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On a magnetic-mesoporous composite loaded with emissive Ru(II) complex for oxygen sensing application: Construction, characterization and emission response to oxygen molecules

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ABSTRACT

This paper was devoted to a magnetic-mesoporous composite loaded with emissive Ru(II) complex for oxygen sensing application. Core–shell structure was used for this composite, with superparamagnetic Fe_3O_4 as the core and silica molecular sieve MCM-41 as the shell, respectively. A Ru(II) complex was covalently grafted into MCM-41 tunnels to minimize photobleaching. This core–shell structured composite was analyzed and confirmed by electron microscope images, XRD, IR, TGA and N_2 adsorption/desorption. Photophysical measurement on this composite suggested that its emission was decreased by increasing O_2 concentration, showing sensing behavior through a dynamic mechanism. Oxygen sensitivity of 5.53 and response time of 6 s were observed from this composite with a non-linear Stern–Volmer working plot.

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1. Introduction

Molecular oxygen is an important life-supporting matter. Its recognition and quantification has been widely admitted in various fields, including medical and chemical industries, environmental monitoring, food preservation and processing [1–4]. Traditional methods, such as Winkler titration and Clark electrode approach, generally give precise and reliable results [3,4]. On the other hand, their necessitation for fine instruments and complicated sample pretreatment make them inappropriate for fast and simple O_2 detection.

As a novel technique, optical sensing has been insensitively focused owing to its advantages such as instant response, simple procedure of sample treatment, needing no reference elements and free of analyte consumption. Additionally, optical sensing signals are readily transmitted over a long distance without suffering from electromagnetic interference. Above features make optical sensing a candidate for on-line monitoring and in-field detection [5,6].

Compared to those based on pure components, oxygen sensing systems based on composite materials have been considered attractive since they combine virtues from each component, showing multifunctional characters [7–12]. Generally, an organic component is good at performance modification and thus serve as a sensing part, while an inorganic component acts as a supporting host owing to its good stability and mechanical strength. There are criteria to be met to achieve desired performance: (1) for a sensing part, long lifetime and wide electron distribution of excited state are desired since these two factors guarantee a complete sensing collision with O_2 molecules. Among the numerous proposals, emissive mental complexes have been proved promising since their MLCT based triplet emission can well satisfy above two factors, (MLCT = metal-to-ligand-charge-transfer) [10–17]. In this case, their excited electrons are localized on ligand π^* orbitals of large conjugation planes. Spin–orbit coupling effect makes their lifetime as long as several microseconds, favoring sensing collision [13,16]; (2) for a supporting host, except for good stability and compatibility with sensing component, high diffusion coefficient and uniform microenvironment are desired to achieve uniform sensing. It seems that a silica based one, MCM-41, satisfies these requirements well owing to its highly ordered hexagonal mesoporous tunnels [11,12].

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Novel composite structures have been proposed to optimize performance, such as core–shell, inner-hollow, Yolk shell, etc. [11–14]. Core–shell structure has been well introduced owing to its simple synthetic method and performance preservation, where each component is properly separated without compromising their features. Never the less, above literatures all miss an important factor of site-specific requirement which should be a common demand for practical applications.

Guided by above consideration, this work is devoted to the design and construction of a core–shell structured composite for site-specific oxygen sensing. Its design and construction route is shown as Scheme 1, where Fe_3O_4, MCM-41 and a Ru(II) complex are chosen as core, shell and sensing part, respectively. For a detailed explanation on this core–shell structured composite, please see Supporting information.

