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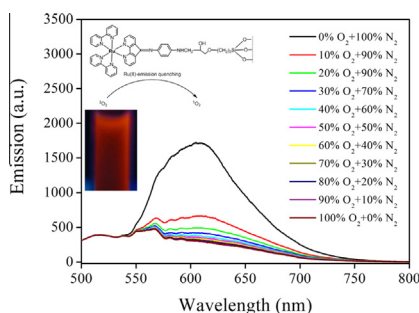
On a magnetic-luminescent nanocomposite for oxygen sensing application: Construction, characterization and sensing performance

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HIGHLIGHTS

- A magnetic-luminescence nanocomposite for oxygen sensing was reported.
- Fe₃O₄ and MCM-41 were chosen as the inner core and the outer shell, respectively.
- A Ru(II) complex was grafted into MCM-41 shell, serving as sensing probe.
- Sensitivity of 5.8 and response time of 16 s were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper was devoted to the construction of a magnetic-luminescence nanocomposite for oxygen sensing application, where superparamagnetic Fe₃O₄ and silica molecular sieve MCM-41 were chosen as the inner core and the outer shell, respectively. A Ru(II) complex was grafted into MCM-41 shell through a coupling ligand N1-(5H-cyclopenta[1,2-b:5,4-b']dipyridin-5-ylidene)benzene-1,4-diamine (denoted as Dafo-Ph-NH₂). The final composite was analyzed by electron microscope images, XRD, IR spectra, thermogravimetry and N₂ adsorption/desorption. Oxygen sensing performance of this composite was evaluated. Sensitivity of 5.8 (the ratio of emission intensity in pure N₂ to that in pure O₂) and response time of 16 s were obtained with good photostability.

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Introduction

The development for concentration quantification of molecular O₂ has always been considered important owing to its importance in various fields such as chemical industry, food processing, medical treatment and environmental monitoring [1,2]. Various candidates have been proposed and tried, such as Winkler titration and Clark electrode approach [3,4]. As a novel quantification method, optical sensing has shown virtues of short response time, low running cost and limited requirement for instrumentation. In

addition, they suffer no drawbacks during sensing operations, such as analyte consumption and complicated pre-treatment procedures, making them attractive for practical applications [5,6].

Efforts are consequently devoted to the design and construction of optical oxygen sensing systems [7–10]. Compared to those based on pure components, organic–inorganic composite materials for sensing purpose are gaining more and more interests since composite materials combine and maintain advantages from each component [11,12]. In this case, organic component usually serves as a functional part, namely a sensing probe, to meet application requirements. Inorganic component, owing to their good mechanical strength and stability, is usually applied as a supporting matrix. When constructing such optical sensing systems, various

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hybrid structures have been proposed so that individual features of each component can be preserved, including core-shell, inner-hollow and Janus structures [13–17]. Among these candidates, core-shell structure has been considered promising owing to its simple preparation route. In addition, each functional component is tightly connected but separated, favoring the design and combination of composites.

There are criteria to be met for both sensing probe and supporting matrix in an ideal oxygen sensing system. Long excited state lifetime and large conjugation chain are usually desired from sensing probe since they are positive to increase collision probability with O₂ molecules, resulting in high sensitivity. It seems that transition metal complexes, especially Ru(II) complexes, are promising ones. It has been pointed out that their onset electronic transitions are metal-to-ligand-charge-transfer (MLCT) ones, where ground state is composed of metal d orbitals and excited state consists of ligand π^* orbitals [13–16]. Such MLCT transitions are usually triplet ones owing to metal turbulence effect, which makes their excited state lifetime as long as several microseconds. As for supporting matrix, high diffusion coefficient, good stability and compatibility with sensing probe are usually desired. Among the numerous candidates, silica molecular sieve MCM-41 is highly recommended owing to its highly regular tunnels, good stability and compatibility [11,12].

Literatures have reported the combination of Ru(II)-based probe and MCM-41 with high sensitivity, short response time and good stability [11,12]. However, few of above precursive efforts has tried site-specific oxygen sensing [17]. Thus, in this effort, we try to construct a composite with core-shell structure for site-specific oxygen sensing, where Fe₃O₄ and MCM-41 are applied as inner core and outer shell, respectively. A Ru(II) complex is covalently grafted into MCM-41 tunnels, serving as sensing probe. This magnetic-luminescence nanocomposite is further considered and evaluated for site-specific oxygen sensing.

Experimental details

Starting chemicals and equipment information

Starting chemicals of this work are listed below. RuCl₃·nH₂O (AR), 1,10-phenanthroline (Phen), benzene-1,4-diamine, Ru(bpy)₂Cl₂, KOH, KMnO₄, tetraethoxysilane (TEOS, AR), odium dodecyl sulfate (SDS, AR), cetyltrimethylammonium bromide (CTAB, AR), FeCl₃ (AR), *p*-toluene sulfonic acid, 3-glycidyloxypropyl trimethoxysilane (GPTS, AR), NH₃·H₂O (28 wt%) and concentrated HCl were all bought from Sigma-Aldrich Corporation. Organic solvents used in this work, such as anhydrous ethanol, toluene, glycol, CHCl₃, *n*-hexane (AR) and tetrahydrofuran (THF), were purchased from Sigma-Aldrich Corporation. They were redistilled before usage. Solvent water was deionized.

