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Study on core–shell–shell structured nanoparticles with magnetic and luminescent features: Construction, characterization and oxygen-sensing behavior

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ABSTRACT

In this paper, we construct core–shell–shell structured nanoparticles, where magnetic Fe_3O_4 nanoparticles are used as the inner core, mesoporous silica functionalized with phosphorescent Ru(II) complex is used as the outer shell, and the middle shell which is composed of amorphous silica is introduced to minimize the negative effect from the inner core on the sensing probes. The obtained magnetic–luminescent composite nanoparticles are characterized by XRD analysis, IR spectrum, electron microscopy, fluorescence microscopy, thermogravimetric analysis and nitrogen adsorption and desorption, confirming the core–shell–shell structure. The magnetic and photophysical properties of the composite nanoparticles are investigated in detail. Data suggest that the nanoparticles show a smaller saturation magnetization value compared with that of Fe_3O_4 nanoparticles. The composite namoparticles are red-emitting ones, and the emission is sensitive towards oxygen concentration variations with sensitivity of 4.1 and response time of 7 s.

1. Introduction

Iron oxide nanoparticles have recently attracted much attention due to their virtues of low toxicity, biocompatibility and environmental friendliness [1,2]. The magnetic character makes iron oxide nanoparticles removable by external magnetic field, which is crucial for site-specific delivery, carrier recycling and similar applications. Above features make magnetic iron oxide nanoparticles a promising candidate in biomedical applications such as drug delivery and targeting, cell sorting and isolating, magnetic resonance imaging, and so on [3,4]. To meet various demands in practical applications, multifunctional iron oxide nanoparticles with desirable chemical and optical characteristics are needed. Since magnetic nanoparticles usually tend to aggregate and thus compromise their dispersal, bare magnetic nanoparticles should be coated or covered with suitable shields [5].

The concept of core–shell structured nanoparticles, which can realize the combination of respective feature from each component or achieve cooperatively enhanced performance, is then proposed to satisfy the above requirements [6,7]. For a representative core–shell structured nanoparticle, the inner core is composed of Fe_2O_3 or Fe_3O_4 nanospheres which provides fundamental magnetic feature. The outer shell is usually composed of amorphous silica due to its low toxicity and good compatibility with biological systems. In addition, the surface of amorphous silica can be chemically modified to attach optical, physical or other functional groups, meeting the multifunctional requirement for practical applications. For example, Wang et al. have reported multifunctional core–shell structured nanoparticles, where magnetic Fe_2O_3 nanoparticles are used as the inner core and SiO_2 doped with phosphorescent Ru(II) complex is used as the outer shell [8]. The phosphorescent emission of those nanoparticles is found to be sensitive towards molecular oxygen, showing oxygen-sensing performance with sensitivity of 1.48. Here the sensitivity is defined as the ratio of emission intensity under pure N_2 to that under pure O_2. This sensitivity value, however, is not satisfactory enough compared with those of oxygen-sensing systems based on silica matrixes and similar phosphorescent Ru(II) probes [9,10], which means that the outer shell of core–shell structured nanoparticles should be further improved to accelerate analyte (O_2) transport and penetration.

Silica mesoporous structures are particularly attractive to serve as the supporting matrix for oxygen-sensing probes since they have homogeneous channels [9,10]. It has been reported that those porous channels can transport analyte efficiently, leading to uniform quenching around sensing probes, high sensitivity and linear response [9]. In addition, the silica mesoporous structures are usually constructed through a sol–gel procedure, which makes their further functionalization more convenient.

In order to improve the oxygen-sensing performance, in this paper, we modified the core–shell structure as a core–shell–shell

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one, where the inner core is composed of Fe_3O_4 nanospheres, the outer shell consists of mesoporous silica (MCM-41 molecular sieve), which is used as the supporting matrix for sensing probes, and the middle shell which is composed of amorphous silica is introduced to minimize the negative effect from the inner core on sensing probes. A conventional Ru(II) complex shown in Scheme 1 is then selected as the sensing probe to evaluate the advantages of the core–shell–shell structure. Their magnetic characterization, morphology and sensing performance are presented and discussed in detail.

2. Experimental section

The fabrication route for the core–shell–shell structured nanoparticles (referred to as Ru-MCM-41@SiO_2@Fe_3O_4) is shown in Scheme 1. 1,10-phenanthroline (referred to as Phen), 3-(triethoxysilyl)propyl isocyanate (referred to as TEPIC) and anhydrous $RuCl_3$ (99.99%) were purchased from Aldrich Chemicals Co. and used without further purifications. $NH_3 \cdot H_2O$, HCl, NH_4AC, *N*,*N*-dimethylformamide (DMF), tetraethoxysilane (referred to as TEOS), $FeCl_3 \cdot 6H_2O$, anhydrous sodium acetate, ethylene glycol, *n*-hexane, chloroform, 4-hydroxybenzaldehyde, cetyltrimethylammonium bromide (CTAB), toluene and ethanol were obtained from Beijing Chemical Company. 1,10-phenanthroline-5,6-dione (referred to as Phen-O) was synthesized according to a literature procedure with 1,10-phenanthroline as the starting material [9]. The precursor Ru(II) complex of $[Ru(Phen)_2]Cl_2$ and $[Ru(Phen)_2Phen\text{-}Ph\text{-}OH]Cl_2$ were synthesized according to a literature procedure [9]. All organic solvents were purified through standard procedures. The water used in this work was deionized.

