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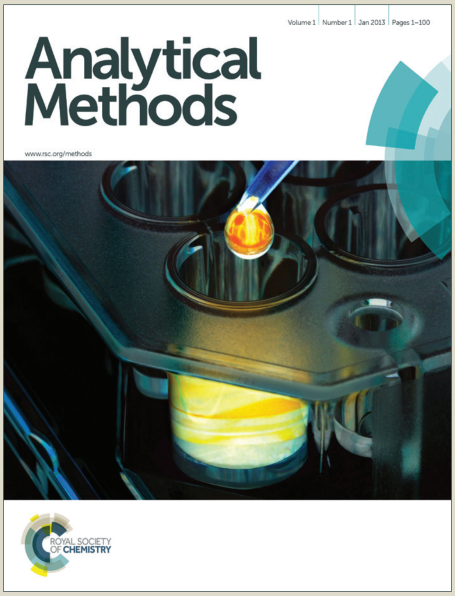

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A New Bifunctional Fluorescent Sensor Based on Naphthalimide-Functionalized Silica Nanoparticles for Detection and Adsorption of Cu^{2+} in Aqueous Solution

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Abstract

A new bifunctional fluorescent sensor for Cu^{2+} based on naphthalimide-functionalized silica nanoparticle (NF-SiO_2) was designed and synthesized. The NF-SiO_2 exhibits excellent fluorescence sensitivity and selectivity towards Cu^{2+} over other metal ions in aqueous media, and it also shows a good adsorption capacity to Cu^{2+}. Moreover, the detection limit of NF-SiO_2 for Cu^{2+} is 1.5×10^{-7} M (S / N = 3) and it can be easily recovered by treatment of a solution of EDTA. These results indicate that this fluorescent sensor may find potential and favorable applications for simple detection and efficient removal of Cu^{2+} in toxicological and environmental fields.

Key words: Commercial silica nanoparticles; Detection; Separation; Trace copper; Integration technology

1 Introduction

Copper ions are widely distributed in the environment, and long-term exposure to them can cause kidney and liver damage.[1] Moreover, a high level of Cu^{2+} in the body can induce a number of diseases including Wilson's disease,[2] Alzheimer's disease,[3] and Meknes syndrome.[4] According to U.S. Environmental Protection Agency, the maximum acceptable concentration of Cu^{2+} in drinking water is about 20 μM.[5] As a result, efficient, economic and viable techniques for selective monitoring or removal of Cu^{2+} in the environmental is highly desirable for protecting human health. Owing to the advantages of simplicity, inexpensive instrumentation and suitability for real-time monitoring of toxic metals, the development of fluorescent sensors for Cu^{2+} detection in the environmental has attracted great research interest in the past few years.[6] However, many traditional fluorescent sensors for Cu^{2+} generally showed effective only in homogeneous aqueous solution and they are not suitable for rapid screening applications or separation, removal and enrichment of Cu^{2+}.[7] Compared to traditional fluorescent sensors for Cu^{2+}, fluorescent solid sensors have many additional advantages such as improving detection selectivity and sensitivity, reusability, and facile integration into detection devices. In addition, a fluorescent solid sensor may endow alternative strategies for developing sensors with the ability of removing, separating and enrichment of heavy metal ions.[8] Therefore, developing fluorescent solid sensor for detection and adsorption of Cu^{2+} or other heavy metal ions is very important and highly desirable.

Up to now, various nanomaterials such as $Fe_3O_4@SiO_2$,[9] gold nanoparticles,[10] nanofibers[11] and silica nanoparticles[12] functionalized by small fluorescent molecules were prepared to detect metal ions or for adsorption purposes. Among them, silica nanoparticles as the matrix material to design fluorescent solid sensors is the most attractive owing to their biocompatibility, stability, large surface area, and easily attaching onto a solid plate such as glass or alumina for utilization as portable sensors.[13] On the other hand, fluoroionophores-functionalized silica nanoparticles as solid chemosensors and adsorbents in heterogeneous solid-liquid phases have many obvious advantages as follows: (1) The silica nanoparticles can be easily isolated from pollutants by filtration, allowing the nanoparticles to be repeatedly utilized as suitable treatment; (2) Fluoroionophores- functionalized silica nanoparticles can separate specific toxic metal ions from the pollutant solution.[12,14]

