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Assembly and luminescence properties of lanthanide-polyoxometalates/polyethyleneimine/SiO_2 particles with core–shell structure

Jun Wang *, Shaohua Fan, Weiqian Zhao, Hongyan Zhang

College of Chemistry, Central China Normal University, Wuhan, 430079, China

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ABSTRACT

In this paper, two lanthanide-polyoxometalate (LnW_{10}) complexes were bonded on the surface of the polyethyleneimine (PEI)-modified silica nanoparticles with different sizes, resulting in the formation of LnW_{10}/PEI/SiO_2 particles. The hybrid core–shell particles were characterized by infrared, luminescent spectra, scanning electronic microscope, and transmission electronic microscope. The particles obtained exhibit the fine spherical core–shell structure and the excellent luminescence properties. The luminescence spectra studies revealed that the formation of LnW_{10}/PEI/SiO_2 particles and the size of particle have an influence on the luminescence properties of lanthanide ions.

1. Introduction

Polyoxometalates (POM), with remarkable chemical, structural, and electronic versatility, are recently stimulating fundamental and applied research for advanced materials with desirable application in catalysis, biology, medicine, magnetic, electrochemistry, photochemistry, and material science [1,2]. They are inorganic metal-oxygen cluster compounds that are outstanding in their topological and electronic versatility [3,4]. Incorporating lanthanide centers into the structural framework of the POM has led to unique and interesting spectroscopic, electrochemical, and magnetic properties. Accommodated with luminescent lanthanide ions (Ln), such as Eu^{3+} and Dy^{3+}, POM can form luminescent coordination complexes with a variety of structures. They are of current interest because of their special electronic and optical properties and potential applications in luminescence devices involving the artificial production of light, such as cathode ray tubes, lamps, and X-ray detectors [5–7].

The design and synthesis of hybrid nanocomposites with special physical and chemical properties have attracted great attention due to their potential applications in photonic crystals, catalysis, diagnostics, nonlinear optics, and pharmacology [8–10]. Among them the core–shell structured materials have been attracting much attention. A variety of approaches have been employed for the manufacture and design of micro- and nanocomposite that consist of either organic or inorganic core coated with shell of different chemical composition [11–14]. The inorganic cores can be coated with layers of various materials by controlled surface reactions on the core particles. In general, approaches for fabricating the hybrid core–shell nanocomposites and controlling nanoscale structures include the synthesis of surface modified nanoparticles and the use of self-assembled polymer or surfactant microstructures as templates for nanostructured core–shell materials. Silica particles can be fabricated controllably into spherical from nano- to micrometer sizes and their surface could be decorated with various composites. Therefore, they are frequently used in core–shell structured materials [13,14]. Recently, we assembled Na_9 [$LnW_{10}O_{36}$] (LnW_{10}) composites on the surface of silica particles modified with 3-aminopropyltriethoxysilane (APS) and investigated their luminescence properties [15,16]. It is interesting for us to employ other polymers to modify the surface of silica nanoparticles and fabricate the luminescent LnW_{10}/SiO_2 particles with defined core–shell structures which may have interesting properties. Polyethyleneimine (PEI) is a kind of water-soluble polyamine and is a cationic polymer with branched structure in which plentiful amine groups can bond with both transition metal ions and negatively charged colloids. Due to the chemical and physisorption properties of PEI, primarily the high cationic charge density, it is able to effectively form nanometric core–shell particles. PEI is widely applied for the assembly of inorganic nanoparticles, such as metal particles, metal oxide particles, metal particles coated with silica, and silica nanospheres [17,18]. The Stöber SiO_2 spheres show some interesting properties such as good chemical stability, low thermal expansion coefficient, and high refractive index that lead to their potential application in optoelectronic devices [19,20]. Therefore, combining the LnW_{10} with promising optical properties and Stöber silica particles decorated with PEI show significance in fabricating optical devices. It is thus of significance to study the optical properties of

* Corresponding author. Tel.: +86 27 67867953; fax: +86 27 67867955.
E-mail address: junwang924@yahoo.com.cn (J. Wang).

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$LnW_{10}/PEI/SiO_2$ particles and local structure of the Eu^{3+} ions in the core–shell nanocomposites.

In this paper, the core–shell structured $LnW_{10}/PEI/SiO_2$ particles with different sizes were fabricated. The experimental results show that SiO_2 modified with PEI possesses the chemisorption ability for LnW_{10} and LnW_{10} particles could be grafted on the silica particles. The hybrid particles exhibit the excellent luminescence properties. The effects of the formation of core–shell particles and the size of particles on the luminescence of Eu^{3+} were investigated in detail. It is found that the control of the size of $LnW_{10}/PEI/SiO_2$ nanoparticles is interesting, which play an important role on their luminescent properties.

2. Experimental sections

2.1. Materials

Tetraethyl orthosilicate, polyethyleneimine (MW. 10,000) were obtained from Beijing Chemistry Co. Ltd, China. Ln_2O_3 (Ln = Eu, Dy) were purchased from Shanghai Yuelong Chemical Reagent Corp.

2.2. Synthesis of colloids and polyoxometalate

The $Na_9[LnW_{10}O_{36}]$ (LnW_{10}, Ln = Eu, Dy) were prepared by the method reported in the literature [21]. Silica particles with different sizes (80 nm noted as $SiO_{2\text{-a}}$, and 240 nm noted as $SiO_{2\text{-b}}$) and were prepared with the Stöber method according to the literature [19].