2.1. Synthesis of Phen-Ph-OH

4-(1H-imidazo[4,5-f] [1,10]phenanthrolin-2-yl)phenol (referred to as Phen-Ph-OH) was synthesized by the following procedure. 1 g of Phen-O, 0.565 g of 4-hydroxybenzaldehyde and 5.86 g of NH_4AC added into 25 mL of HAC. The mixture was heated to reflux for 5 h. After cooling, the mixture was poured into 300 mL of cold water. The solution was neutralized to pH=7. The solid was filtered and washed with plenty of water. The crude product was further purified by recrystallization from hot ethanol:water (V:V=3:7). Yield: 1.1 g (70%). ^1H NMR (300 MHz, $CDCl_3$): 7.03–7.11 (d, 2H), 7.75–7.82 (m, 2H), 8.13–8.17 (d, 2H), 8.89–8.97 (dd, 2H), 8.94–9.01 (dd, 2H), 10.04 (O–H), 13.47 (N–H). IR (KBr): 3389 cm^{-1} (stretch OH).

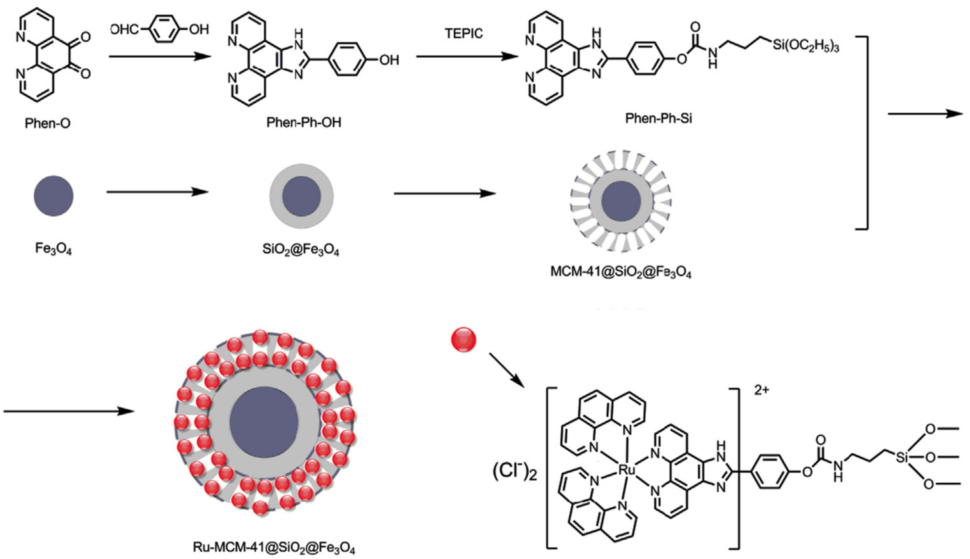
2.2. Synthesis of Phen-Ph-Si

4-(1H-imidazo [4,5-f] [1,10] phenanthrolin-2-yl)phenyl 3-(triethoxysilyl) propylcarbamate (referred to as Phen-Ph-Si) was synthesized by the following procedure. 0.1 g of Phen-Ph-OH was added into 4 mL of TEPIC under N_2 atmosphere. The mixture was treated with ultrasonic bath for 20 min and then heated to 80 °C for 3 days. After cooling, the mixture was poured into 50 mL of cold *n*-hexane (0 °C). The obtained yellow solid product was filtered and washed with *n*-hexane. This crude product was further purified by recrystallization from the mixed solvent of $CHCl_3$:*n*-hexane (V:V=2:8). Yield: 0.12 g (67%). ^1H NMR (300 MHz, $CDCl_3$): 0.57–0.62 (t, 2H), 1.13–1.18 (t, 9H), 1.57–1.58 (m, 2H), 3.05–3.07 (m, 2H), 3.78–3.81 (q, 6H), 7.37 (d, 2H), 7.85–7.91 (m, 2H), 8.24–8.29 (d, 2H), 8.94 (dd, 2H), 9.05 (dd, 2H), 12.97 (NH). IR (KBr): 1689 cm^{-1} (C=O stretch). Anal. Calcd for $C_{29}N_5O_5H_{33}Si$: C, 62.23; H, 5.94; N, 12.51. Found: C, 62.17; H, 6.02; N, 12.39.

2.3. Preparation of MCM-41@SiO_2@Fe_3O_4

The precursor of MCM-41@SiO_2@Fe_3O_4 was obtained by the following procedure. Fe_3O_4 nanospheres were prepared through a literature procedure [11]. Then the fresh Fe_3O_4 nanospheres (0.05 g) were treated by ethanol under ultrasonic bath for 30 min. A volume of 10 mL deionized water, 0.5 mL of $NH_3 \cdot H_2O$ and 0.05 mL of TEOS were added into the fresh Fe_3O_4 solution. The solution was mechanically stirred for 5 h under N_2 protection at room temperature. The resulting solid was collected and obtained as SiO_2@Fe_3O_4 which was used directly for the next procedure without further purification.

Above obtained fresh SiO_2@Fe_3O_4 was added into the solution of 0.15 g of CTAB, 0.6 mL of $NH_3 \cdot H_2O$ and 40 mL of deionized water. The mixture was mechanically stirred for 30 min at room temperature. Then 0.4 mL of TEOS was added into the solution under vigorously stirring. The final solution was mechanically stirred for 8 h under N_2 protection at room temperature. The resulting solid product was carefully collected and dried in vacuum at 60 °C for 12 h. The remaining template reagent of CTAB was removed by the following extraction procedure. Above obtained product was added into the mixed solution of 5 mL of



Scheme 1. The fabrication route for the core–shell–shell structured nanoparticles of Ru-MCM-41@SiO_2@Fe_3O_4