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Bifunctional composite microspheres of silica/lanthanide-polyoxometalates/Au: Study on luminescence and catalytic properties

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ABSTRACT

In this paper, the synthesis and properties of composite silica microspheres grafted with gold nanoparticles and lanthanide-polyoxometalates are described. This synthesis employs polyethyleneimine as the crosslink polymer to immobilize the Au nanoparticles and lanthanide-polyoxometalates on silica spheres, which results in the formation of bifunctional composite microspheres of silica/lanthanide-polyoxometalates/Au. The composite material was found to be catalytically active in the oxidation of styrene, and benzaldehyde and styrene oxide were the main products. Catalyzed oxidation of styrene demonstrates the size-dependent activity of catalysts and the smaller catalyst shows the higher selectivity. Moreover, the composite particles show bright red luminescence under UV light, which could be seen by naked eyes. The luminescence properties of composite material and the effect of Au nanoparticles on the luminescence of Eu ion were investigated, and energy could be more effectively transferred from ligand to lanthanide ion when Au nanoparticles were grafted on silica spheres. The integration of luminescent components and Au particles makes it possible to label catalyst and monitor the catalyzed reactions.

1. Introduction

Polyoxometalates (POMs), as early transition metal oxide clusters, bear many properties that make them attractive for applications in catalysis, biology, magnetism, optics, and medicine [1–3]. Within the class of POMs, the polyoxoanions accommodating luminescent lanthanide are an important subclass. Luminescent lanthanide-substituted POMs (Ln-POMs) are of both fundamental and technical interest due to their characteristic luminescence properties, such as extremely sharp emission bands, long lifetime, large Stokes shift and potential high internal quantum efficiency. They have potential applications in luminescence devices and biomedical applications involving the labels, cathode ray tubes, lamps, bioimaging, bioassay, and nanomedicine [4–6]. However, the application of lanthanide-POMs in optical devices and biomedical applications depends on the fabrication of nanomaterials. Therefore, Ln-POMs need to be grafted on various particles sometimes. Stöber silica nanoparticles are highly hydrophilic and easy to prepare, separate, surface modify, and label. They can be fabricated controllably into spheres from nano- to micrometer sizes and their surface could be decorated with various composites [7,8]. Therefore, they could be used in core–shell structure materials to support luminescent particles. Luminescent composite nanoparticles could be prepared by incorporation of luminescent materials during particle formation or by coupling of luminescent materials to the particle surface. In our previous study, we assembled Ln-POM composites on the surface of silica particles modified with bridging organics and investigated their core–shell structures and luminescence properties [9–11]. It is interesting for us to fabricate more functional particles base on lanthanide-POM and investigate their properties further.

Recently, bifunctional nanoparticles with core–shell structures have gained significant interest due to the properties that arise from the combination of different compositions of particles on the nanoscale. Bifunctional nanoparticles could integrate two formerly distinct functionalities into a single entity with superior and sometimes unprecedented properties. Au–Fe_3O_4 nanoparticles represent an example for a hybrid system which exhibits the plasmonic and catalytic (Au) and magnetic (Fe_3O_4) activities [12–14]. The combination of Au with metals such as Pd or Pt offers the attractive option for label-free in situ monitoring of Pd or Pt catalyzed reactions by using surface-enhanced Raman scattering [15,16]. Despite the progress achieved of bifunctional particles, it is still a challenge to synthesize bifunctional hybrid particles with nanostructures. Among these noble metals, gold particles have recently been attracting rapidly growing interests because of their optical properties such as surface plasmon resonance (SPR) and catalytic activity [17,18]. Gold nanoparticles could be attached on silica with high surface area to prevent aggregation during the reaction to be catalyzed, which show the high catalytic activity [19,20]. Moreover, it is known that Au is a kind of plasmonic material which could affect the luminescence properties and enhance fluorescence quantum yield [21]. Therefore, it is interesting for

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us to integrate Au nanoparticles and luminescent Ln-POMs into a single entity and fabricate the bifunctional nanoparticles. The integration of luminescent lanthanide-POM components and Au metal particles onto biocompatible silica spheres makes it possible to label catalyst, monitor the catalyzed reactions and improve luminescent properties. The development of synthetic methods for making core–shell nanostructures consisting of Au and luminescent particles has emerged as an attractive research area in material chemistry, which has the application in labeling, optics and catalysis. Therefore, it shows the important significance to develop the method to fabricate bifunctional composite particles containing Au nanoparticles and lanthanide-POM, and investigate on the catalysis properties of Au and the effect of Au nanoparticles on the luminescence properties of lanthanide-POM.

In this paper, we report a construction of bifunctional silica microspheres grafted with Au nanoparticles and Ln-POM. As a result, the composite microspheres show the high performance in catalytic oxidation of styrene. Meanwhile, the microspheres show the strong red luminescence which could be observed by naked eyes under UV. The effect of the size and incorporation of Au nanoparticles on the luminescence of Eu^{3+} was investigated. It is found that energy could be more effectively transferred from ligand to lanthanide when Au nanoparticles were grafted on silica spheres.