2.3. Assembly of $LnW_{10}/PEI/SiO_2$ nanocomposites

SiO_2 particles were coated with PEI according to the literature [22]. Briefly, SiO_2 particles were coated with PEI in 0.1 M KCl aqueous solutions, and the pH was adjusted to 8.0 with 0.1 M HCl. The mass ratio of PEI to SiO_2 was about 1:10. After 3 h, the centrifugation/wash cycles were operated to remove unabsorbed PEI. Then, 1 g silica particles coated with PEI was followed by the addition of the 50 ml LnW_{10} aqueous solutions (2 mg/ml). Finally, the $LnW_{10}/PEI/SiO_2$ nanocomposites were washed with water three times to remove unadsorbed LnW_{10}.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were measured with a Nicolet Nexus 470 FT/IR infrared spectrophotometer with the KBr pellet technique. Scanning electron microscopy (SEM) images were taken by a JEOL 6700-F apparatus at 5.0 kV. Transmission electron microscope (TEM) micrographs were obtained on a Philips/Tecnai 20 G2 S-Twin apparatus at 200 kV after dilute dispersions of the particles were dropped onto copper grids. The excitation and emission spectra were taken on a Spex spectrofluorometer using xenon lamp as excitation source. All the measurements were performed at room temperature.

3. Result and discussion

3.1. The illustration of the formation of $EuW_{10}/PEI/SiO_2$ particles

The illustration of the formation of $EuW_{10}/PEI/SiO_2$ particles was shown in Fig. 1. The surfaces of silica were covered by OH groups. The surface Si–OH groups play an important role in bonding LnW_{10} to form shells on silica surface. PEI can easily adsorb on SiO_2 surface through the hydrogen bonding between amino-group of PEI molecules and –OH group of SiO_2 surface [18]. PEI was bonded onto the surfaces of silica particles in the manner of "grafting onto", then lanthanide polyanions were grafted on the amide bond by an electrostatic bond between the amino-group and the negatively charged polyoxometalate.

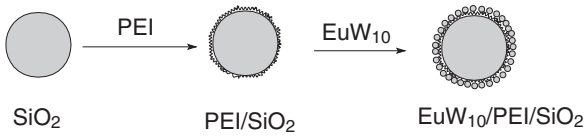

Fig. 1. The illustration of the formation of $EuW_{10}/PEI/SiO_2$ particles.

3.2. IR spectrum

The FT-IR spectrum of $EuW_{10}/PEI/SiO_{2\text{-b}}$ particles was shown in Fig. 2. Besides the characteristic peak of the Si–O–Si stretching vibration at 1100 cm^{-1}, it shows the bands at 993 and 820 cm^{-1} which are attributed to the antisymmetric and symmetric –Si–OC_2H_5 stretching modes, respectively. The broad absorptions in the range of at 3000–3800 (max = 3450 cm^{-1}) is attributed to the silanols on the surface of silica particles [23]. The particles show a characteristic peak at 1640 cm^{-1}, which are ascribed to the characteristic N–H bending vibrations. The peaks at 1468, 1420 and 1380 cm^{-1} correspond to $-CH_3$ and $-CH_2$ bending vibrations. The characteristic peaks of polyoxometalates EuW_{10} appeared at 951 cm^{-1}, 860 cm^{-1}, and 781 cm^{-1}, which are due to the W–O_d, W–O_b–W and W–O_c–W transitions, respectively.

3.3. SEM and TEM

The SEM images of $EuW_{10}/PEI/SiO_{2\ (a,\ b)}$ particles and the size distribution of particles are shown in Fig. 3. As expected, this method led to well-defined spherical nano- and micrometric-particles in the cases. It shows that the samples obtained were non-agglomerated spherical particles with slightly rough surfaces. The $EuW_{10}/PEI/SiO_{2\ (a,\ b)}$ nanoparticles are directly observed by TEM, as shown in Fig. 4. It showed the particles with a basic core–shell spherical morphology. In the image, the particles display dark cores surrounded by thin gray shell which is the EuW_{10}/PEI layer grafted on the silica, indicating the core–shell structure of $EuW_{10}/PEI/SiO_2$. The structure of hybrid particle is roughly consistent with the expected model of such particles from the idealized picture presented in Fig. 1.

3.4. Luminescence properties

The $EuW_{10}/PEI/SiO_{2\ (a,\ b)}$ particles exhibit strong luminescence which was observed by naked eyes under UV lamp, indicating that EuW_{10} particles were grafted on the silica particles. The formation and structures of EuW_{10} on the silica particles can be further confirmed by the luminescence characteristics of Eu^{3+}. The excitation spectra of EuW_{10} solid and $EuW_{10}/PEI/SiO_{2\ (a,\ b)}$ particles were shown in Fig. 5 (normalization). The excitation spectrum of EuW_{10} solid shows a strong

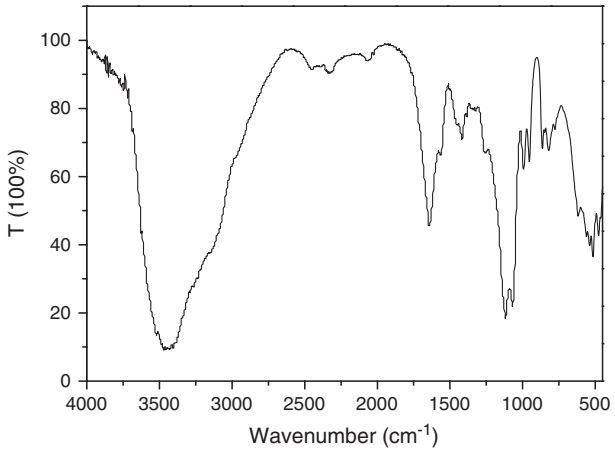

Fig. 2. IR spectrum of $EuW_{10}/PEI/SiO_{2\text{-b}}$.