Journal of Luminescence 202 (2018) 502–507

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Design of hybrid inorganic-organic nanosensor based on Fe_3O_4 as the core and recovery features

Nengtao Wu[a], Yiping Tang[b], Min Zeng[d,*], Jinwei Gao[c,d], Xubing Lu[d], Yuhui Zheng[a,*]

[a] *Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China*
[b] *College of Material Science and Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, PR China*
[c] *Guangdong Provincial Engineering Technology Research Center For Transparent Conductive Materials, South China Normal University, Guangzhou 510006, PR China*
[d] *Institute for Advanced Materials, Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, PR China*

ARTICLE INFO

Keywords:
Fluorescent sensor
Magnetic particle
Metal ions
Hybrid material

ABSTRACT

An efficient way to assemble $Fe_3O_4@SiO_2\text{-}NH_2$ nanocomposite has been developed by coupling (3-aminopropyl) trimethoxysilane onto surface of core-shell structure through facile impregnation of $Fe_3O_4@SiO_2$ decorated with amino groups. The key step during the synthesis involves the incorporation of organic fluorophore and amines are treated with 1,8-naphthalic anhydride. The achieved hybrid inorganic-organic nanoparticle gives rise to blue emissions and shows enough stability. Furthermore, Cu^{2+} can be recognized by the organic building block via coordination reaction and the "on-off" quenching effect is observed. The nanosensor provides a response concentration range (1–6 μM) to Cu^{2+} with the detection limit of 0.65 μM. Owing to the magnetic properties, the hybrid nanoprobe can be easily retrieved from aqueous solution for repeated uses via magnetic separation (35 s). This approach will offer an alternative way for designing novel detection systems in biological related fields.

1. Introduction

Due to the fast development of industrialization, Cu^{2+} plays more and more important roles in biological systems of plants, living cells and humans. Its higher concentration will cause a series of physical diseases and it may also induce unexpected threats especially when its level exceeds the cellular necessity [1]. It is closely related to Alzheimer's disease [2], lipid metabolism [3,4], and inflammatory disorders [5]. Therefore, highly selective and sensitive detection of Cu^{2+} will be compulsory in view of physiological and biomedical fields [6]. A few fluorescent dyes or organic structures have been developed for the specific recognition of metal ions [7,8]. Following this idea, naphthalimide derivatives have been studied extensively as responsive sensors because of striking fluorescence properties, such as high quantum yield, particular emission wavelengths and chelating ability [9–12]. However, organic chromophores are difficult to handle in practical uses in terms of poor thermal stability and low mechanical properties. Hence, organic-inorganic hybrid systems have been designed since they can demonstrate both merits of organic and inorganic moieties [13–19]. Functional hybrids are nanoscale materials lying between the organic moieties and inorganic networks. The mild chemistry synthesis strategies such as sol-gel treatments will allow the assembly of inorganic and organic phases at the nanometer range. The general method to construct composite material is the direct inclusion of incorporated chromophores into sol-gel derived matrices. However, leaching problem frequently occurred because no effective chemical bonds would combine the organic units and the sol-gel hosts. In addition, clustering of emissive species would be difficult to control since weak forces existed between the two phases (inorganic and organic). In this study, covalent grafting of the organic building block (1,8-naphthalic anhydride) to the silica matrices through C-N linkages will allow us to avoid the above-mentioned drawbacks.

Magnetite (Fe_3O_4), a common magnetic iron oxide, has received considerable interests due to its physiochemical features and magnetic properties [20,21]. Very recently, Fe_3O_4-based superparamagnetic nanoadsorbents have been developed and the adsorption performances for Cd^{2+} were discussed [22]. Huang et al. incorporated Fe_3O_4 into polyacrylamide hydrogels with the assistance of cellulose. Thermal stability and shear resistance were significantly improved [23]. Another recent study was focused on the construction of chitosan layer modified Fe_3O_4 core, then graphene shell was formed through electrostatic assembly. Based on such core-shell composite, four proteins were enriched with better adsorption capacity [24]. Jiang et al. reported the removal and recovery of phosphate from water via Fe_3O_4@alkali-treated calcium silicate composite and a wide pH range (2.5–13) was achieved [25]. Additionally, functional magnetic silica nanoparticles have been paid

---

[*] Corresponding authors.
E-mail addresses: zengmin@scnu.edu.cn (M. Zeng), yhzheng78@scnu.edu.cn (Y. Zheng).

https://doi.org/10.1016/j.jlumin.2018.06.018
Received 29 April 2018; Received in revised form 30 May 2018; Accepted 8 June 2018