2. Experimental section

2.1. Reagents and materials

$HAuCl_4 \cdot 3H_2O$, polyethyleneimine (PEI, 30% solution, wt 10,000), styrene and tert-butyl hydroperoxide (TBHP) are analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

2.2. Fabrication of $SiO_2/EuW_{10}/Au$ nanoparticles

The Stöber SiO_2 spheres (140 nm SiO_2 noted as $SiO_{2\text{-a}}$, and 550 nm SiO_2 noted as $SiO_{2\text{-b}}$) were synthesized by following the Stöber method [22]. $Na_9[EuW_{10}O_{36}]$ (EuW_{10}) were synthesized according to the literature [23]. SiO_2 particles were firstly decorated with PEI according to the literature with slight modification [24]. Briefly, 1.5 g silica particles and 0.5 g PEI were dispersed in 70 ml 0.1 M KCl aqueous solution, and the pH was adjusted to 7.0 with dilute HCl. The SiO_2 particles decorated with PEI suspension were stirred vigorously at room temperature for 24 h, and then the products were recovered by centrifugation and washed with water three times. Then 30 ml EuW_{10} (150 mg) solution was added in the 100 ml suspension of SiO_2 decorated with PEI and stirred for 12 h at room temperature. Finally, the SiO_2/EuW_{10} suspension was centrifuged and washed three times to remove unabsorbed EuW_{10}. This yielded the white SiO_2/EuW_{10} nanoparticles. Au nanoparticles were prepared by the literature method [25]. 1 g SiO_2/EuW_{10} particles were dispersed in 100 ml aqueous solution. Then 100 ml Au nanoparticles solution was added to the above SiO_2/EuW_{10} suspension and stirred for 12 h at room temperature. Finally, the suspension was centrifuged, washed with water and dried. The purple $SiO_2/EuW_{10}/Au$ particles were obtained.

2.3. Preparation of SiO_2/EuW_{10} and $SiO_2/EuW_{10}/Au$ particles modified electrode

The glassy carbon electrode (GCE) was polished with gamma alumina powders, then washed with ethanol and distilled water in an ultrasonic bath, and finally dried with N_2 gas. Ten microliters sonicated SiO_2/EuW_{10} or $SiO_2/EuW_{10}/Au$ suspension in nafion/ethanol (V: V = 1:20) was dropped on the pretreated bare GCE using a micropipette tip and dried in air.

2.4. Catalytic evaluation

The oxidation of styrene was studied as a model reaction to probe the catalytic activity of gold nanoparticles. In a typical catalytic test, 160 mg as-synthesized $SiO_2/EuW_{10}/Au$ particles and 10 mmol styrene were added to 12 ml toluene and stirred for 30 min at room temperature in a round-bottom flask equipped with a condenser. After the temperature rose to 80 °C, 3.0 ml tert-butyl hydroperoxide (TBHP) was added in drops to initiate the reaction. Samples taken from the catalytic reaction were centrifuged, and the supernatant fluids were identified by gas chromatography/mass spectrometry detector (GC-MSD).

2.5. Characterizations

Fourier transform infrared (FT-IR) spectra were measured with a Nicolet Nexus 470 FT/IR infrared spectrophotometer with the KBr pellet technique. The UV–vis absorption spectra of the samples were measured with a UV-2550 apparatus. Transmission electron microscope (TEM) images of the samples were obtained with a Philips/Tecnai 20 G2 S-Twin apparatus at 200 kV. Scanning electron microscopy (SEM) images were taken by a JEOL 6700-F apparatus at 15 kV. Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance X-ray diffractometer equipped with Cu Kα radiation. The excitation and emission spectra were taken on a Spex spectrofluorometer using xenon lamp as excitation source. Cyclic voltammograms (CVs) were obtained on the CHI660D electrochemical work station. GC-MSD was tested on Thermo-DSQ II.

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectra of $SiO_{2\text{-a}}/EuW_{10}/Au$ and $SiO_{2\text{-a}}/EuW_{10}$ particles are shown in Fig. 1. For $SiO_{2\text{-a}}/EuW_{10}$ particles, the strong broad band at the wavenumber region of 3300–3500 cm^{-1} is the characteristic peak of $-NH_2$ and $-OH$ stretching vibrations, which is overlapping in the region. The bands between 1570 cm^{-1} and 1640 cm^{-1} can be assigned as $-NH_2$ and $-NH$ bending vibrations. The particles show the presence of Si–O–Si (asymmetric stretch) at around 1090 cm^{-1}. The spectra also show the presence of organic peaks due to C−H bending vibrations in the regions 1400–1500 cm^{-1}. The characteristic peaks of polyoxometalates EuW_{10} appeared at 951 cm^{-1}, 860 cm^{-1}, 776 cm^{-1}, which are due to the W–O_d, W–O_b–W and W–O_c–W transitions, respectively [26]. A significant change in the spectra, as observed in Fig. 1, is the shape and position of $-NH_2$ and $-NH$ bending vibrations of $SiO_{2\text{-a}}/EuW_{10}/Au$, which are different from those of $SiO_{2\text{-a}}/EuW_{10}$. The significant difference indicated that

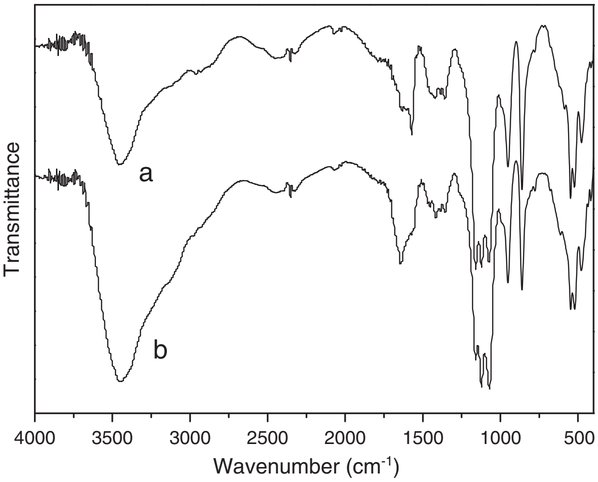

Fig. 1. FT-IR spectra of $SiO_{2\text{-a}}/EuW_{10}/Au$ (a) and $SiO_{2\text{-a}}/EuW_{10}$ (b).