2. Experimental

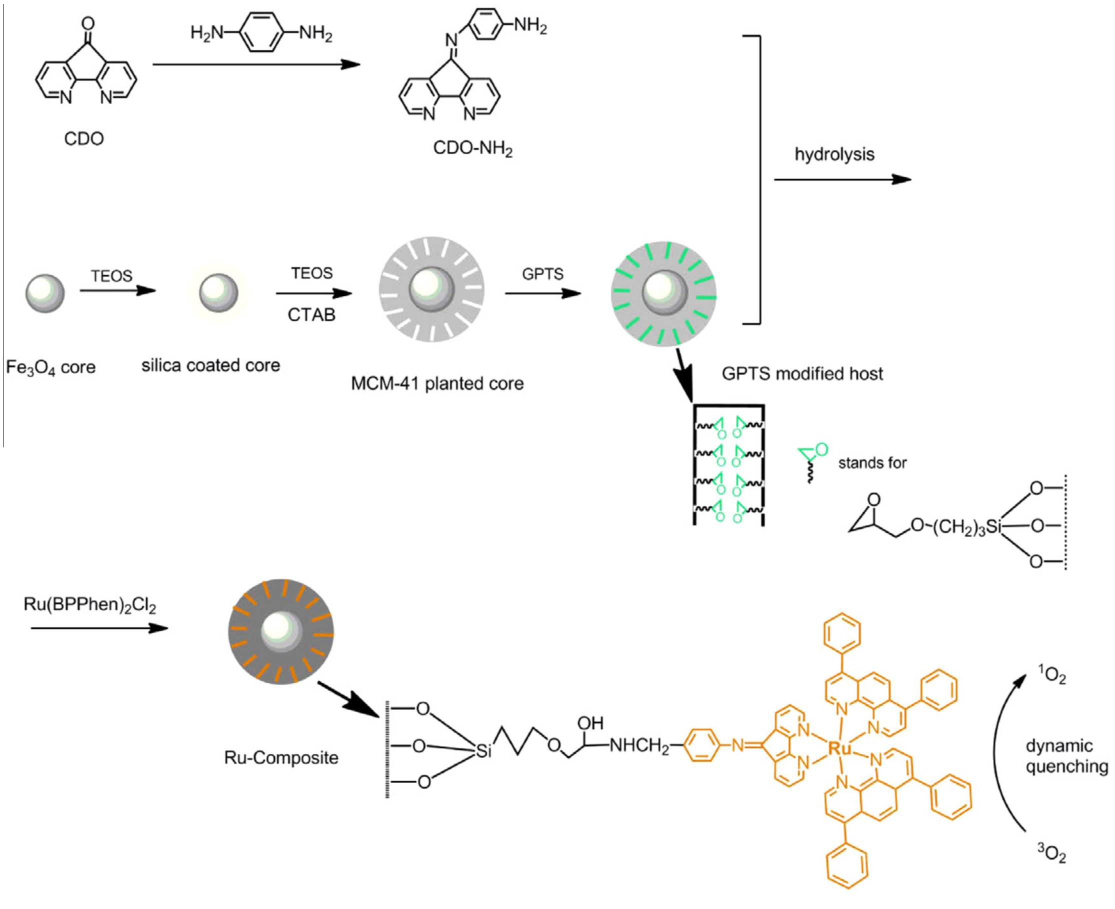
2.1. General information of measurement and reagent

Equipment information for sample characterization is summarized as follows. A Agilent 1100 MS series/AXIMA CFR MALDI/TOF MS spectrometer was responsible for mass spectra. NMR spectra were recorded on a Varian INOVA 300 spectrometer. IR spectra were taken from a Bruker Vertex 70 FTIR spectrometer (400–4000 cm^{-1}, KBr pellet technique). XRD patterns were plotted by a Rigaku D/Max-Ra X-ray diffractometer (λ = 1.5418 Å). Magnetic curves were obtained from a MPM5-XL-5 superconducting quantum interference device. Thermal stability was analyzed with a Perkin-Elmer thermal analyzer. Mesoporous structure was analyzed by a Nova l000 analyzer using Barrett–Joyner–Halenda (BJH) model. A Hitachi S-4800 microscope and a JEOL JEM-2010 transmission electron microscope were applied for sample morphology scan. Photophysical parameters were taken by a Hitachi F-4500 fluorescence spectrophotometer and a 355 nm light generated from the third-harmonic-generator pump, with pulsed Nd: YAG laser as excitation source and a two-channel TEKTRONIX TDS-3052 oscilloscope as recorder, respectively.

Regents for sample synthesis are summarized as follows. 1,10-Phenanthroline (Phen), 4,7-diphenyl-1,10-phenanthroline (DPPhen), benzene-1,4-diamine, tetraethoxysilane (TEOS, AR), odium dodecyl sulfate (SDS, AR), *p*-toluene sulfonic acid, cetyltrimethylammonium bromide (CTAB, AR) and 3-glycidyloxypropyl trimethoxysilane (GPTS, AR) were supplied by Jiaxin Chemicals and Reagents Company (Jinan, China) and used as received. $FeCl_3$ (AR), $KMnO_4$, KOH, $RuCl_3{\cdot}3H_2O$ (AR), concentrated HCl and concentrated ammonia were bought from Jiamei Chemicals and Reagents Company (Chongqing, China). Organic solvents such as $CHCl_3$, CH_2Cl_2, ethanol, toluene, glycol, *n*-hexane (AR), N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Jiaxin Chemicals and Reagents Company (Jinan, China) and purified with standard procedures. Solvent water was deionized.

2.2. CDO-NH_2

A coupling ligand CDO-NH_2 was synthesized using CDO and benzene-1,4-diamine as starting chemicals [15,16]. First, Phen was oxidized by $KMnO_4$ in the presence of KOH following a literature procedure to give CDO as yellow powder [16]. Then, CDO, benzene-1,4-diamine and *p*-toluene sulfonic acid (1:1:0.1, molar ratio) were dissolved in anhydrous toluene and heated to



Scheme 1. Design and construction route of Ru-Composite.

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