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Fabrication of free-standing fluorescent mesoporous silica films for detection of nitrobenzene

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ABSTRACT

We report a facile two-step strategy for grafting lanthanide complexes onto the surface of nanocrystalline cellulose-templated mesoporous silica films to prepare luminescence mesoporous silica films, which retain both chiral nematic order of the cellulose nanocrystals and fluorescence of the lanthanide complexes are successfully co-assembled after removal of the cellulose and grafting lanthanide complexes. The films exhibit well-defined fluorescence combining the assembly lanthanide complexes. The mesoporous channels of fluorescent mesoporous silica films are more accessible to the analytes compared with traditional fluorescent materials. So, our fluorescent mesoporous silica films were used as fluorescent sensor for the detection of nitrobenzene.

Introduction

Photonic materials have attracted widespread attention due to their unique property of spatial periodicity in microstructure on the scale of optical wavelength [1,2], and the excellent features render them promising for potential applications in waveguides [3], optical switches [4] and fluorescent probes [5]. Among these numerous photonic materials, mesoporous silica materials with chiral nematic structure have paid close extensive attention due to their ordered structures let them possess photonic properties [6–8].

Clever incorporation of different functional dopants into photonic crystals will improve useful multifunctional applications in frequency filters, waveguides, signal modulators, optical switches and fluorescent sensors [8–10]. Incorporation of luminescent dopants into photonic materials could improve their optical responses for fabricating wave-guide-based devices [11,12]. Trivalent lanthanide (Ln(III)) activated luminescent complexes possesses unique electronic structure which enables Ln(III) ions to emit photons efficiently in the wide spectral region from ultraviolet to visible or infrared with narrow bandwidth, long lifetimes and emission and large apparent Stokes shifts [13], makes them show distinct fluorescence effect compared to quantum dots and organic dyes [14,15]. Because of these excellent fluorescence properties, Ln(III)-based fluorescent materials have been widely configured as an optical probe system for rapid, sensitive detection of trace analyte via fluorescence change [16,17]. Therefore, sophisticated rare earth complex materials with photonic structures show potential use in fields of sensor, photo-fluorescence display technology, and optical amplifiers [18,19].

Cellulose nanocrystals (CNCs) are renewable biopolymer, which can be obtained by acid hydrolysis of bulk cellulose [20–24]. CNCs can organize into liquid crystal phase in water which makes CNCs act as the biotemplate to construct mesoporous films with 1-D photonic structure by evaporation-induced self-assembly (EISA) [25,26]. Photonic and porous structures can be tunable by changing the concentration of silica precursors. After removal of CNCs, highly ordered mesoporous structures are obtained with high surface area and spindle helical twist of the chiral nematic [27]. These materials often exhibit brilliant iridescent colors due to the 1D photonic structure, which leads them to selectively reflect circularly polarized light with wavelengths [28].

The lanthanides doped oxides photonic materials have been reported previously [18,29,30]. Eu(III)-doped Gd_2O_3 inverse opal photonic crystals were successfully synthesized based on a self-assembly technique and a sol–gel method showing interesting modulation effects and photo-fluorescence properties. And Chu et al. synthesized free-standing chiral nematic mesoporous films of Y_2O_3: Eu(III) using a hard template method. Although these materials showed interesting modulation effects and photo-fluorescence properties, multi-step fabricate procedure and removal of the template process dramatically impacted chiral

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nematic organization, and decreased the porosity of the materials. Recently, MacLachlan and co-workers reported to incorporate silver nanoparticles [31] and CdS quantum dots [5] into chiral nematic CNC-templated silica films, which exhibited interesting optical properties and potential applications in fluorescence detection. The materials were able to show chiral nematic organization and porosity. Fluorophore has been embedded in the chiral nematic mesoporous films, which may affect the chiral nematic organization and limit its application values for fluorescent recognition and fluorescent image. During preparation, the Fluorophore nanoparticles may be not well dispersed. Furthermore, the removal of template (calcination or acid hydrolysis) would interfere the fluorescent nanoparticles intensely. To overcome these problems, we used Ln(III) complex grafting on the surface of the mesoporous silica films, which not only maintain the mesoporous structure, but also keep the fluorescence of the Ln (III). Although, multi-step procedure to fabricate materials is often difficult to achieve and expensive for production scale-up, our two-steps grafting method is quite simple for fabricating mesoporous silica films, and the renewable resources act as template, both of which are important for developing applications of the fluorescent mesoporous silica films.

Due to the unique electronic properties of lanthanide (Ln) ions originated from the 4f electrons, the mesoporous silica films undergo fluorescence quenching when exposed them to nitrobenzene, suggesting their potential applications in optical sensor.

In this paper, we reported our work. At the beginning of self-assemble into the substrate of CNC-templated silica, subsequently two-step modified by TTA–Si and Eu(III), which generated free-standing iridescent, luminescent films. To the best of our knowledge, our work provided the demonstration of assembly of binary mesoporous hybrid materials fabricated with CNCs. The synthetic approach for the modified materials is depicted in the Schematic. Characterizations and detailed studies of the properties of all materials were investigated and compared. Finally, our films were applied as the sensor for sensitive determination of nitrobenzene in solution or vapor.

