Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 151 (2015) 100–103

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Short Communication

Novel multi-component hybrids through double luminescent lanthanide unit functionalized zeolite L and titania

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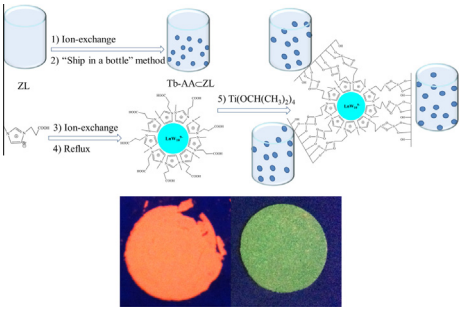
HIGHLIGHTS

- Double lanthanide luminescent species are functionalized to assembly multi-component hybrid systems.
- Functionalized zeolite and titania are assembled with ionic liquid compound as linker.
- These hybrids exhibit the multi-color luminescence.

GRAPHICAL ABSTRACT

Multi-component luminescent hybrids are assembled with double lanthanide species functionalized zeolite L (ZL) and titania with ionic liquid compound as linker.



ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form 19 June 2015
Accepted 22 June 2015
Available online 23 June 2015

Keywords:
Hybrids
Lanthanide polyoxometalate
Terbium complex
Functionalized zeolite L
Ionic liquid
Luminescence

ABSTRACT

Zeolite L (ZL) is functionalized with inside-outside double modification paths (gas disperse ("ship in bottle") and covalently grafting) with two kinds of luminescent lanthanide species (Tb^{3+} complex of acetylacetone (AA), lanthanide polyoxometalate ($NaLnW_{10}O_{36}{\cdot}32H_2O$, abbreviated as LnW_{10}, Ln = Eu, Tb)) to prepare the hybrid materials. The prepared hybrids show the red and green luminescence, which provides a useful path to obtain multi-component lanthanide hybrids.

1. Introduction

Much research work on lanthanide inorganic–organic hybrid materials has been done in the past decades [1,2]. The hybrid materials enable both inorganic and organic dopants to be incorporated with relatively high thermal stability. Among which the functionalized nanoporous host materials belong to important kinds of hybrid system. Mesoporous silica such as MCM-41, SBA-15, POMs and microporous zeolites can behave as the host for lanthanide complexes [3–8], whose host–guest hybrid materials present versatile post-synthetic paths and interesting luminescence properties and embody them great potential for practical application [9–12]. Zeolites are crystalline microporous materials with highly regular nanometer-sized channels or cavities inside, which is widely used in the host–guest assembly of organolanthanide complexes for supramolecular organization of guest molecules or nanostructures [13,14]. Especially zeolite L (ZL) crystals play a

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http://dx.doi.org/10.1016/j.saa.2015.06.068
1386-1425/

great role in the construction of luminescent materials due to their perfect one-dimensional and strictly parallel channels arranged in hexagonal symmetry and has proven to be an ideal host of hybrid materials with intriguing properties [15,16]. ZL is easily to be functionalized with targeting groups for its surface is covered with a large number of hydroxyls and luminescent lanthanide complexes can be inserted into the one-dimensional channels via the "ship in a bottle method" [17].

Here, we prepare zeolite L and then functionalize it with terbium ions by ion exchange reaction and introduce acetylacetone ligand (AA) by gas diffusion called "ship-in-bottle" method. Meanwhile, ionic liquid compound 1-methyl-3-propionyloxy imidazolium bromide (IL) is synthesized. Finally, through the condensation process and coordination reaction, the multi- component hybrid system is assembled, as formulated as AA-Tb ZL-Ti-IL-LnW_{10}.

2. Experimental section

2.1. Materials

Chemical pure and highly crystalline Zeolite L (ZL) crystals were synthesized according to the reported procedure. $LnNO_3{\cdot}6H_2O$ (Ln = Eu/Tb) were obtained by dissolving their respective oxides in concentrated nitric acid (69.2%). Acetylacetone (98%, AA, Aladdin), sodium aluminate (Aladdin), sodium hydroxide (Aladdin), potassium hydroxide (Aladdin), and colloidal silica (40%, Ludox HS-40, Sigma), tetraisopropyl titanate ($Ti(OCH(CH_3)_2)_4$, Aladdin) were used without further purification. And the chemicals were analytically pure and purchased from China National Medicines Group and used as received.

2.2. The synthesis of IL

Highly purified IL were synthesized according to a previously reported procedure [18]. 100 mmol of 3-bromopropionic acid was first dissolved in 10 mL absolute ethyl alcohol, and then equal amount of substance 1-methyl imidazole was added to the solution stirred for 8 h at 348 K. The coarse product was washed with ether by three times and then taken down on a rotary evaporator to remove excess solvent to obtain a pale yellow ionic liquid, referred to as IL. The yield was 80%. For IL: 1H NMR (400 MHz, DMSO-d^6): δ (9.25, s, 1H), δ (7.70, s, 1H), δ (7.60, s, 1H), δ (4.44, t, 2H), δ (2.92, t, 2H), δ (3.93, s, 3H).

