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MIL-53(Al)/Eu^{3+} luminescent nanocrystals: Solvent-adjusted shape-controllable synthesis and highly selective detections for Fe^{3+} ions, $Cr_2O_7^{2-}$ anions and acetone

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ABSTRACT

Luminescent aluminum-based coordination polymers, MIL-53(Al)/Eu^{3+} nanocrystals, were successfully fabricated by a simple mixed solvothermal method without the addition of any surfactants or capping agents. The product was characterized by XRD, SEM, TEM, IR, and EDS technologies. Experiments uncovered that the morphology of luminescent MIL-53(Al)/Eu^{3+} nanocrystals could be tuned by changing the volume ratio of mixed solvents; and the as-obtained nanocrytals presented shape-dependent fluorescent properties. Sheet-like nanocrystals prepared from the system containing the DMF/H_2O/ethanol volume ratio of 20:5:5 (V_{total} = 30 mL) presented the strongest PL emission and the biggest BET surface area. It was found that the as-obtained luminescent MIL-53(Al)/Eu^{3+} nanocrystals could be prepared into fluorescent probes for the selective detections of Fe^{3+} and $Cr_2O_7^{2-}$ ions in aqueous systems and acetone in $CHCl_3$ since its emission peak could be quenched by these matters. Simultaneously, the mechanism to cause the fluorescent quenching was discussed.

1. Introduction

In recent decade, metal organic frameworks (MOFs) have been paid much attention in chemistry and materials science since they display a high extent of adjustability on the size and morphology, which is favorable for tailoring the physical and chemical properties of MOFs [1–4]. Among various MOFs, those with unique luminescent properties drew increasing interest, due to their intriguing topological architectures and the potential use for analytical sensors, display devices, nonlinear optics, and white-light production [4–8]. In particular, MOFs containing lanthanide ions (Ln-MOFs) become one of the research hotspots because of their unique optical performances including visible color observable with the naked eye, large Stokes shift, high color purity, strong luminescence intensity and long luminescence lifetimes originated from specific 4f electron structure [9–11]. Since the PL spectra of Ln-MOFs can be affected by some guests such as cations, anions, and organic small molecules, Ln-MOFs can be prepared as the fluorescent probes for the detection of ions and organic small molecules in solutions, as well harmful organic vapors in air and in biomedicine [12–18]. For instance, Fe^{3+} ion, Cr(VI) and acetone are several species that are often detected. It is well known that iron element acts an important role in the vital movement. Its deficiency or overloading can cause various biological disorders, including hepatic cirrhosis, endotoxemia, and hereditary hemochromatosis [19–21]. As a heavy metal ion, Cr(VI) bears very high toxicity and must be severely controlled in water systems. Acetone is also a harmful matter though it is widely used as the solvent in industry and laboratory. When its concentration reaches certain level in the body through the way of inhalation, ingestion, and/or dermal exposure, the nervous system will be harmed. Herein, some clinic symptoms appear, such as fatigue, headache, vomit, and even coma [22,23].

Many studies have uncovered that the property of a material can be tuned by its shape and size. To realize the shape-/size- controlled synthesis of the material, some additives such as surfactant and complexant are often used during the reaction process. In 2014, our group successfully realized phase- and shape- controlled synthesis of $CePO_4$ nanocrystals without the assistance of any additive, through changing the original EG/H_2O volume ratio [24]. Similarly, it should also be probable to realize the shape-controlled synthesis of Ln-MOFs nanostructures in a simple system only through tuning the volume ratio of mixed solvents. In fact, Li and Du had discussed the role of solvents in coordination supramolecular system [25]. They considered that the solvents could affect the coordination assemblies of specific reactants from both thermodynamic and kinetic aspects. As a result, diverse

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crystalline products could be yielded. During reactions, the solvent could act four roles besides as the medium: (1) ligand, (2) guest, (3) ligand and guest, (4) structure-directing reagent. In the former three instances, the solvent acts as the component incorporated within the crystalline lattice to affect the resulting structure. In the last case, the solvent does not exist in the product but indeed, insensibly influence the lattice structure, crystal growth, and crystalline morphology of the final product [25].

Usually, the approaches to obtain luminescent MOFs mainly include the direct combination of organic linkers and lanthanide metal ions [26,27], the post-treatment of non-luminescent MOFs in the system containing Ln^{3+} ions and the in situ Ln-doping during the formation of MOFs [28,29]. In the current work, we successfully prepared luminescent MIL-53(Al)/Eu^{3+} nanocrystals via the in situ Ln-doping route from a DMF-water-ethanol mixed system with $Al(NO_3)_3{\cdot}9H_2O$, $Eu(NO_3)_3$, 1,4-benzenedicarboxylic acid (1,4-H_2BDC) at 130 °C for 8 h. Experiments uncovered that the morphology of luminescent MIL-53(Al)/Eu^{3+} nanocrystals could be tuned by changing the volume ratio of mixed solvents; and the as-obtained nanocrystals presented shape-dependent fluorescent properties. It was found that the as-obtained luminescent MIL-53(Al)/Eu^{3+} nanocrystals could be prepared into fluorescent probes for selective detections of Fe^{3+} and $Cr_2O_7^{2-}$ ions in aqueous systems and acetone in $CHCl_3$ since its PL peak could be quenched by these matters. Simultaneously, the mechanism to cause the fluorescent quenching was discussed.

2. Experimental section

All reagents and chemicals were analytically pure, bought from Sinopharm Chemical Reagent Co. Ltd., and used as received without further purification. Distilled water was used throughout the experiments.