Recently, a few reports are available regarding fluoroionophores-functionalized silica nanoparticles for detecting Zn^{2+},[15] Hg^{2+},[16] Pb^{2+},[17] Cd^{2+},[18] and Pd^{2+},[19] however fluoroionophores-functionalized silica nanoparticles for Cu^{2+} is still limited.[20] It is still desirable to develop a new fluorescent solid sensor based on silica nanoparticles for detection and adsorption of Cu^{2+} in aqueous media. One of the most common issues faced in developing a new recyclable and reversible solid fluorescent sensor is the chemical and light stability of fluorophores. Among various fluorophores, 1,8-naphthalimide has been widely used as a signaling handle for the design of fluorescent sensors because of its advantageous optical characteristics, such as a large stokes shift, high fluorescence quantum yield, modest excitation and emission wavelengths, high photostability, and high stability towards chemicals.[21]

Consequently, 1, 8-naphthalimide derivatives as fluorescent probes, conjugated silica nanoparticles to prepare fluorescent solid sensors for detecting and removing metal ions has received much attention. For example, Zhang and co-workers reported a new fluorescent solid sensor by clicking alkyne-functionalized naphthalimide derivatives onto azide functionalized SBA-15 and realized a sensitive and selective solid sensor for Hg^{2+} in aqueous solution.[22] Qian et al. used a fluorescent sensor based on silica nanoparticles, naphthalimide derivative and 2, 6-bis (aminomethyl) pyridine for simultaneous detection and separation of trace Hg^{2+} in water and serum.[23] Qian group reported a highly selective heterogeneous fluorescent sensor based on mesoporous silica microspheres for palladium ions.[19] However, to the best of our knowledge, few fluorescent solid sensors based on silica nanoparticles and 1, 8-naphthalimide derivatives for copper ions is available in the literature.[24] Furthermore, the present study about fluorescent solid sensors based on silica nanoparticles for detection and separation of heavy metal ions were mainly focused on the selection of silica nanoparticles, the synthesis of small fluorescent molecules containing hydroxyl, amino and other functional groups, and the method for modifying surface of silica nanoparticles. Nevertheless, commercial and cheap silica nanoparticles (150RMB/500g, 15nm, Aladdin Chemical Reagent Co., Ltd.) as matrix to synthesis fluorescent solid sensors have not been extensively investigated and it is very meaningful in practical application.

Considering the importance of detecting and separating the trace concentration of Cu^{2+} in the environment, we focused on the synthesis and property of naphthalimide derivatives functionalized commercial silica nanoparticle and investigate its selective sensing, adsorption ability and reutilization. As expected, commercial silica nanoparticle as the matrix material also exhibited excellent performance for detection and removal of Cu^{2+} from aqueous solution and this kind of material may pave a simple way to fabricate a fluorescent solid sensor for detection other heavy metal ions.

2 Experimental

2.1 Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Silica nanoparticle (15nm), (3-isocyanatopropyl)-trithoxysilane, 2-chloroacetyl chloride, 4-bromo-1, 8-naphthalic anhydride, piperazine, 8-aminoquinoline and 2-aminoethanol were purchased from Aladdin Chemical Reagent Co., Ltd. Compound **1** was synthesized according to the procedure reported.[25] The stock solutions of metal ions for fluorescence discrimination were prepared from $AgNO_3$, $PbCl_2$, $CoCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 7H_2O$, NaCl, $CuCl_2$, $NiCl_2 \cdot 6H_2O$, KCl, $FeCl_3$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $MgCl_2 \cdot 6H_2O$ using doubly distilled water. ^1H NMR measurements were performed on a Bruker AVB-500 MHz NMR spectrometer (Bruker biospin, Switzerland). The MS analysis was performed on an Agilent 1100 series mass spectrometer. UV-Vis absorption spectra were recorded with a UV2450 (Shimadzu Co., Japan). Fluorescence measurements were carried out on an F-7500 FL spectrophotometer (Hitachi Ltd, Japan) with excitation slit set at 10 nm and emission at 10 nm. A Dupont-1090 thermal gravimetric analysis (TGA) instrument and scanning electron microscope (SEM, JSM-7800F, JEOL, Japan) was used for characterization of fluorescent solid sensors.

