



Research paper

Recyclable nitrite ion sensing nanocomposites based on a magnetic-emissive core–shell structure: Characterization and performance



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ABSTRACT

In this paper, two nitrite ion sensing nanocomposites based on a magnetic-emissive core–shell structure were designed and synthesized, using Fe₃O₄ particles as core, a silica molecular sieve (MCM-41) as supporting matrix and two rhodamine derivatives as chemosensors, respectively. These two composite sensing samples were characterized carefully by means of electron microscopy, mesoporous analysis, magnetic response, IR spectra and thermal stability analysis. Emission of these two composite sensing samples was found quenchable by nitrite ion, with limit of detection as low as 1.2 μM. Detailed analysis suggested that these chemosensors followed a static sensing mechanism towards nitrite ion through an additive reaction. These chemosensors could be recycled and recovered by sulphamic acid after nitrite ion sensing.

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1. Introduction

The World Health Organization (WHO) has claimed a maximum limit for nitrite salts in drinking water as 65 μM which are usually used as antistaling reagent for meat and fish preservation. Nitrite in high concentration may react with amines in living bodies and release carcinogenic nitrosamines, increasing risks of cancers and deformities [1–4]. As a target analyte in analytical chemistry, nitrite can be precisely quantified by many modern analytical methods, including capillary electrophoresis, electrometry, chromatography and spectrofluorimetry [5–9]. Regardless of their precise results, these techniques are not suitable for on-line monitoring and in-site detection owing to their requirement for fine instruments and complicated sample pretreatment. In this case, optical sensing has emerged as an attractive analytical method in virtue of its low need for instruments, simple pretreatment procedure and non-invasive character. More interestingly, optical signals are free of electromagnetic interference and thus can be transmitted over a long distance, making optical sensing an attractive candidate for on-line monitoring [10].

Previous reports have explored nitrite optical sensing systems based on fluorescent organic dyes and sensitizers [11–15].

Rhodamine and its derivatives, for example, have been reported as a class of emission turn-off chemosensors since they react with nitrite ion and yield non-emissive nitroso products [14]. For most sensing systems, their chemosensor is usually immobilized and dispersed in a supporting matrix, such as silicates, polymers, metal oxides etc., so that the self-quenching between chemosensor molecules can be minimized, homogeneous microenvironment around chemosensor molecules can be guaranteed [16–18]. A silica molecular sieve, MCM-41, has been proved superior to other candidates owing to its advantages of chemical inertness, high compatibility with dopants, large surface-area-to-volume ratio and highly ordered tunnels which guarantee fluent analyte diffusion and transportation.

Regardless of their promising sensing performance, most nitrite optical sensing systems are not recyclable since they are unable to be re-aggregated after being dispersed in testing samples. This issue may be solved by a hybrid composite material which combines and preserves characters of all its components [19,20]. Magnetic samples have been proved effective in magnetic targeting, sample sorting and isolating [21–23]. A composite material that combines a magnetic component and a nitrite ion sensing chemosensor may realize a recyclable nitrite ion sensing system [24,25].

Given the above consideration, two magnetic-emissive composite samples are designed, aiming at good sensing performance and recyclability. A typical core–shell structure is applied in them,

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using Fe_3O_4 particles as core, MCM-41 as supporting matrix and two rhodamine derivatives as chemosensors, respectively. A full characterization on these two composite samples, along with their nitrite ion sensing performance and recyclability, is reported.

2. Experimental details

2.1. General information

A schematic presentation for the design and construction of these two composite samples, Core&MCM-41&RB and Core&MCM-41&RSB, is shown as Scheme 1. Starting reagents were bought from Shanghai Chemical Company (Shanghai, China) which were used as received, including Lawesson's reagent, rhodamine B, $\text{NH}_3 \cdot \text{H}_2\text{O}$ (28 wt%), tetraethoxysilane (TEOS), anhydrous hydrazine (95 wt%), 3-glycidyloxypropyltrimethoxysilane (GPTS), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), ferric trichloride, anhydrous sodium acetate, concentrated HCl, ethylene glycol and other inorganic metal salts. Organic solvents were provided by Dafa Chemical Company (Tianjin, China) which were redistilled and purified with standard operations, including toluene, *n*-hexane, ethanol, CH_3CN and tetrahydrofuran (THF). Solvent water was deionized.

NMR, IR and mass spectra of samples were collected from a Varian INOVA 300 spectrometer, a Bruker Vertex 70 FTIR ($400\text{--}4000\text{ cm}^{-1}$, KBr pellet technique) and a Agilent 1100 MS series/AXIMA CFR MALDI/TOF (matrix assisted laser desorption ionization/time-of-flight) MS (COMPACT), respectively. XRD patterns were obtained on a Rigaku D/Max-Ra X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$). Emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Emission decay lifetimes were determined using a F900 fluorescence spectrophotometer. Sample morphology analysis was finished on a Hitachi S-4800 microscope and a JEOL JEM-2010 transmission electron microscope, respectively. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Magnetic nature was obtained using a MPM5-XL-5 superconducting quantum interference device (SQUID) magnetometer. Thermal degradation and stability were analyzed by a Perkin-Elmer thermal analyzer. Mesoporous structure was analyzed on a Nova 1000 analyzer with Barrett-Joyner-Halenda (BJH) model [19].

