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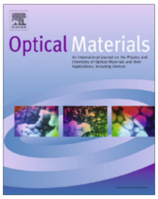

A magnetic mesoporous nanocomposite modified with a ruthenium complex for site-specific molecular oxygen sensing: Construction and characterization

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ABSTRACT

In this paper, we constructed a core–shell structured organic–inorganic hybrid composite, where superparamagnetic ferroferric oxide and silica molecular sieve MCM-41 were used as the inner core and the outer shell, respectively. A Ru(II) complex was covalently grafted into these MCM-41 tunnels. Electron microscopy images, XRD analysis, IR spectra, thermogravimetry and N_2 adsorption/desorption analysis were applied to confirm this Ru(II)-functionalized hybrid composite. Emission of this composite decreased with increasing O_2 concentrations, which made itself an O_2 sensing system. High selectivity (12.2), linear working curve (linearity = 0.99) and short response time (12 s) were obtained from this composite.

1. Introduction

Nanocomposite materials are gaining more and more research interests since they combine and preserve virtues of each component, offering shinning characters compared to their corresponding inorganic or organic counterparts [1,2]. Generally, organic components serve as a functional component to meet application requirements. Inorganic components usually have high mechanical strength and good stability and thus can be applied as a supporting matrix for organic components [2,3]. These organic and inorganic components are combined together through various hybrid structures, core–shell, Janus and hollow for example, to meet applications for optical sensing, solar cells, optoelectronic devices, catalysts and so on [2–4].

Many nanocomposite materials for optical sensing have been explored owing to their advantages of fast response, low cost and low requirement for instrumentation. Those for O_2 sensing are particularly interesting since the recognition/quantification of O_2 concentration has been considered important in various branches of chemical industry and engineering, food processing, medicine and environmental protection [5,6]. Compared to traditional O_2 quantification techniques such as Winkler titration and Clark electrode approach, optical oxygen sensing composites are free of drawbacks such as analyte consumption, complicated pre-treatment procedures and fine instrumentation, which makes them attractive for practical application [7,8].

An optical sensing composite is usually composed of a sensing probe and its supporting matrix [9–12]. This supporting matrix disperses probe molecules and allows smooth analyte diffusion, favoring linear response and good sensitivity. There are criteria to be met for an ideal supporting matrix, including high diffusion coefficient, good compatibility with probe and high photostability. These criteria in turn guarantee fast analyte transportation, homogeneous probe dispersal and reliable sensing signals. Among the numerous candidates for supporting matrix, silica molecular sieve MCM-41 has been recommended since it can well satisfy above requirements [11,12].

As for sensing probe, transition metal complexes, especially Ru(II)-based ones, are usually applied since their long-lived excited state can increase collision probability with O_2 molecules, offering a better sensitivity [13–16]. It has been reported that ground state electrons usually localize on metal center, while excited state electrons migrate to diamine ligand. Their onset electronic transition thus has metal-to-ligand-charge-transfer (MLCT) character. It is rational to assume that an increased conjugation chain in diamine ligands can further increase collision probability with O_2 molecules.

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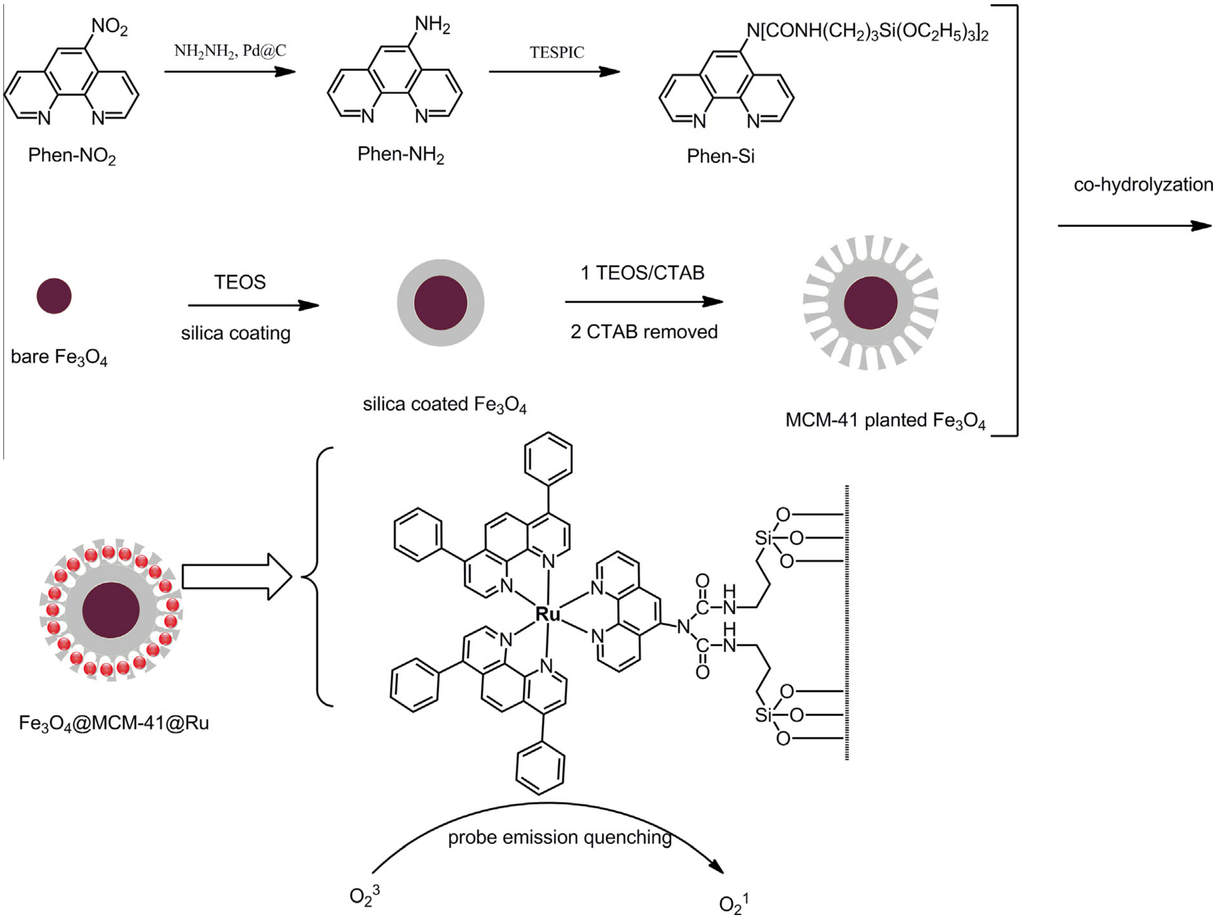