2.2 Preparation of compound NF

(Preferred position of Scheme 1)

(3-Isocyanatopropyl)triethoxysilane (0.30 g, 1.2 mmol) and triethylamine (0.17 mL, 1.2 mmol) was added to a solution of compound **1** (0.51 g, 1.0 mmol) in 20 mL anhydrous dichloroethane. Under a nitrogen atmosphere, the mixture was heated to 80 °C in a round-bottom flask equipped with a condenser for 24 h. After the dichloroethane had been evaporated under reduced pressure, the residue was purified by silica gel column chromatography (EtOAc: CH_2Cl_2 = 2:3) to give compound NF (0.51 g, yield: 67%). ^{1}H NMR (500 MHz, CD_3Cl) δ(ppm): 11.47 (s, 1H), 8.85-8.77 (m, 2H), 8.59-8.55 (m, 2H), 8.44 (d, 1H, J = 8.5 Hz), 8.17 (d, 1H, J = 8.5 Hz), 7.72 (t, 1H, J = 8.0 Hz), 7.57-7.52(m, 2H), 7.46-7.44 (m, 1H), 7.31 (d, 1H, J = 8.0 Hz), 4.47-4.39 (m, 4H), 3.81-3.77 (m, 6H), 3.48-3.46 (m, 6H), 3.12-3.11 (m, 2H), 3.04 (s, 4H), 1.82 (s, 1H), 1.60-1.54 (m, 2H), 1.20-1.18(m, 9H), 0.62-0.60 (m, 2H). ^{13}C NMR(125 MHz, CD_3Cl) δ(ppm): 168.5, 164.4, 163.9, 156.3, 155.9, 148.5, 139.0, 136.2, 134.2, 132.6, 131.2, 130.2, 129.9, 128.0, 127.3, 126.2, 125.8, 123.2, 121.8, 121.6, 116.8, 116.6, 114.9, 62.4, 62.1, 58.4, 53.5, 53.3, 43.4, 39.3, 23.2, 18.2, 7.5. ESI *m/z* $[M+H]^+$ 757.4.

2.3 Preparation of NF-SiO_2

Compound NF (100 mg) was dissolved in anhydrous toluene (15 mL) and the silica nanoparticle (200 mg) was added as a solid. The suspension of silica nanoparticles was stirred under reflux conditions for 24 h in toluene. Then, the collected solid was washed repeatedly with ethanol to rinse away any surplus compound NF. After drying at 50 °C overnight, a yellow powder was obtained.

3 Results and discussion

3.1 FT-IR analysis

(Preferred position of Figure 1)

The successful conjugation of compound NF onto the surface of the silica nanoparticles can be confirmed by infrared spectroscopy. Fig. 1 shows the FTIR spectra of silica nanoparticles (Fig. 1a), naphthalimide-modification silica nanoparticles (Fig. 1b) and compound NF (Fig. 1c). From Fig. 1(a) and (b), it can be seen that both the materials contain the typical Si-O-Si bands around 1070-1200 and 460 cm^{-1}, associated with the formation of a condensed silica network. A broad band centered at 3480 cm^{-1} and a strong peak around 1650 cm^{-1} assigned to O-H bonds in silanol groups and adsorbed water molecules. Compared with the spectrum of compound NF (Fig. 1a), the peaks at 1693 cm^{-1} found in the spectrum of NF- SiO_2 (Fig. 1b) can be assigned to the stretching vibration of amide groups. The presence of a strong band at 1544 cm^{-1} is due to the C=C stretching, which comes from the benzene ring. The band at 1378 cm^{-1} is C-N stretching. All these bands confirm the conjugation of compound NF onto the surface of SiO_2.

3.2 TGA analysis of SiO_2 and NF-SiO_2

(Preferred position of Figure 2)

Thermogravimetric analysis (TGA) is a good and reliable method measuring weight changes in a material as a function of temperature under a controlled atmosphere. Thermogravimetric analysis of SiO_2 shown in Fig. 2a indicates that weight loss of 2.0 wt % (up to 800 ^oC) resulted from desorption of water molecules from silanol groups of SiO_2. From the TGA weight loss curve in Fig. 2b, the decomposition of organic layer was observed above 200 ^oC. Comparing with Fig. 2a, it can be seen that the content of the NF grafted to the SiO_2 is about 6.0 wt%, which is 0.08 mmol g^{-1}. In addition, compared with some reported fluoroionophores -functionalized SiO_2 material for detecting heavy metal ions,[15-20] the commercial and cheap silica nanoparticles can also provide high loading efficiency.

