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Synthesis and fluorescent pH sensing properties of nanoscale lanthanide metal-organic frameworks with silk fibroin powder as polymer ligands

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A B S T R A C T

A series of novel nanoscale lanthanide metal-organic frameworks with silk fibroin powder as polymer ligands were successfully obtained and studied. The silk fibroin powder was first modificated by pyromellitic acid, and then coordinated to lanthanide ions. The size of the metal-organic frameworks can be designed to the range 190–1000 nm through adding different quality of lanthanide ions. The nanoscale materials have excellent photoluminescent properties and exhibit rapid response in detection of pondus hydrogenii. Especially at acidic conditions, the characteristic emission peaks of lanthanide ions are in linear relation with pondus hydrogenii and meet linear equation. This work not only provides an effective strategy for preparation of luminescent nanoscale metal-organic frameworks using biopolymer as ligands on a molecular level but also offers a way to prepare ratiometric fluorescent pondus hydrogenii sensor for biomedical applications.

1. Introduction

Luminescent metal-organic frameworks (MOFs) are a new type of inorganic-organic hybrid materials made from an assembly of metal ions with organic linkers [1–3] and certainly very promising as multifunctional luminescent materials [4,5]. They have attracted extensive attention by their diverse applications in light-emitting devices, display, imaging, biomedicine, fluorescence detection and sensors [6–9]. Not only the metal centers and organic linkers can produce luminescent emissive sources, the metal-organic charge transfer and the guest solvent molecules can also generate luminescence. There is an increasing trend in the exploration and discovery of functional luminescent MOFs. As well known, lanthanide ions, especially Eu(III) and Tb(III), have excellent fluorescence properties [10–12], which make such ions very appealing for the preparation of luminescence MOFs (Ln-MOFs). Now, the MOFs studied and used are mostly bulk single crystal materials and the size greatly restricts their applications in the biology, biomedicine and thin films fields. Nanoscale MOFs (nano-MOFs) have a bright future for their applications in tissue and cell imaging, as well as drug delivery monitoring and treatment, theranostic nanomedicine in which the nanoscale materials are essential for their internalization into cells, and will be expected to be fabricated into thin films for their straightforward and instant sensing devices in the future [13–15].

To date, however, only a few approaches for the fabrication of nano-MOFs are developed. One is the controlled precipitation of self-assembled MOFs by microwave-assisted or sonochemical syntheses to accelerate the nucleation and increase the seed number, thus inhibiting the MOF crystal growth [16,17]. The second is using the addition of capping agents with the same chemical functionality as the linkers [18]. The third is the confined assembly process within specific nanoscale spheres. For example, self-assembly of nano-MOFs can be confined into droplets by micro-emulsion or controlled on the surface of substrates by templates [19,20]. Especially, little work is available on the preparation of nano-Ln-MOFs which, however, present considerable potential as nanoplatforms for biological and biomedical applications [21,22].

Recently, some luminescent nano-Ln-MOFs have been reported. They have excellent applications in the fields of fluorescence

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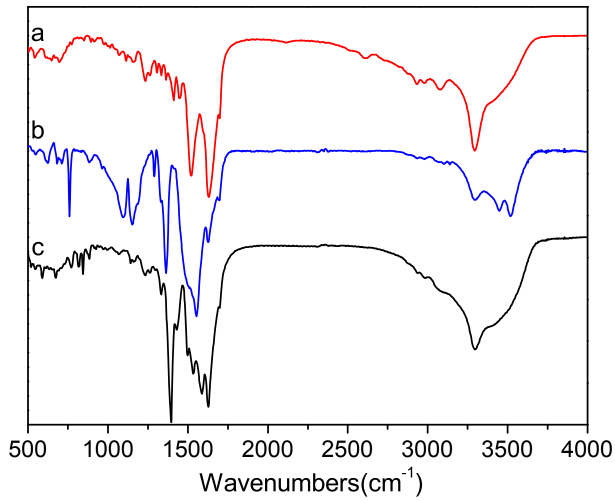

Fig. 1. FT IR spectra of (a) the silk fibroin powder; (b) the silk fibroin powder modificated by PMA; (c) the nano-Eu-MOFs.

detection, ratiometric nanothermometer, luminescent thin films and so on [23–28]. But the combine of nano-Ln-MOFs and biopolymer for biological and biomedical applications still has large work to do. Silk fibroin from the *Bombyx mori* silkworm exhibits attractive potential applications as biomechanical materials due to its unique mechanical and biological properties including its biocompatibility and biodegradability. Many recent researches on the fabrication of various silk fibroin-based composites materials have been reported in the field of biotechnology [29–31]. Herein, we improved an effective strategy for preparation of luminescent nano-Ln-MOFs using silk fibroin powder as ligands on a molecular level. The silk fibroin powder was coordinated to lanthanide ions with pyromellitic acid (PMA) as bridging ligands. The novel nano-Ln-MOFs exhibit rapid response in detection of pH, and offer a way to prepare ratiometric fluorescent pH sensor for biomedical applications because of the good biocompatibility of silk fibroin powder.

