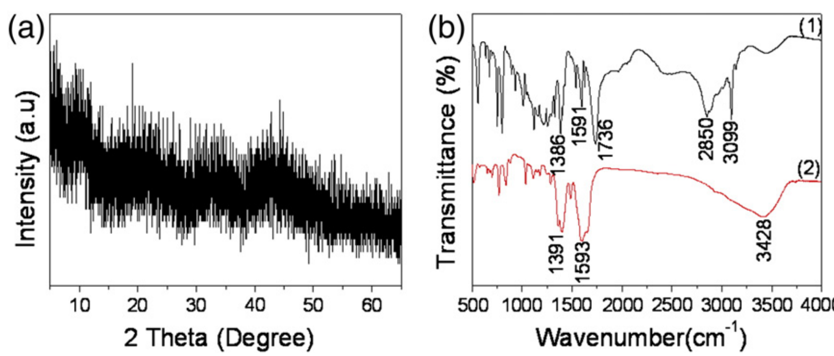

Fig. 2. (a) XRD pattern of the as-prepared product; (b) FTIR spectra of (1) the pyridine-2, 5-dicarboxylate ligand and (2) the as-prepared product.

experiments is a modified household microwave oven equipped with a refluxing apparatus. After being irradiated for 5 min in the open air and cooled to room temperature naturally, the precipitates were centrifuged and washed three times with ethanol. Finally, the products were dried at 60 °C in air for 6 h.

Fig. 1 shows the SEM images of the product. Fig. 1(a) is the overview images of the sample. It clearly shows that the product is composed of uniform microspheres with diameters of 200–400 nm. From the enlarged image shown in Fig. 1(b), it can be seen that the microspheres are with smooth surface. To further investigate the

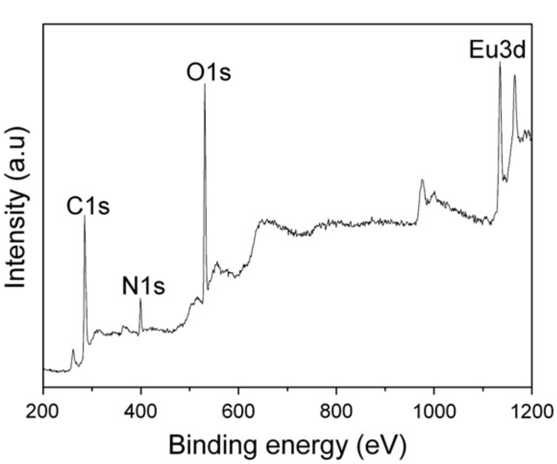

Fig. 3. XPS spectrum of the as-prepared product.

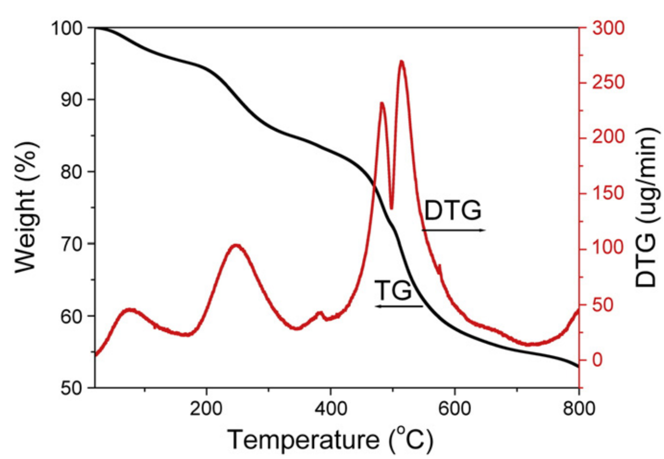

Fig. 4. TG-DTG curves of the as-prepared product.