3.3 SEM image of SiO_2 and NF-SiO_2

(Preferred position of Figure 3)

Fig. 3 shows the typical SEM images of the silica nanoparticles before and after surface modification. It can be seen that the unfunctionalized silica nanoparticles was regular in shape (Fig. 3a). After surface modification, the surface of silica nanoparticles does not show any serious cracks or degradation. Moreover, from SEM images of naphthalimide derivatives functionalized silica nanoparticle, it clearly indicated that the silica nanoparticles structures were maintained during the modification process, however, the silica nanoparticles diameter increased slightly.

3.4 UV-vis spectra properties of NF-SiO_2

(Preferred position of Figure 4)

In order to provide the compelling evidence of the coordination between NF-SiO_2 and Cu^{2+}, we measured the UV-vis spectra of NF-SiO_2 with varying Cu^{2+} concentration. As shown in Fig.4, upon the addition of Cu^{2+} to NF-SiO_2, an absorption band at 239nm is significantly enhanced, and a broad band at 409nm slightly increased. It suggested that N atoms of 8-aminoquinoline group and the piperazine linker can chelate with Cu^{2+} ions.

3.5 Fluorescence spectra properties of NF-SiO_2

(Preferred position of Figure 5)

Fig. 5 shows the fluorescence spectra of NF-SiO_2 in the presence of different amounts of Cu^{2+} ions. With an excitation wavelength of 413 nm, the fluorescence emission peak occurs at 529 nm. From Fig. 5, it can be seen that the fluorescence intensity of NF-SiO_2 is progressively quenched as the concentration of Cu^{2+} gradually increases. The results show that Cu^{2+} has a particular effect on the fluorescence intensity of NF-SiO_2. Upon the addition of 500 μM Cu^{2+}, a strong decrease of the emission intensity can be observed, due to the Cu^{2+} ions complexion with N atoms of 8-aminoquinoline group and the piperazine linker, which can be tentatively explained in terms of electron transfer from the excited 1, 8-naphthalimide fluorophore to the complexed Cu^{2+} ions. On the basis of the results of fluorescence intensity at 529 nm, the relationship between the concentration of Cu^{2+} ions and fluorescence intensity is established, and it can be expressed by the following equation of the calibration line: $F = 490.784 - 34.646 \times [Cu^{2+}]$ ($R^2 = 0.995$). In addition, Cu^{2+} ions can be determined in concentration rang of 1-10 μM and the detection limit of NF-SiO_2 for Cu^{2+} was 1.5×10^{-7} M (S / N = 3), which was far below the U.S. EPA limit of 20 μM. This phenomenon makes the NF-SiO_2 ideal fluorescent sensors for detection Cu^{2+}.

3.6 Selectivity of NF-SiO_2

(Preferred position of Figure 6)

Due to the selectivity is a very important factor for fluorescent solid sensor, we also tested the fluorescence response of NF-SiO_2 to various common metal ions. Fig. 6 shows the fluorescence response of NF-SiO_2 to various common metal ions in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ ethanol by excitation with 413 nm. The sensor shows exclusive selectivity for Cu^{2+}, and no obvious fluorescent response to the other metal ions (Na^+, K^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}). However, the emission intensity is very slightly decreased to some metal ions such as Ag^+ and Ni^{2+}, and very slightly increased in the presence of Zn^{2+}, Co^{2+}, and Fe^{3+} ions. These results suggested that NF-SiO_2 could recognize Cu^{2+} ions with high selectivity against other metal ions under physiological conditions.