2. Experimental

2.1. Materials and physical measurements

$EuCl_3·6H_2O$, $TbCl_3·6H_2O$, PMA used for the preparations were reagent grade without further purification. Silk fibroin powder was made in our laboratory. A Bruker Tensor 27 Fourier transform infrared spectroscopy was employed to measure the IR spectra. Scanning electron microscopy (SEM) images of the nano-MOFs were obtained using a Quanta FEG250 scanning electron microscope (FEI, USA). Fluorescence spectra were recorded with an F-2500 fluorescence spectrophotometer (Hitachi, Japan). The digital photos were taken under a 365 nm UV light. The pH of the nano-MOFs solution was measured using a PHS-3C acidometer (Yueping, China).

2.2. Synthesis of fluorescent nano-Ln-MOFs (Ln = Eu, Tb and Eu/Tb)

PMA 4 g and sodium hypophosphite 1.5 g were dissolved in 30 mL deionized water, and keep stirring for 30 min with 0.3 g silk fibroin powder immersed in the mixture solution. Then the silk fibroin powder was pressed at the pressure of 15 kg/cm^2, dried 5 min at 80 °C, and baked 3 min at 160 °C. The 0.3 g silk fibroin powder modificated by PMA was obtained and then divided into six parts. Every part of silk fibroin powder (0.05 g) was immersed in 15 mL deionized water containing different quantity of $EuCl_3·6H_2O$ (0.005, 0.01, 0.02, 0.03, 0.04 and 0.05, respectively). The resulting mixture was sealed in a 20 mL Teflon-lined stainless-steel autoclave

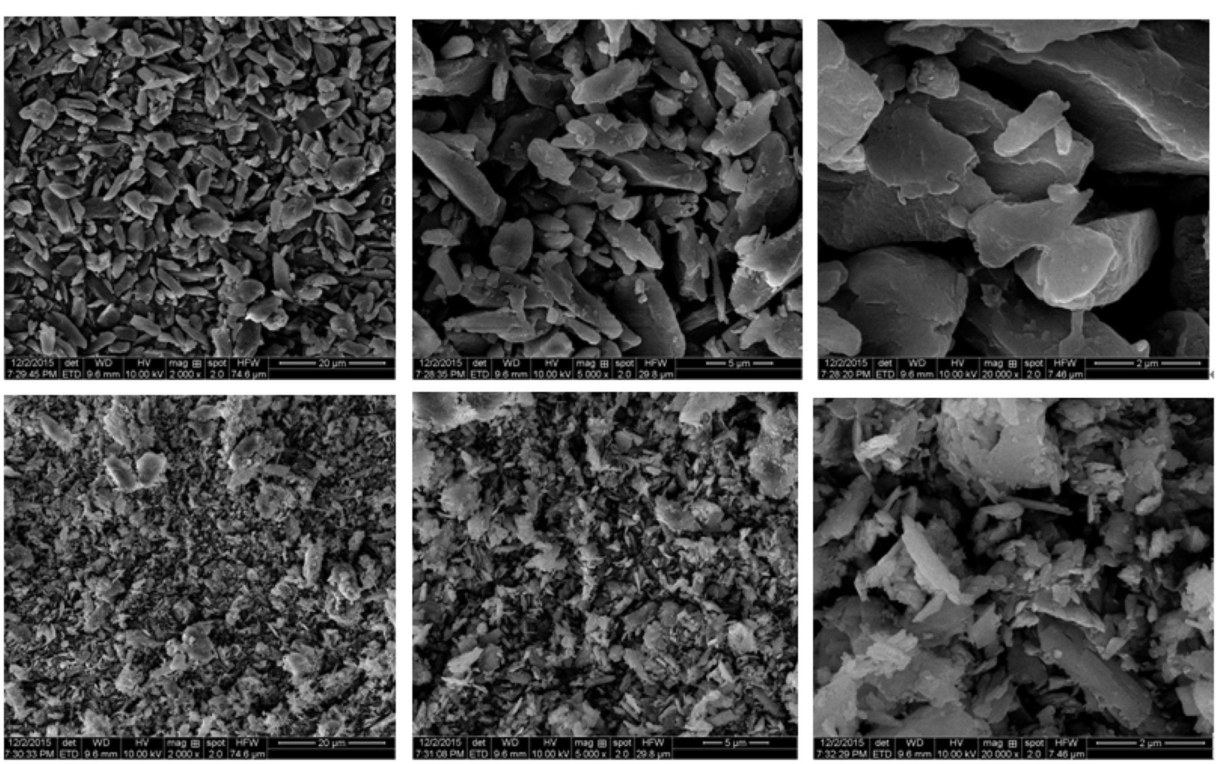

Fig. 2. SEM images of the silk fibroin powder (top) and nano-Eu-MOFs (bottom).