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Hierarchical porous cellulose/lanthanide hybrid materials as luminescent sensor[☆]

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ABSTRACT

Photoluminescent hybrid materials containing carboxymethyl cellulose and lanthanide ions (Eu^{3+} , Tb^{3+}) were prepared by a facile method under ambient conditions. Lanthanide ions were covalently grafted to the cellulose framework through coordination with the carboxylic groups of the cellulose. Hybrid materials were fabricated as hydrogel and aerogel. As shown by SEM and pore parameters, aerogel materials which were obtained by supercritical CO_2 drying show hierarchical porous structure. The photoluminescence spectrum of the hybrid materials shows the characteristic red emission of Eu^{3+} ion and green emission of Tb^{3+} . Further luminescent investigations reveal that these hybrid materials can detect Fe^{3+} with relative selectivity and high sensitivity, which suggests that the hybrid materials could be a promising luminescent probe for selectively sensing Fe^{3+} ion.

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1. Introduction

In recent years, the emergence of newly-developed hybrid materials containing photoluminescent lanthanide complexes has greatly promoted the advancement of cell imaging, sensing, optoelectronic devices and so on, because lanthanide complexes show unique luminescence properties such as large Stokes shifts, sharp emission profiles, and long-lived excited states.¹ Unfortunately, poor thermal stability, precious primary material, complicated preparation processes and toxic precursors restrict the application of traditional lanthanide hybrid materials. Due to the fascinating features such as low cost, abundant source, environmental friendliness and biodegradability, natural polysaccharides are considered as ideal matrix in the preparation of novel lanthanide hybrid materials.²

Cellulose, the most abundant natural biopolymer on the earth, is renewable, biodegradable, and affordable. The good thermal and chemical stability of cellulose, due to its strong intra- and intermolecular hydrogen bonds, are favorable characteristics for the applications such as nanocapsules microspheres and support of

nanocatalyst.^{3–5} However, insolubility of cellulose leads to numerous obstacles and limitation in the processing and application.⁶ To solve the problem of insolubility of cellulose, the grafting of hydrophilic group has been treated as one of the most immediate and the most effective method.⁷ The most representative cellulose derivative is carboxymethyl cellulose (CMC) formed by the carboxymethylation of the hydroxyl group of cellulose.⁸ With the grafting of carboxyl groups, the solubility of cellulose has been greatly improved. In addition, inorganic metal ions can be covalently grafted to the cellulose framework through coordination with the carboxylic groups of the cellulose.^{9,10} Inorganic materials are widely used for the construction of biomaterials since the incorporation of rigid inorganic materials can improve the mechanical strength as well as stability. Besides, the metal ions' concentration also has an immense impact on CMC aerogels' structure.¹¹

To date, luminescent hybrid materials are widely used as chemosensors for the fluorescence detection of cations, anions and small molecules. These luminescent hybrid materials feature unique advantages in response time, sensitivity and operability.^{12–17} In this regard, the selective and sensitive sensing of Fe^{3+} ions is of practical significance,^{18,19} since many vital cell functions of either human or other animals depend closely on the specific amount of Fe^{3+} involved, which can not only facilitate the formation of haemoglobin and muscle but also improve the brain functions.²⁰ However, to the best of our knowledge, there are few

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reports about the hierarchical porous hybrid material combining both lanthanide and carboxymethyl cellulose. Herein, we wish to report photoluminescence studies and honeycomb-like hierarchical porous structure of cellulose/lanthanide hybrid materials (Ln = Eu, Tb). These new hybrid materials showed the promising application in the highly selective and sensitive sensing of Fe^{3+} ions.

2. Experimental

2.1. Materials

Europium(III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) and terbium(III) chloride hexahydrate ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) were all purchased from Aladdin Industrial Corporation, Shanghai, China. Carboxymethyl cellulose (CMC) was supplied by J&K Scientific Corporation, Beijing, China. Hydrochloric acid (HCl) and absolute alcohol were used of analytical grade, and without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of Ln^{3+} -CMC hydrogel and aerogel

The hydrogel and aerogel materials in this work were obtained according to the previously reported procedure.²

Hydrogel. A 2 wt% solution of sodium carboxymethyl cellulose in deionized water was added dropwise at room temperature to a LnCl_3 solution (0.1 mol/L; 100 mL) under stirring using a syringe with a 1.0 mm diameter needle. Then, gel microspheres were matured in the Ln^{3+} for 24 h, separated from the cationic solution and washed with distilled water. The average diameter of the prepared hydrogel materials is about 4 mm as shown by SEM.