3.7 Reversibility and adsorption ability of NF-SiO_2

(Preferred position of Figure 7)

Reversibility is an important aspect for a fluorescent solid sensor to be widely employed in the detection of specific analyses, and so a reversibility experiment of the sensor has been carried out. It is well known that EDTA has a strong ability to coordinate with Cu^{2+}. Therefore, EDTA was chosen to test the reversibility of NF-SiO_2. The addition of Cu^{2+} to the solution of NF-SiO_2 caused fluorescence to be quenched. Upon addition of an excess amount of EDTA to the mixture of NF-SiO2 and Cu^{2+}, the fluorescent emission intensity of the system was immediately recovered to the original level, indicating that EDTA could replace the receptor to coordinate with Cu^{2+} (Fig. 7). Thus, the reversibility of the sensor meets the requirement for practical application.

In addition, a preliminary investigation on the use of NF-SiO_2 as a sorbent for removing Cu^{2+} from waste water was carried out. The NF-SiO_2 (10 mg) was added into 1 mL of neutral water containing Cu^{2+} (1 μM) and stirred for 1h. The Cu^{2+} loaded composite silica nanoparticles were then isolated from the solution by centrifugation. Inductively coupled plasma mass spectrometry (ICP-MS) was used to detect the amount of Cu^{2+} left in the solution. Measurements suggested that less than 5% of the original Cu^{2+} remained in the solution. The result indicates that NF-SiO_2 can be used as a potential sorbent in water for Cu^{2+} removal and has potential in environmental.

Conclusion

In summary, a new bifunctional silica nanoparticles sensor with naphthalimide group as the fluorophore for Cu^{2+} has been designed. This nanosensor showed excellent fluorescence sensitivity and selectivity towards Cu^{2+} over other metal ions. Covalently grafted compound **NF** onto the surface of silica nanoparticles makes the nanosensor easy to recover and recycle. Moreover, the fluorescence of NF-SiO_2 is turned on when adding EDTA to the mixture of Cu^{2+} and NF-SiO2 solution. Thus, the “on -off -on’’ fluorescence sensing behavior strengthens the application of NF-SiO_2 to work as a potential device with logic gate functions.

Acknowledgements

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Figure captions:

Scheme 1 Synthesis of NF and NF- SiO_2.

Fig. 1 FT-IR spectra of SiO_2 (a), NF-SiO_2 (b) and NF (c).

Fig. 2 TGA curves of SiO_2 (a) and NF-SiO_2 (b).

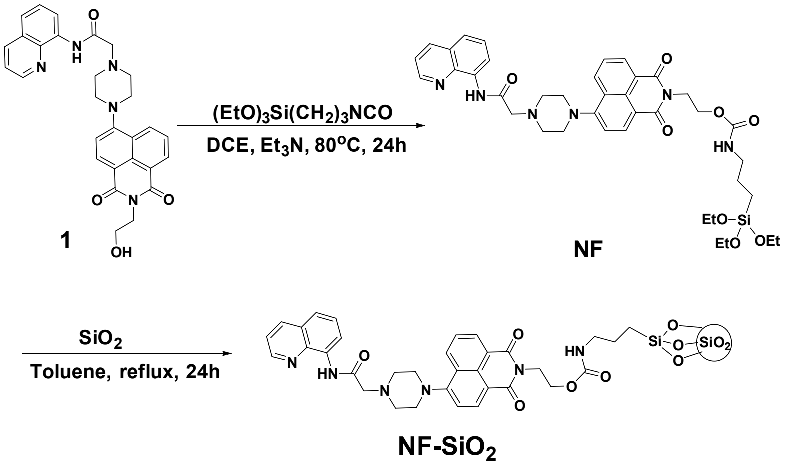
Fig. 3 SEM images unfunctionalized silica nanoparticles (a) and naphthalimide derivatives functionalized silica nanoparticle (b).

Fig.4 Absorption spectra of NF-SiO_2 (0.25 mg/mL) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol in the presence of different amounts of Cu^{2+} ions (from 0 to 6 μM).

Fig. 5 (a) Fluorescence spectra of the NF-SiO_2 (0.25 mg/mL) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol in the presence of different amounts of Cu^{2+} ions (from 0 to 500 μM); (b) Florescence intensity of NF-SiO_2 at 529nm versus the concentration of Cu^{2+} ions; the excitation wavelength was 413nm.

Fig.6 Fluorescence quenching ration I / I_0 of the NF-SiO_2 (0.25mg/mL) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol at 529nm after addition of 500 μM Cu^{2+} and 500 μM other metal ions (Na^+, K^+, Ag^+, Cd^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+}, Fe^{3+}) ; the excitation wavelength was 413nm.