Experimental

Materials

All the solvents and reagents were analytical reagent and used without further purification unless otherwise stated. Degreasing cotton provided by Sinopharm Chemical Regent Co. Ltd. (Shanghai, China) and it was used as a raw material for production of nanocrystalline cellulose (CNC). All other chemicals, including tetramethoxysilane (TMOS, >95%), sulphuric acid (H_2SO_4, 95–98%), 2-Thenoyltrifluoroacetone (TTA, 98.0%), NaH(60%), Eu $(NO_3)_3$(99.9%), 3-(triethoxysilyl)-propyl-isocyanate (TEPIC, 95.0%), tetrahydrofuran (THF, 99%), ethanol (>99.7%), toluene (>99.5%) were purchased from Everbright Chemical Inc. (Nanjing, China).

Synthesis

Preparation of cellulose nanocrystals (CNCs)

1 g of commercial degreasing cotton was hydrolyzed in 50 wt.% concentration sulfuric acid (15 ml) with vigorous stirring for 100 min at 45 °C. Deionized water was added to terminate hydrolysis. Then the CNCs suspension was allowed to settle for stratification overnight. Subsequently, the lower layer was centrifuged after decanting the clear upper layer. After centrifugation, CNCs was put into dialysis membrane tubes (11,000–15,000 molecular weight wiped off) and dialyzed in running deionized water for 1–4 days. Then CNCs from the dialysis membrane tubes was dispersed by ultrasound treatment for 10 min and was diluted to the desired concentration.

Preparation of free-standing mesoporous silica films

Mesoporous silica films were prepared according to previously reported literature methods [25]. In a typical procedure, CNC/silica composite films were prepared by first sonicating a 3 wt.% aqueous CNC suspension for 10 min. Then TMOS was added dropwise to the suspension, and the mixture was left to stir at room temperature for 2 h to obtain a homogeneous solution. The mixtures were poured into polystyrene Petri dishes and left to dry under ambient conditions for complete drying. Then the obtained CNC/Silica composites were calcinated under flowing air at a rate of 2 °C min^{-1} to 100 °C, held at the temperature for 2 h, then raised to 540 °C at 2 °C min^{-1}, and held at the temperature for 6 h. After cooling the samples to room temperature, free-standing mesoporous silica films were recovered, and noted as MSF.

Synthesis of the cross-linking precursor (TTA–Si)

For the new free-standing fluorescent mesoporous silica films, first a TTA–Si was prepared. The synthesis of TTA–Si was briefed as the method in literature [32]. 2-Thenoyltrifluoroacetone (TTA) (1 mmol, 0.222 g) was dissolved in 20 ml of tetrahydrofuran (THF), and then NaH (2 mmol, 0.048 g) was added into the solution. After two hours, 3-(triethoxysilyl)-propyl-isocyanate (TEPIC, 2.0 mmol, 0.495 g) was added dropwise into the solution. The mixture was heated to reflux at 65 °C for 12 h in N_2 protection. After isolation and purification, a yellow viscous liquid was obtained, and noted as TTA–Si.

Preparation of new free-standing fluorescent mesoporous silica films

0.2 g of free-standing mesoporous silica films were then reacted with different volumes of TTA–Si in 50 ml toluene at room temperature overnight. The films were washed thoroughly with toluene and ethanol to remove any physically adsorbed TTA–Si, and dried under vacuum overnight at 50 °C in order to obtain the free-standing fluorescent mesoporous silica films (MSF-TTA). Modified mesoporous silica films were then added into an appropriate amount of $Eu(NO_3)_3$ ethanol solution under continuous stirring (the molar ratio of Eu(III): TTA–Si = 1:3). The resulting films were dried overnight at 40 °C under vacuum. The resulting fluorescent mesoporous hybrid films were assigned the following codes: MSF, MSF-1, and MSF-2 denoting pristine mesoporous films and fluorescent mesoporous hybrid films with different TTA–Si and Eu(III) (MSF-1 added 100 μl of TTA–Si, and MSF-2 is 200 μl of TTA–Si.).

Characterization

FTIR spectra (4000–400 cm^{-1}) were collected on a Nicolet NEXUS-470 FT-IR apparatus (U.S.A.). Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100 (HR) at an accelerating voltage of 200 kV with a LaB6 filament, Thermo Scientific. Samples were prepared by first grinding the film into a fine powder, suspending in ethanol, and then dropcasting onto a carbon-coated TEM grid. The thermogravimetric analysis (TGA) of samples were measured using a Diamond TG/DTA Instruments (STA 449C Jupiter, Netzsch, Germany) under a nitrogen atmosphere up to 800 °C with a heating rate of 10.0 °C min^{-1}. The surface area was determined using N_2 adsorption isotherms on the sorbent using a Micromeritics TriStar II 3020 analyzer (Micromeritics Instrument Corporation, USA). All materials were dried under reduced pressure at 50 °C for 12 h and were outgassed for 6 h at 100 °C prior to N_2 adsorption analysis, which was carried out at −196 °C. The surface area was obtained by a multi-point analysis of the volume of nitrogen adsorbed as a function of relative pressure.