Scheme 1. Design strategy and synthetic route of Fe_3O_4@MCM-41@Ru.

Never the less, these optical oxygen sensing composites all failed to realize site-specific oxygen sensing. Recently, magnetic component has been incorporated into composites for site-specific guiding [17]. Thus, in this paper, we intend to combine a magnetic component into oxygen sensing composite so that site-specific oxygen sensing can be achieved. The corresponding design strategy and synthetic route are shown in Scheme 1 which will be later explained in detail.

2. Experimental details

2.1. General information

All starting compounds and reagents used in this work are summarized as follows. $RuCl_3{\cdot}nH_2O$, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline (Bphen, AR), hydrazine (90%), tetraethoxysilane (TEOS, AR), 5% Pd/C catalyst, odium dodecyl sulfate (SDS, AR), 3-(triethoxysilyl)-propyl isocyanate (TESPIC, AR), cetyltrimethylammonium bromide (CTAB, AR), $FeCl_3$ (AR), H_2SO_4, HNO_3 and other inorganic salts were purchased from Nanyun Chemicals and Reagents Company (Zhengzhou, China). Organic solvents used in this work, including anhydrous ethanol, $CHCl_3$, toluene, *n*-hexane (AR), CH_3CN and tetrahydrofuran (THF), were bought from Yixi Chemical Company (Zhengzhou, China) and purified by standard procedures prior to use. Solvent water was deionized.

Instruments for sample characterization and performance measurement are listed as follows. NMR, IR and mass spectra were taken from a Varian INOVA 300 spectrometer, a Agilent 1100 MS series/AXIMA CFR MALDI/TOF MS spectrometer and a Bruker Vertex 70 FTIR spectrometer (400–4000 cm^{-1}, KBr pellet technique), respectively. XRD patterns were measured with a Rigaku D/Max-Ra X-ray diffractometer ($\lambda = 1.5418$ Å). Morphology was shot by a Hitachi S-4800 microscope and a JEOL JEM-2010 transmission electron microscope, respectively. Magnetic property was analyzed by a MPM5-XL-5 superconducting quantum interference device. N_2 adsorption and desorption isotherms were plotted by a Nova l000 analyzer, using Barrett–Joyner–Halenda (BJH) model. Thermal degradation was studied by a Perkin–Elmer thermal analyzer. Emission spectra were recorded by a Hitachi F-4500 fluorescence spectrophotometer. Oxygen sensing performance was discussed on the basis of steady emission quenching. All operations were carried out at room temperature without further specifications.

2.2. Synthesis of Phen-Si

Silane coupling ligand Phen-Si was synthesized with Phen-NO_2 as a starting compound. Phen-NO_2 was firstly synthesized according to a literature procedure [12]. Then Phen-NO_2 (20 mmol), 5% Pd/C catalyst (0.2 g) and hydrazine (10 mL) were dissolved in ethanol (25 mL) and heated to reflux under N_2 protection for 10 h. After cooling, this mixture was filtered. The resulting solution was vaporized. Crude product was recrystallized in hot ethanol/H_2O (V:V = 2:1) to give Phen-NH_2 as yellow powder. ^1H NMR($CDCl_3$, 300 MHz): δ 6.05 (s, 2H), 6.81 (s, 1H), 7.47 (m, 1H), 7.70 (m, 1H), 8.01 (d, 1H), 8.62 (m, 2H), 9.01 (d, 1H). MS *m*/*z*: $[m+1]^+$ calc. for $C_{12}H_9N_3$, 195.1; found, 196.1.