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A novel permanganate-sensitive fluorescent nano-chemosensor assembled with a new 8-hydroxyquinoline-functionalized SBA-15

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ABSTRACT

A novel fluorescence nano-chemosensor for MnO_4^- anion has been developed by assembly of fluorescent aluminum complex of 8-hydroxyquinoline (8-HQ) within the channels of modified SBA-15 (SBA-SPS-QAl). The ordered porous structure of SBA-15 is still retained after hybridization by chemosensor material. A remarkable fluorescent quenching of SBA-SPS-QAl was attributed to the effect of MnO_4^- anion. The linear detecting range of the hybrid mesoporous chemosensor is 0.16–4.6 μmol L^{-1} of MnO_4^- anion and the lowest detection limit is 0.2 ng mL^{-1} in the aqueous solution. SBA-SPS-QAl showed a selective and sensitive fluorescent quenching response toward MnO_4^- ion in comparison with N_3^-, NO_3^-, CN^-, HCO_3^-, Cl^-, F^-, $H_2PO_4^-$, SO_4^{2-}, $Cr_2O_7^{2-}$, IO_3^- and I^- ions, which was because of the higher stability of its inorganic complex with permanganate anion.

1. Introduction

Recent advances in mesostructured materials and nanotechnologies have let to the designing new methods in construction of the optical sensors and biosensors, and also the development of highly sensitive potentiometric sensors. In recent years, moreover, large-scale nano-structured materials such as SBA-15 and MCM-41 have attracted significant interest in development of the optical chemical sensors [1–4]. Among the mesoporous silica compounds, SBA-15, possessing hexagonal arrays of uniform pores with ultra large pore diameters, large surface area, high pore volume and thicker pore walls, is characterized with highly ordered two-dimensional symmetry. The compound also shows excellent homogeneity and chemical/mechanical stability [5,6]. These properties change the compound to a potential candidate for interacting with guest species on the surface.

Chemical sensors are molecular receptors that change the chemical information into useful analytic signals upon binding to specific guests. These devices have attracted attention owing to their potential for easy detection and quantification of the pollutant species in many fields of application, such as waste management, environmental chemistry, clinical toxicology, and bioremediation of radionuclides [4–12]. The design of host molecules that can recognize and sense anions selectively through electrochemical or optical responses has received considerable attention in recent years because of the important roles played by the anions in biological, industrial, and environmental processes [13,14].

Among all these sensors, the optical ones allowing on-site, real time qualitative or semi quantitative detections without the use of any substantial or complicated instrumentation have been regarded as very promising methods in determination of pollutant species in environmental analysis [15–18].

Our team has recently reported a number of chemosensors and optical sensors for ions such as Zn^{2+} [19], Hg^{2+} [20], $P_2O_7^{4-}$ [21], Tb^{3+} [22–24], Er^{3+} [25] and in the present work, we wish to introduce a functionalized fluorescent mesoporous material,

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in which 8-hydroxyquinoline aluminum complexes are covalently grafted to the surface of SBA-15 via a sulfonamide bond SBA-SPS-QAl. This simple nano-chemosensor acts based on the effective coordinating ability of 8-hydroxyquinoline complexes with specific anions and the excellent structure properties of SBA-15 [16,26]. Our investigation showed that this material has high selectivity and sensitivity toward MnO_4^- anion over other anions and hence it may be used to construct a nano-sensor device to directly sense this anion in some especial environmental samples.

2. Experimental

2.1. Materials

All chemicals were of the reagent-grade from Fluka and Merck Chemical Companies. Pluronic P123 with average molecular weight of 5800 was purchased from Aldrich. Tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) were purchased from Merck. All of the other reagents and solvents were of analytical reagent grade and used as received.

All fluorescent measurements were carried out on a Perkin-Elmer LS50 luminescence spectrometer. Absorption spectra were studied on a Shimadzo UV 2100 PC UV-visible spectrometer. FTIR spectra were obtained on a Vector 22 Bruker spectrometer with samples prepared as KBr pellets.

2.2. Synthesis of SBA-SPS-AlQ$_x$

SBA-SPS-QAl was prepared according to the literature [27] as depicted in Fig. 1A. As it can be seen in Fig. 1A, 8-hydroxyquinoline was grafted to the surface via formation of a sulfonamide bond between 8-hydroxyquinoline-5-sulfonyl chloride and surface amine groups of amino propyl functionalized SBA-15 and then, the final product was obtained via complexation reaction between 8-HQ functionalized SBA-15 and Al^{3+} ions and additional 8-HQ ligands (designated as SBA-SPS-QAl).