Aerogels. The hydrogel microspheres were successively immersed in a series of ethanol-water baths of increasing alcohol concentration (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%) during 1 h each and the hydrogels were transformed to alcogels. These alcogel microspheres were dried under supercritical CO_2 conditions (7.4 MPa, 31.5 °C) in a Polaron 3100 apparatus to obtain aerogels. The preparation procedure is shown in Scheme 1.

2.3. Characterizations

Scanning electron micrographs and chemical composition (elemental maps) of the aerogel microspheres were obtained using a NOVA NANOSEM-450 apparatus after gold metallization.

The infrared (IR) spectra of samples were recorded on a BRUKER TENSOR 27 spectrometer in the wavenumber range of 4000–400 cm^{-1} using KBr pellets.

Thermogravimetric analysis was performed with STA449F31 apparatus under N_2 (20 mL/min, 25–800 °C, 5 °C/min) on a 10 mg sample.

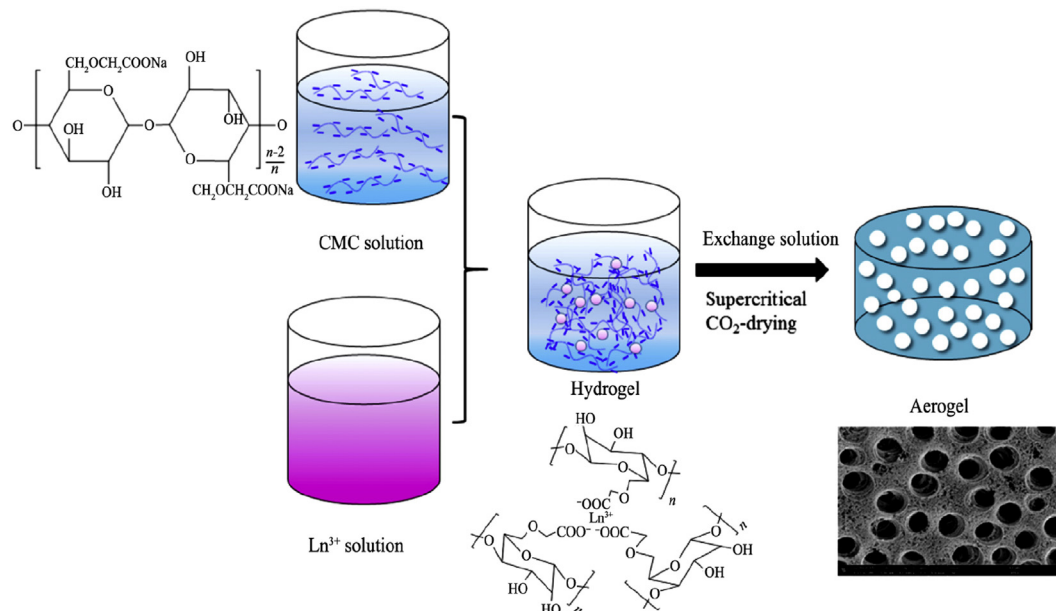
The photoluminescence spectra were acquired using Hitachi F-7000 with a xenon lamp as an excitation source at room temperature.

Nitrogen adsorption/desorption isotherms were recorded using JWGB-BK132F apparatus at 77 K after outgassing the sample at 323 K under a vacuum until a stable 4×10^{-5} Pa pressure was obtained without pumping.

Biocompatibility assessment. To assess the biocompatibility of the Ln^{3+} -CMC, RAECs (rat aortic endothelial cells) were grown with the prepared powder of aerogels ground with agate mortar and the cell viability was measured by MTT viability assay, a colorimetric measure of mitochondrial activity.²¹ Cells were cultured in a 96-well plate (Costar, approximately 4×10^3 cells per well) with DMEM medium containing 10% FBS and different concentrations of the power dispersed in deionized water for 24 h. Then, 20 mL of MTT solution (5 $\mu\text{g}/\text{mL}$ MTT in phosphate buffer solution, pH 7.4) was added to each well and incubated for 4 h at 37 °C. After removing the medium, intracellular formazan crystals were extracted into 150 mL of DMSO and quantified by measuring the absorbance of the cell lysate at 490 nm. Cell viability was expressed as a percentage of the control.²²

2.4. Luminescence sensing of metal ions

Ln^{3+} -CMC hydrogel were treated with different types of metal ions, including K^+ , Ni^{2+} , Cu^{2+} , Co^{2+} , and Fe^{3+} (10 mmol/L). Then, the sample were dried in vacuum overnight at 80 °C and 0.07 MPa. To better understand the fluorescence response of Ln^{3+} -CMC to



Scheme 1. Schematic illustration for the formation process of Ln^{3+} -CMC aerogels.

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