2.3. Synthesis of four kinds of lanthanide polyoxometalates (LnW_{10})

$Na_9LnW_{10}O_{36}{\cdot}32H_2O$ ((LnW_{10})) can be abbreviated to LnW_{10} (Ln = Eu, Tb). The synthesis of POMs was prepared with the method reported by Peacock and Weakley [19]. Firstly, 100 mmol of $Na_2WO_4{\cdot}2H_2O$ was dissolved in 10 mL deionized water, the solution was heated to 358 K, and then adjust the pH of about 7–8 with glacial acetic acid. 1 mmol aqueous solution of $Ln(NO_3)_3{\cdot}6H_2O$ (0.8 mL) was added to the solution dropwise by stirring. In the process of adding, a lot of white precipitate immediately generated, stop the heating and cooling to room temperature in the end. The product was obtained by filtration, and then dried under normal atmospheric conditions. The colorless crystals is LnW_{10} (Ln = Eu/Tb).

2.4. Preparation of AA-Tb⊂ZL

Tb⊂ZL was synthesis according to the ion-exchange synthesis procedure as follows. 100 mg of ZL was stirred in 1.2 mL of a 0.05 M aqueous solution of $TbCl_3{\cdot}6H_2O$ for 12 h at 353 K. The product was collected by centrifugation, washed with deionized water by three times and then dried for 5 h at 353 K under normal atmospheric conditions. The organic–inorganic hybrid materials AA-Tb⊂ZL was synthesized by "ship in a bottle" method. After Tb⊂ZL was degassed and dried at 423 K for 2 h to get rid of the solvent molecules and water molecules, it was exposed to the TTA/AA vapor at 453/393 K for 18 h. The product was washed with CH_2Cl_2 by three times, and dried at 333 K for 4 h under vacuum.

2.5. Preparation of AA-Tb⊂ZL-Ti-IL-LnW_{10} (Ln = Eu/Tb)

0.9 mmol IM^+Br^- was firstly suspended in 20 mL of ethanol solution, 0.1 mmol LnW_{10} was then added for ion exchange, and refluxed in normal atmospheric conditions at 343 K for 24 h. 0.9 mmol of $Ti(OCH(CH_3)_2)_4$ and 100 mg ZA/L was added and refluxed at 343 K for another 6 h. Stop heating, 3.6 mmol deionized water was used to promote the hydrolysis reaction stirring at room temperature. The molar compositional ratio of the resulting gel was $1LnW_{10}$:9IL:$9Ti(OCH(CH_3)_2)_4$:$36H_2O$. The product was washed with anhydrous ethanol by three times and then dried for 10 h under vacuum. The resulting material is dried at 60 °C under vacuum overnight, whose scheme for the predicted composition is illustrated in Fig. 1.

2.6. Physical characterization

X-ray powder diffraction patterns (XRD) were recorded on Rigaku D/max-Rb diffractometer equipped with Cu anode; the data were collected within the 2θ range of 5–70°. Scanning electronic microscope (SEM) images were obtained with a Hitachi S4800. Fourier transform infrared spectra (FTIR) were measured within KBr slices from 4000 to 400 cm^{-1} region using a Nexus 912 AO446

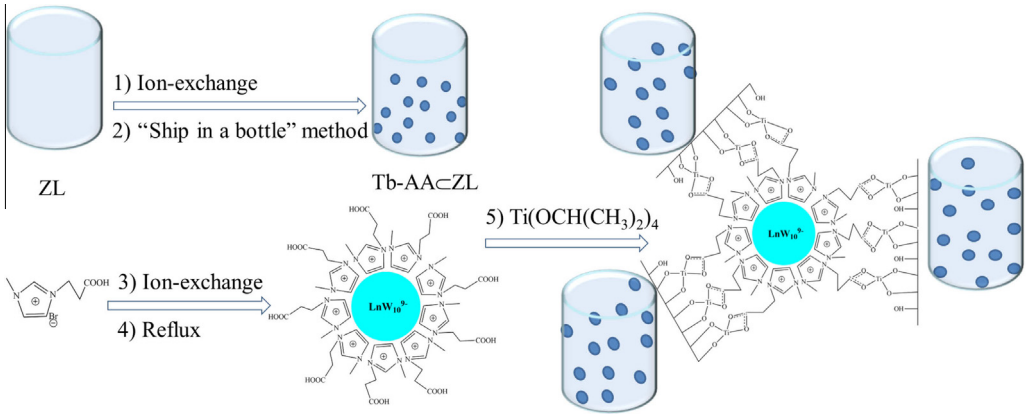

Fig. 1. The scheme for the synthesis and predicted composition of AA-Tb⊂ZL-Ti-IL-LnW_{10} (Ln = Eu, Tb) hybrids.