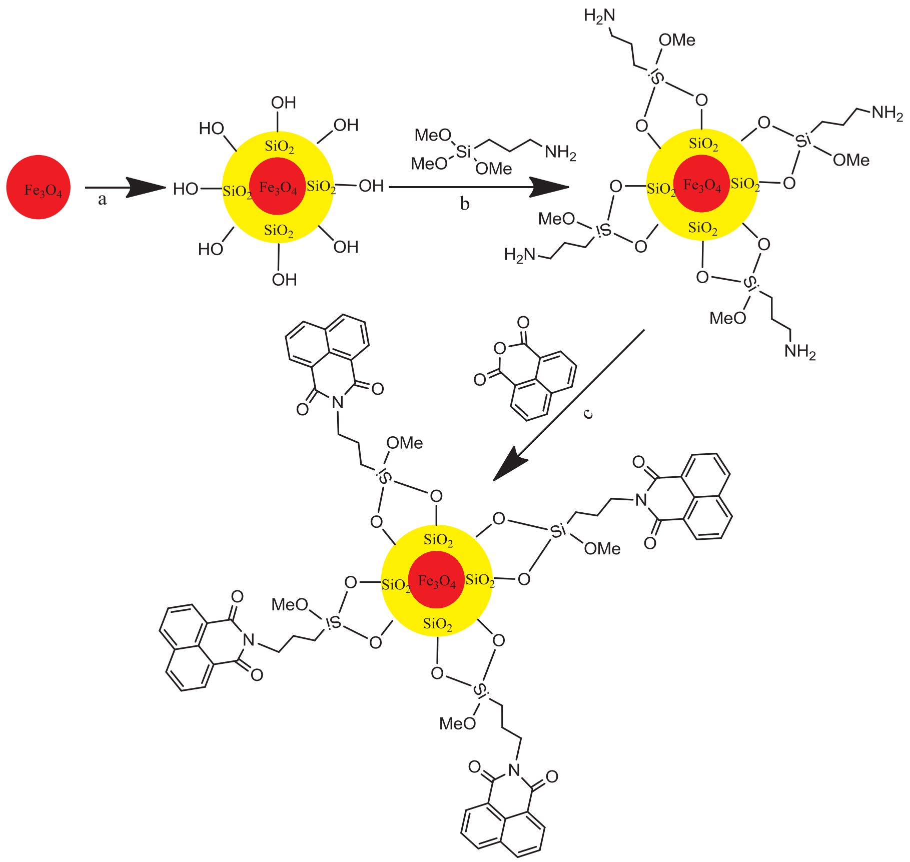

Fig. 1. Scheme representation of the assembly of hybrid nanomaterial ($Fe_3O_4@SiO_2$-NA) (a) sodium silica, HCl (from pH = 12 to pH = 7); sonication (b) EtOH, heating at 60 °C for 10 h (c) reaction in N,N-dimethylformamide (DMF) at 85 °C; stirring for 3.5 h.

much attention based on their compatibility, multiple modes and stability against degradation [26]. In this work, a new nanostructure possessing both magnetism and luminescence has been developed. After Fe_3O_4 nanoparticle was prepared, the core-shell structure of $Fe_3O_4@SiO_2$ was synthesized by the hydrolysis and poly-condensation of sodium silicate. In the next step, amino groups were introduced by the linkages with (3-aminopropyl)trimethoxysilane. Finally, 1,8-naphthenic anhydride (abbreviated as NA) as the molecular scaffold was incorporated and this structure modification led to blue emissions for the sample of $Fe_3O_4@SiO_2$-NA (Fig. 1). Although naphthalimide has been used as sensing molecules for Cu^{2+} ions, this kind of hybrid inorganic-organic system including dual functions (magnetism and luminescence) has never been explored for this metal detection potentials.

2. Experimental

2.1. Materials

Ferric chloride ($FeCl_3{\cdot}6H_2O$,99%), tetraethyl orthosilicate (TEOS, 99.9%), ferrous chloride ($FeCl_2{\cdot}4H_2O$,99.5%), sodium sulfite (Na_2SO_3,97%), ammonia($NH_3{\cdot}H_2O$,25%), sodium silicate ($Na_2SiO_3{\cdot}9H_2O$), (3-aminopropyl)trimethoxysilane(97%), 1,8-naphthalicanhydride (98%)and N,N-Dimethylformamide (DMF) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All the other chemicals were used without further purification.

2.2. Synthesis of Fe_3O_4 nanoparticles

The magnetite nanoparticles were prepared by the conventional co-precipitation method with some modifications [27]. $FeCl_3{\cdot}6H_2O$ (2.3185 g), Na_2SO_3(1.0850 g) and $FeCl_2{\cdot}4H_2O$ (0.8821 g) were dissolved in deionized water (50 mL) within a round bottom flask under stirring at 85 °C. Insoluble impurities were filtered and ammoniac solution 25% (3 mL) was added quickly to the solution. The color of bulk solution turned from orange to black immediately and Fe_3O_4 nanoparticles are generated. The magnetite precipitates were washed twice with deionized water and (95%) ethanol. The final magnetite nanoparticles were precipitated by magnetic decantation and then dried in a vacuum.

2.3. Synthesis of nanostructured silica coated magnetite

The silica coated magnetite were prepared by the literature with some modifications [28]. Sodium silicate (0.3325 g) was dissolved in deionized water (25 mL) and the pH value of the solution was controlled to 12. The sodium silicate solution and Fe_3O_4 nanoparticles (0.3528 g) prepared in the above were poured into a beaker under stirring. The mixture was ultrasonicated for 30 min. Since the solution was alkaline, HCl solution was added dropwise to adjust the pH value to 6–7. The precipitates were washed several times with deionized water by magnetic decantation and then dispersed in 50 mL of ethanol and(3-aminopropyl) triethoxysilane (1.0 mL) was added to the reaction solution. The mixture was stirred at 60 °C for 10 h. The magnetic nanoparticles being surface modified with amine groups were collected by magnetic separation. Then the $Fe_3O_4@SiO_2$-NH_2 was washed with distilled water and ethanol, then dried in a vacuum.

2.4. Surface functionalization of silica coated magnetite with 1,8-naphthalic anhydride

1,8-naphthalic anhydride (0.10 g) and DMF(50 mL) were added in a