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Tubular solids of lanthanide-doped polyoxometalates in micrometer-scale: synthesis and NIR-luminescent properties

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ABSTRACT

A series of lanthanide-doped polyoxometalate microtubes, Ln-SiW₁₂ (Ln=Nd, Dy and Yb), have been synthesized, and characterized by X-ray diffraction, elemental analysis and thermogravimetric analysis. In the microtubes, the lanthanide cations combine with polyanions through electrostatic interaction. Furthermore, the lanthanide-doped microtubes were chelated with 8-hydroxyquinoline (HQ) in a post-synthesis step (designed as LnQ-SiW₁₂). The LnQ-SiW₁₂ show characteristic near-infrared (NIR) luminescence, corresponding to Ln³⁺ ions due to efficient energy transfer from Q to the Ln³⁺ ions through antenna effect.

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1. Introduction

Lanthanide compounds possess appealing applications in optical material, magnetic materials and superconducting materials [1–6]. The luminescent properties of lanthanide ions display advantages in that they absorb and emit light over narrow wavelength ranges with high quantum yields [7–13].

Polyoxometalates (POMs) are a unique class of metal oxide clusters, which have enormous structural diversities with stability of definite structures [14–21]. Especially, they possess potential applications in various fields such as catalysis, medicine, magnetism and photoelectric materials [22]. Materials in micro/nanometer-scale with hollow interior are attracting more and more attention for scientists, owing to their potential applications, for example, in electronic, magnetic, optical and sensing materials [23–30]. POMs with tubular structures may exert both merits of POMs and tubes. Therefore, design and synthesis of POM-based tubular materials in micro/nano-scale are fascinating [31–36].

In this work, our aim is to obtain lanthanide near-infrared (NIR) luminescence tubular materials through an integration of lanthanide (III) into the tubular morphology of POMs. As is known, the 4f–4f transition of the lanthanide ions are partly forbidden, therefore, design and preparation of efficient sensitization systems for lanthanide-based emitters remain a challenge. A useful strategy to

overcome this drawback is the complexation of lanthanide ions with some ligands to enhance luminescence through the so-called “antenna effect” or sensitization process. 8-hydroxyquinoline (HQ) is an effective chelating ligand to complex trivalent lanthanide ions. Furthermore, coordination complexes of HQ are often strongly emissive either in solution or in solid phases, so it is a good candidate for preparation of Ln-based luminescent materials [37]. Based on this consideration, we have prepared lanthanide-doped 12-tungstosilicate microtubes, Ln-SiW₁₂ and LnQ-SiW₁₂ (Ln=Nd(III), Dy(III), Yb(III)). The preparation and NIR luminescent properties of the Ln-SiW₁₂ and LnQ-SiW₁₂ microtubes are reported here.

2. Experimental section

2.1. Materials and equipments

Hydrated LnCl₃ salts (Ln=Nd, Dy and Yb) were obtained by dissolving Ln₂O₃ in hydrochloric acid (HCl) followed by removal of HCl through evaporation. Silicotungstic acid (H₄[SiW₁₂O₄₀]), HCl, KCl, 8-hydroxyquinoline(C₉H₇NO) and ethanol were of analytical grade, and were used directly without any further purification. All aqueous solutions were made with deionized water.

Fourier transform infrared (FT-IR) spectra were recorded on a D/MAX-IIIIC instrument; elemental analyses were carried out on Euro Vector EA 3000 and Vario EL instruments; environmental scanning electron microscopy (ESEM) images were acquired with an XL30 field emission environmental scanning electron microscope

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(ESEM-FEG); powder X-ray diffraction (PXRD) patterns were obtained with a D/max-IIIc diffractometer; thermogravimetric analysis measurements (TG) were performed with a Perkin-Elmer TGA7 instrument; X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 spectrometer with an Al-K α (1486.6 eV) achromatic X-ray source; Metal element analyses were carried out on a Thermo iCAP 6000 inductively coupled plasma-atomic emission spectrometer (ICP-AES). The excitation and emission spectra of the Ln-SiW₁₂ and LnQ-SiW₁₂ microtubes were measured at room temperature (RT) with an Edinburgh Analytical Instrument FLS920 equipped with a stable spec-xenon lamp (450 w) as the light source.

2.2. Preparation of Ln-SiW₁₂ (Ln=Nd, Dy and Yb) microtubes

In a typical preparation procedure, 3 g of silicotungstic acid (H₄[SiW₁₂O₄₀]) was put in a beaker having an internally scratched bottom, and 10 mL of deionized water was added under stirring. Then the solution was heated in a water bath of 85 °C for 10 min, and 0.5 g of KCl was added. After reacting for 5 min, hydrated LnCl₃ salts (1 g) were added in the solution. When hydrated LnCl₃ salts were completely dissolved, the solution was cooled at room temperature (25 °C) for about 10 min, from which the Ln-SiW₁₂ microtubes were crystallized, and collected by filtration, dried under air for 24 h (Yield: 1 g).

2.3. Preparation of LnQ-SiW₁₂ (Ln=Nd, Dy and Yb) microtubes

The as-prepared Ln-SiW₁₂ microtubes were dipped in an HQ ethanol solution (0.5 mol/L) which was heated in a 75 °C water bath till the white microtubes changed color to yellow, followed by removal of ethanol through evaporation. The LnQ-SiW₁₂ microtubes were washed several times with ethanol to remove surplus HQ.