2.2. Synthesis of chemosensors RB-NH₂ and RSB-NH₂

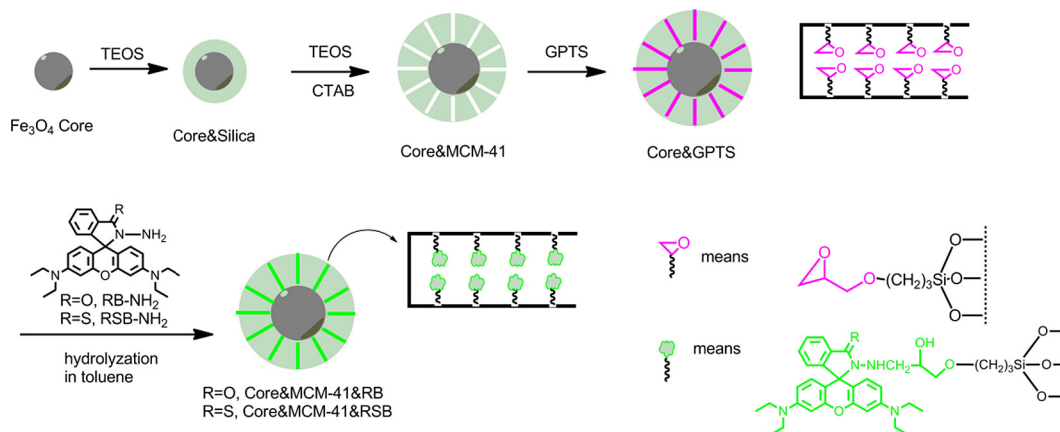
Chemosensor 2-amino-3',6'-bis(diethylamino)spiro[isindoline-1,9'-xanthen]-3-one (RB-NH₂) was synthesized following a

literature method [19]. POCl_3 (5 mL) was dissolved in CH_2Cl_2 (10 mL) and dropwise added into rhodamine solution in CH_2Cl_2 (15 mmol in 30 mL). This solution was heated at $60\text{ }^\circ\text{C}$ for 8 h under N_2 condition. Solvent and excess POCl_3 were extracted under reduced pressure. Solid product was directly mixed with anhydrous acetonitrile (100 mL) and anhydrous hydrazine (10 mL). This mixture was stirred at $0\text{ }^\circ\text{C}$ for 1 h and then at room temperature for 10 h under N_2 condition. Solvent and excess hydrazine were extracted under reduced pressure. Crude product was recrystallized in ethanol/water ($V:V = 2:8$). $^1\text{H NMR}$ (CDCl_3), δ (ppm): 1.30 (t, 12H, NCH_2CH_3), 3.22 (q, 8H, NCH_2CH_3), 3.73 (s, 2H, N-NH_2), 6.31 (dd, 2H, xanthen-H), 6.39 (d, 2H, xanthen-H), 6.44 (d, 2H, xanthen-H), 7.12 (dd, 1H, Ar-H), 7.43 (dd, 2H, Ar-H), 8.16 (dd, 1H, Ar-H). EI-MS m/e : calc. for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_2$, 456.2; found, 456.3 [m]⁺.

Chemosensor 2-amino-3',6'-bis(diethylamino)spiro[isindoline-1,9'-xanthen]-3-thione (RSB-NH₂) was synthesized by treating RB-NH₂ with Lawesson's reagent [26,27]. A mixture of RB-NH₂ (5 mmol), Lawesson's reagent (8 mmol) and anhydrous toluene (25 mL) was heated at $120\text{ }^\circ\text{C}$ for 10 h under N_2 condition. Solvent was extracted under reduced pressure. Crude product was purified on a silica gel column with CH_2Cl_2 as eluent. $^1\text{H NMR}$ (CDCl_3), δ (ppm): 1.33 (t, 12H, NCH_2CH_3), 3.27 (q, 8H, NCH_2CH_3), 3.79 (s, 2H, N-NH_2), 6.30 (dd, 2H, xanthen-H), 6.41 (d, 2H, xanthen-H), 6.47 (d, 2H, xanthen-H), 7.15 (dd, 1H, Ar-H), 7.44 (dd, 2H, Ar-H), 8.17 (dd, 1H, Ar-H). EI-MS m/e : calc. for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{OS}$, 472.2; found, 472.5 [m]⁺.

2.3. Construction of supporting matrix Core&GPTS

The supporting matrix for chemosensors, denoted as Core&GPTS, was synthesized as follows [19]. Firstly, a mixture of glycol (100 mL), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.2 g), SDS (1.5 g) and NaAc (8.0 g) was stirred at room temperature for 30 min and poured into a Teflon flask. After being heated at $200\text{ }^\circ\text{C}$ for 8 h, solid sample was collected and obtained as Fe_3O_4 particles. Then these Fe_3O_4 particles (0.1 g) were dispersed in ethanol (20 mL) and exposed to ultrasonic bath. The following reagents were added sequentially, including ethanol (20 mL), deionized water (10 mL), concentrated ammonia (0.5 mL) and TEOS (0.1 g). This turbid liquid was stirred at room temperature for 6 h, then solid product was separated and washed with deionized water to yield Core&Silica. Ethanol (30 mL), deionized water (40 mL), CTAB (0.15 g), concentrated ammonia (0.5 mL) and TEOS (0.4 g) were sequentially mixed with Core&Silica and stirred at room temperature for 6 h. The resulting solid product was re-dispersed in ethanol (100 mL) and concentrated HCl (5 mL) and stirred at room temperature for 3 days to eliminate



Scheme 1. A schematic presentation for design and construction of Core&MCM-41&RB and Core&MCM-41&RSB.

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