Fig.7 Fluorescence spectra of NF-SiO_2 (0.25 mg/mL) in the presence of Cu^{2+} (500 μM) and EDTA (1 mM) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol; the excitation wavelength was 413nm.



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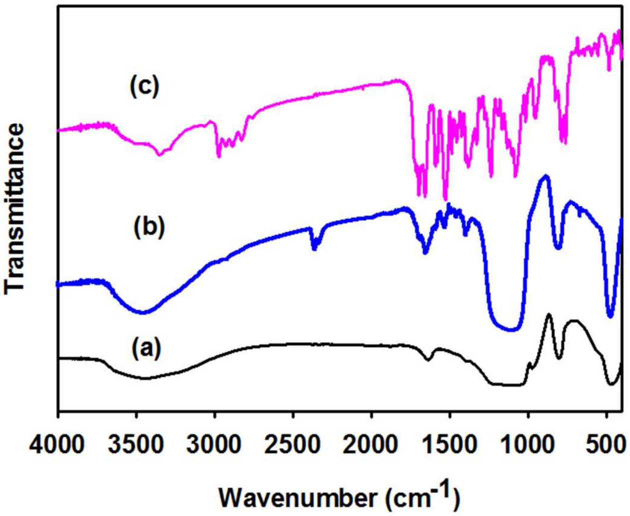

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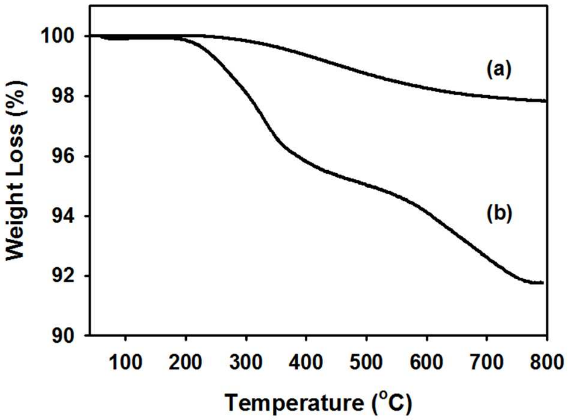

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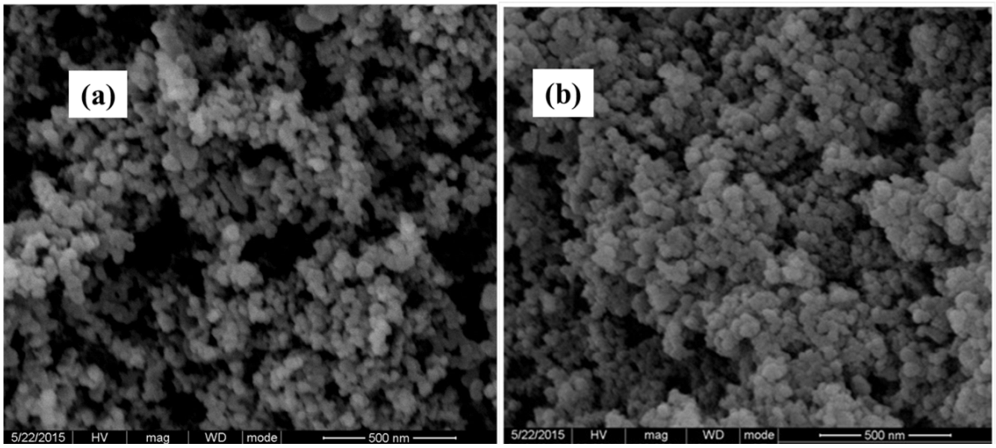

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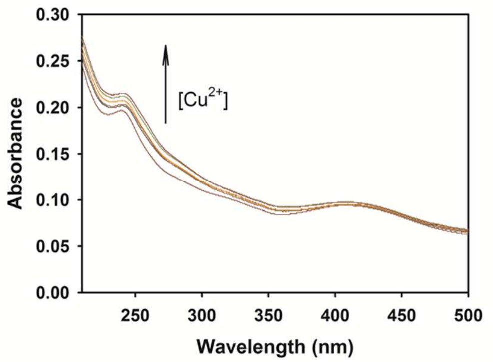