2.1. Synthesis of MIL-53(Al)/Eu^{3+} nanocrystals

A mixed solvothermal route was employed for synthesis of MIL-53(Al)/Eu^{3+} nanocrystals. In a typical experimental process, proper amounts of $Al(NO_3)_3{\cdot}9H_2O$, $Eu(NO_3)_3$, 1,4-benzenedicarboxylic acid (1,4-H_2BDC) were firstly dissolved into N,N-Dimethylformamide (DMF) with certain volume. After stirring for 10 min, water and ethanol with appropriate volumes were added. The total volume of the mixed solution was 30 mL. Then, the mixed solution was transferred into a Teflon-lined stainless steel autoclave with a 50 mL capacity and heated at 130 °C for 8 h. Subsequently, the autoclave was allowed to cool naturally to room temperature. The precipitate was collected by centrifugation at 8000 rpm for two minutes, washed several times with distilled water and anhydrous ethanol in turn and finally dried in vacuum at 60 °C for 12 h. The related experimental parameters and results were listed in Table 1.

As controls, MIL-53(Al) nanocrystals were also synthesized under the same conditions without the presence of Eu^{3+} ions (see Table 1).

2.2. Characterization

The X-ray powder diffraction patterns of the products were carried out using a Bruker D8 Advance X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 0.154060$ nm), employing a scanning rate of 0.02°/s and 2θ ranges from 5° to 50°. Field emission scanning electron microscopy (FESEM) images and energy dispersive spectra (EDS) of the products were taken on a Hitachi S-4800 field emission scanning electron microscope, employing the accelerating voltage of 5 kV or 15 kV (15 kV for EDS). Transmission electron microscopy (TEM) images were obtained with a Hitachi HT7700 transmission electron microscope, employing an accelerating voltage of 120 kV. Fourier transform infrared (FTIR) spectra were obtained on a Shimadzu FTIR-8400S spectrometer by pressing a small amount of sample and KBr crystal into a plate. Photoluminescence (PL) spectra were recorded on a FLSP 920 with a Xe lamp at room temperature, employing the excitation wavelength of 335 nm from a He–Cd laser. Quantum yields were measured with 3-D Fluorescence Spectrometer of Horiba FL-3 with the exciting wavelength of 310 nm. The Brunauer–Emmett–Teller (BET) tests were carried out via a Quantachrome autosorb IQ-C nitrogen adsorption apparatus. All of the as-prepared samples were degassed at 150 °C for 8 h prior to the nitrogen adsorption measurements. The inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima5300DV-ICP, PerkinElmer) was employed to analyze the contents of various metal ions. UV–vis absorption spectra were obtained on UV-Metash 6100 UV–vis spectrophotometer (Shanghai).

2.3. Influences of ions and organic solvents on the luminescent property of MIL-53(Al)/Eu^{3+}

To investigate the influence of metal ions on the PL property of MIL-53(Al)/Eu^{3+} nanocrystals, sheet-like MIL-53/Eu^{3+} nanocrystals prepared from the system containing the DMF/H_2O/ethanol volume ratio of 20:5:5 were employed as the luminescent matter. Various metal cation solutions with the concentration of 2.0×10^{-2} mol L^{-1} were prepared through dissolving a proper amount of metal chlorate salts into deionized water, respectively. Meanwhile, 1.0 g L^{-1} of MIL-53/Eu^{3+} suspension was also obtained by dispersing MIL-53/Eu^{3+} powders into proper amounts of deionized water under the ultrasonic assistance. Subsequently, 1.0 mL of the above suspension was introduced into 1.0 mL 2.0×10^{-2} mol L^{-1} of MCl_n solution (M = K^+, Na^+, Sr^{2+}, Fe^{2+}, Mg^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+}, In^{3+}, and Cr^{3+}) at room temperature. After the mixed system was placed for 5 min without shaking, the PL spectrum of the system was measured. Similarly, the influences of some anions on the PL property of MIL-53(Al)/Eu^{3+} nanocrystals were also investigated through adding their sodium salts with the concentration of 2.0×10^{-2} mol L^{-1}, including F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, $C_2O_4^{2-}$, HPO_4^{2-}, CO_3^{2-}, CrO_4^{2-}, and $Cr_2O_7^{2-}$.

To study the influence of organic solvents on the PL property of MIL-53(Al)/Eu^{3+} nanocrystals, 3 mg of sheet-like MIL-53(Al)/Eu^{3+} nanocrystals were separately dispersed in 3 mL of different solvents, including water, methanol, ethanol, isopropanol, acetone,

Table 1
the related experimental parameters and results.

Entry	$Al(NO_3)_3{\cdot}9H_2O$	$Eu(NO_3)_3$	1,4-H_2BDC	DMF/H_2O/ethanol (mL/mL/mL)	T/°C	t/h	Results
1	0.19 mmol	0.01 mmol	0.4 mmol	10/10/10	130	8	Porous spheres
2	0.19 mmol	0.01 mmol	0.4 mmol	20/5/5	130	8	nanosheets
3	0.19 mmol	0.01 mmol	0.4 mmol	5/20/5	130	8	Coin-like nanoflakes
4	0.19 mmol	0.01 mmol	0.4 mmol	5/5/20	130	8	Porous spheres
5	0.2 mmol	/	0.4 mmol	10/10/10	130	8	Porous spheres
6	0.2 mmol	/	0.4 mmol	20/5/5	130	8	nanosheets
7	0.2 mmol	/	0.4 mmol	5/20/5	130	8	Coin-like nanoflakes
8	0.2 mmol	/	0.4 mmol	5/5/20	130	8	Porous spheres