Equipment information is summarized as follows. 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) were used to record NMR, MS and IR spectra, respectively. Magnetic property was obtained from a MPM5-XL-5 superconducting quantum interference device. XRD measurement was performed by a Rigaku D/Max-Ra X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$). N₂ adsorption and desorption measurement was taken with a Nova 1000 analyzer, using Barrett-Joyner-Halenda (BJH) model. Sample morphology was recorded with a Hitachi S-4800 microscope and a JEOL JEM-2010 transmission electron microscope, respectively. Sample thermal degradation was analyzed by a Perkin-Elmer thermal analyzer. Emission spectra were recorded through a Hitachi F-4500 fluorescence spectrophotometer. Emission decay dynamics were

obtained from a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd:yttrium aluminum garnet (YAG) laser as excitation source. A two-channel TEKTRONIX TDS-3052 oscilloscope was used to record decay data. Oxygen sensing evaluation was discussed on the basis of steady emission quenching. Above operations were carried out in the air at room temperature with no specifications.

Synthesis of Dafo-Ph-NH₂

N1-(5H-cyclopenta[1,2-b:5,4-b']dipyridin-5-ylidene)benzene-1,4-diamine (denoted as Dafo-Ph-NH₂) was prepared following a two-step procedure described as follows. First, 5H-cyclopenta[1,2-b:5,4-b']dipyridin-5-one (Dafo) was prepared with Phen as starting reagent following a literature procedure [17]. Then, Dafo (1 mmol), benzene-1,4-diamine (1.2 mmol), *p*-toluene sulfonic acid (0.1 mmol) and toluene (15 mL) were mixed together and heated to reflux for 8 h under N₂ protection. Crude production was purified by recrystallization from ethanol/toluene to give Dafo-Ph-NH₂ as deep red powder. ¹H NMR (CDCl₃): δ 8.77(s, 1H), 8.64(s, 1H), 8.25(s, 1H), 7.37 (s, 2H), 7.03–6.98 (m, 3H), 6.81–6.79 (m, 2H), 5.03(s, 2H). MS *m/z*: [m+1]⁺ calc. for C₁₇H₁₂N₄, 272.1; found, 273.1.

Construction of GPTS-MCM-41@Fe₃O₄

Our supporting matrix GPTS-MCM-41@Fe₃O₄ was prepared following a four-step procedure described as follows. First, Fe₃O₄ magnetic core was fabricated with FeCl₃·6H₂O as starting reagent [17,18]. The mixture of FeCl₃·6H₂O (2.7 g), SDS (1.0 g), NaAc (7.2 g) and glycol (100 mL) was held still at room temperature for half an hour and then poured into a Teflon flask. This flask was sealed into an autoclave and heated to 200 °C for 8 h. After cooling, solid product (Fe₃O₄ particles) was filtered off and washed with plenty of water.

Then this magnetic core was coated with amorphous silica. The mixture of Fe₃O₄ particles (0.1 g) and ethanol (20 mL) was exposed to ultrasonication for half an hour. Ethanol (20 mL), deionized water (10 mL) and concentrated ammonia (0.5 mL) were then added and stirred. TEOS (0.1 g) was slowly added. This resulting mixture was stirred at room temperature for 5 h and centrifuged. Crude product (SiO₂@Fe₃O₄) was collected and washed with plenty of water.

Silica molecular sieve MCM-41 was further planted on SiO₂@Fe₃O₄ following below step. SiO₂@Fe₃O₄ (0.2 g), CTAB (0.15 g), deionized water (40 mL), concentrated ammonia (0.5 mL) and ethanol (30 mL) were mixed together and exposed to ultrasonication for 15 min. Then TEOS (0.4 g) was dropwise added into this mixture and allowed to react at room temperature for 8 h. The resulting mixture was centrifuged and dispersed in ethanol (100 mL) and concentrated HCl (5 mL). This mixture was stirred at room temperature for 2 days to remove template reagent CTAB. The resulting solid product (MCM-41@Fe₃O₄) was collected and washed with plenty of water.

MCM-41@Fe₃O₄ was finally modified with a silane coupling reagent GPTS as follows. The mixture of MCM-41@Fe₃O₄ (0.1 g), GPTS (0.05 g) and anhydrous toluene (15 mL) was heated to reflux under N₂ protection for 10 h. The resulting solid sample (GPTS-MCM-41@Fe₃O₄) was centrifuged, collected and washed with plenty of benzene and ethanol.

Construction of Ru-MCM-41@Fe₃O₄

With above fabricated supporting matrix GPTS-MCM-41@Fe₃O₄, our final site-specific oxygen sensing composite Ru-MCM-41@Fe₃O₄ was constructed following a two-step procedure. The mixture of

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