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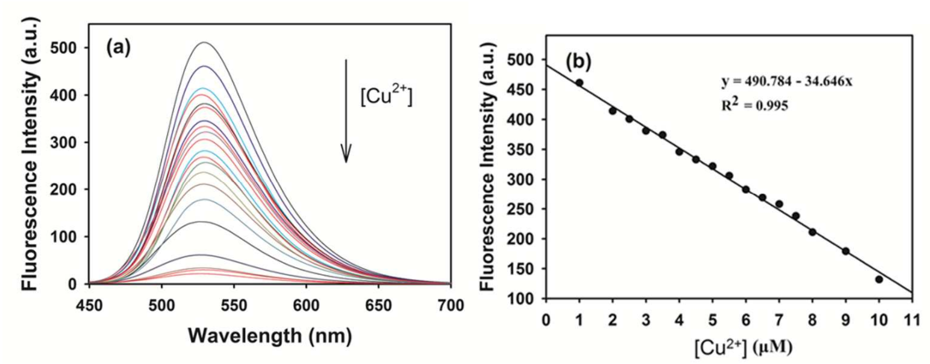

Fig. 5 (a) Fluorescence spectra of the NF-SiO_2 (0.25 mg/mL) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol in the presence of different amounts of Cu^{2+} ions (from 0 to 500 μM); (b) Florescence intensity of NF-SiO_2 at 529nm versus the concentration of Cu^{2+} ions; the excitation wavelength was 413nm.

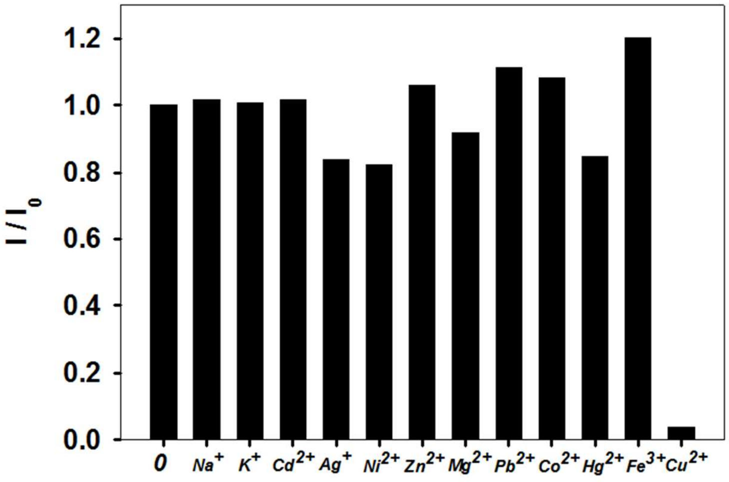

Fig.6 Fluorescence quenching ration I / I_0 of the NF-SiO_2 (0.25 mg/mL) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol at 529nm after addition of 500 μM Cu^{2+} and 500 μM other metal ions (Na^+, K^+, Ag^+, Cd^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Hg^{2+}, Fe^{3+}) ; the excitation wavelength was 413nm.

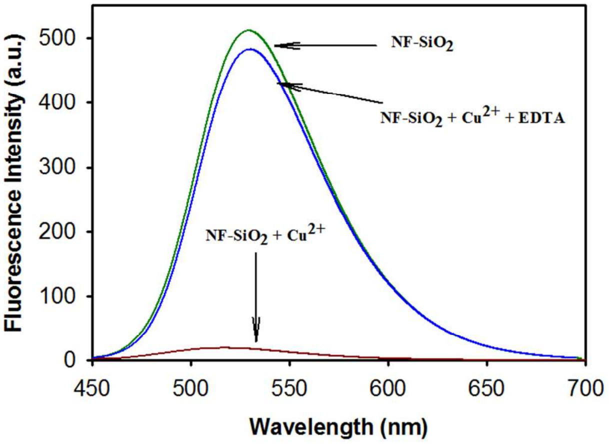

Fig.7 Fluorescence spectra of NF-SiO_2 (0.25 mg/mL) in the presence of Cu^{2+} (500 μM) and EDTA (1 mM) in PBS buffer solution (25 mM, pH = 7.4) containing 50% (v/v) H_2O/ethanol; the excitation wavelength was 413nm.