3. Results and discussion

3.1. Characterization of Ln-SiW₁₂ microtubes

Tubular morphologies of the Ln-SiW₁₂ microtubes are well observed by optical micrographs (Fig. S1). The color of Nd-SiW₁₂ microtubes is lavender, and the color of other Ln-SiW₁₂ microtubes

is white. ESEM-FEG images reveal that an average length is around 2.5 mm, and inner diameters and wall thicknesses of the Ln-SiW₁₂ microtubes are in the ranges of 30–85 μ m and 10–25 μ m, respectively (Fig. 1).

The FT-IR spectra obtained from the Ln-SiW₁₂ microtubes (Fig. S2) show four characteristic vibration absorption bands below 1000 cm⁻¹, assigned to $\nu_{as}(W-O_d)$, $\nu_{as}(Si-O_a)$, $\nu_{as}(W-O_b-W)$ and $\nu_{as}(W-O_c-W)$ of the Keggin anion, respectively. The FT-IR spectra verify the saturated Keggin structure in the Ln-SiW₁₂ microtubes.

XRD patterns found for the Ln-SiW₁₂ microtubes (Fig. S3) are in good agreement with those of the SiW₁₂ microtubes, indexed to the orthorhombic phase of K₄SiW₁₂O₄₀ (JCPDS 70-1714), with slight differences in some peak positions and/or intensities. These results prove that the crystalline structure of K₄SiW₁₂O₄₀ is still maintained in the Ln-SiW₁₂ microtubes.

TG measurements were carried out to determine the number of water molecules in the Ln-SiW₁₂ microtubes. All the TG curves show two steps of weight-loss. The first weight-loss stage in the range of 57–300 °C corresponds to the loss of about four crystal water molecules, and the second weight-loss stage in the range of 300–600 °C corresponds to the loss of about two coordinated water molecules (Fig. S4).

Element analyses gave the percentages of the Ln³⁺ cations in the Ln-SiW₁₂ microtubes: Nd³⁺, 1.34%; Dy³⁺, 1.51%; Yb³⁺, 1.60%. According to these results, a general formula of K_{4-3n}Ln_n[SiW₁₂O₄₀]·6H₂O (n=0.25–0.3) is given for the Ln-SiW₁₂ microtubes.

3.2. Characterization of LnQ-SiW₁₂ microtubes

ESEM-FEG images and optical micrographs of the LnQ-SiW₁₂ microtubes are shown in Fig. 2 and Fig. S5.

All the TG curves obtained from the LnQ-SiW₁₂ microtubes are shown in Fig. S6. The FT-IR spectra obtained from LnQ-SiW₁₂ microtubes are shown in Fig. S7. The vibration absorption at 1650–1450 cm⁻¹ is assigned to the aromatic ring skeleton. The peaks around 1390 and 1320 cm⁻¹ are attributed to the C–N bonds. The absorption vibration of C–O at around 1250 cm⁻¹ is also observed [38]. The characteristic absorption peaks of the Q molecule below 1000 cm⁻¹ may be overlapped by those of polyoxometalates.

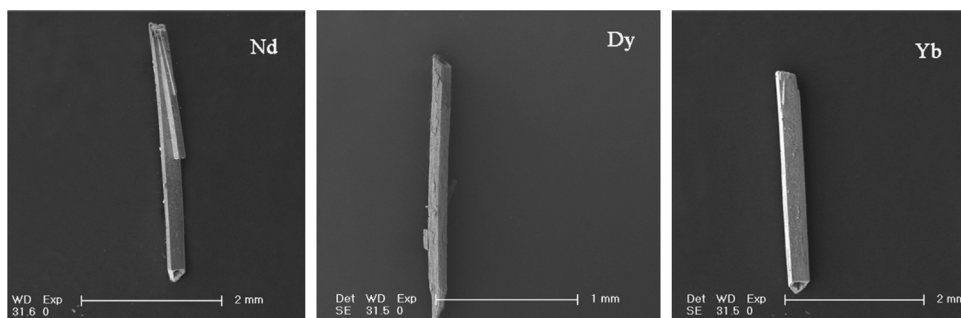


Fig. 1. The ESEM images of the Ln-SiW₁₂ (Ln=Nd, Dy and Yb) microtubes.

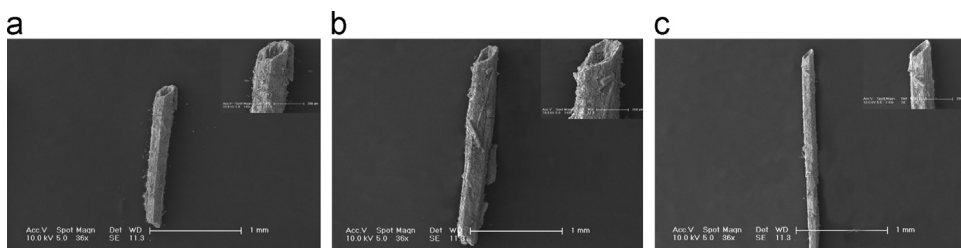


Fig. 2. The ESEM-FEG images of (a) NdQ-SiW₁₂, (b) DyQ-SiW₁₂ and (c) YbQ-SiW₁₂ microtubes.

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