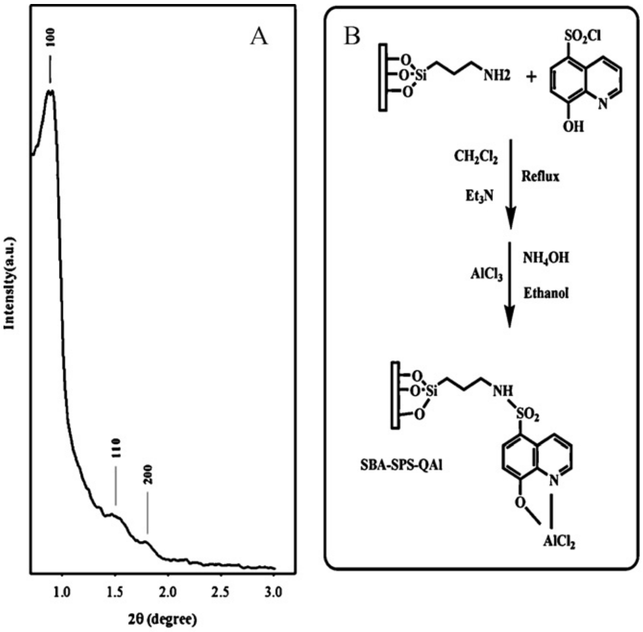
3. Results and discussion

The low angle XRD patterns of the prepared SBA-15 showed a single intensive reflection at 2θ angle around 0.85° and two additional peaks correspond to the higher ordering (1 1 0) and (2 0 0) reflections, which was associated with a two-dimensional hexagonal (p6mm) structure similar to the typical SBA-15 materials (Fig. 1B).

The nitrogen adsorption–desorption isotherms of SBA-SPS-Q showed a type-IV isotherm with an obvious H1-type hysteresis loop that was representative of the mesoporous cylindrical (Fig. 2). The respective specific surface areas (BET method), pore diameters (BJH method) and total pore volumes were given in Fig. 1.

Fig. 3A illustrates the SEM image of SBA-SPS-Q and shows uniform particles of about 1 μm. The TEM image (Fig. 3B) show hexagonal arrays of mesopores and provide further proof that the prepared material has a typical 2D P6mm hexagonal structure.

FT-IR spectra of SBA-SPS-Q confirmed the incorporation of 8-hydroxyquinoline (8-HQ) in the SBA-15 framework (Fig. 3C). The peaks at 1610, 1580, 1500, 1471 and 1387 cm^{-1} were related to the C=N and C=C ring skeletal vibrations of the grafted 8-HQ ligand and the band appearing at 1334 cm^{-1} could be ascribed to the asymmetric vibration of O=S=O group of sulfonamide bond that linked to the 8-HQ moiety of the surface of functionalized SBA-15 [28–30].



Textural Parameters of prepared compounds [a]

Sample	S_{BET} ($m^2\ g^{-1}$)	V ($cm^3\ g^{-1}$)	D_{BJH} (nm)
SBA-15	464	0.5578	5.4
SBA-SPS-Q	79	0.1885	5.2

[a] S_{BET} is the BET surface area; V is the total pore volume; D_{BJH} is the average pore diameter calculated using BJH method

Fig. 1. (A) Synthesis rout of SBA-SPS-QAl; (B) XRD patterns for SBA-15.

3.1. Preliminary experiments

In order to evaluate whether SBA-SPS-QAl could be used as a selective fluorescent nano-chemosensor for MnO_4^- anion, in preliminary experiments the complexation of SBA-SPS-QAl with a number of anions was spectrofluorometrically investigated in an aqueous solution at 25.0 ± 0.1 °C. A solution of SBA-SPS-QAl (0.04 g L^{-1}) in an aqueous solution was titrated with microliter amounts of 1.0×10^{-4} mol L^{-1} solutions of anions spectrofluorometrically. Fluorescence titration experiments were recorded by excitation at 360 nm. As shown in Fig. 4A, when titrations with MnO_4^- were performed a significant decrease in the fluorescence intensity of the chemosensor was obtained. No significant fluorescence changes were observed when F^-, $H_2PO_4^-$ and other ions were tested.

3.2. Absorption studies

Fig. 4B shows typical UV–vis titration curves of SBA-SPS-QAl with different concentrations of MnO_4^- added. The UV–vis absorption spectra of the SBA-SPS-QAl showed two absorption maxima at approximately 377 and 259 nm. The mode of coordination of SBA-SPS-QAl with MnO_4^- was investigated by spectrophotometric titration at 298 K (0.03 g L^{-1}) suspended in aqueous medium. The pH of the solution was 7. It is apparent from Fig. 4B that the absorption intensity of SBA-SPS-QAl at 259 nm and 377 nm gradually decreases as the concentration of MnO_4^- increases

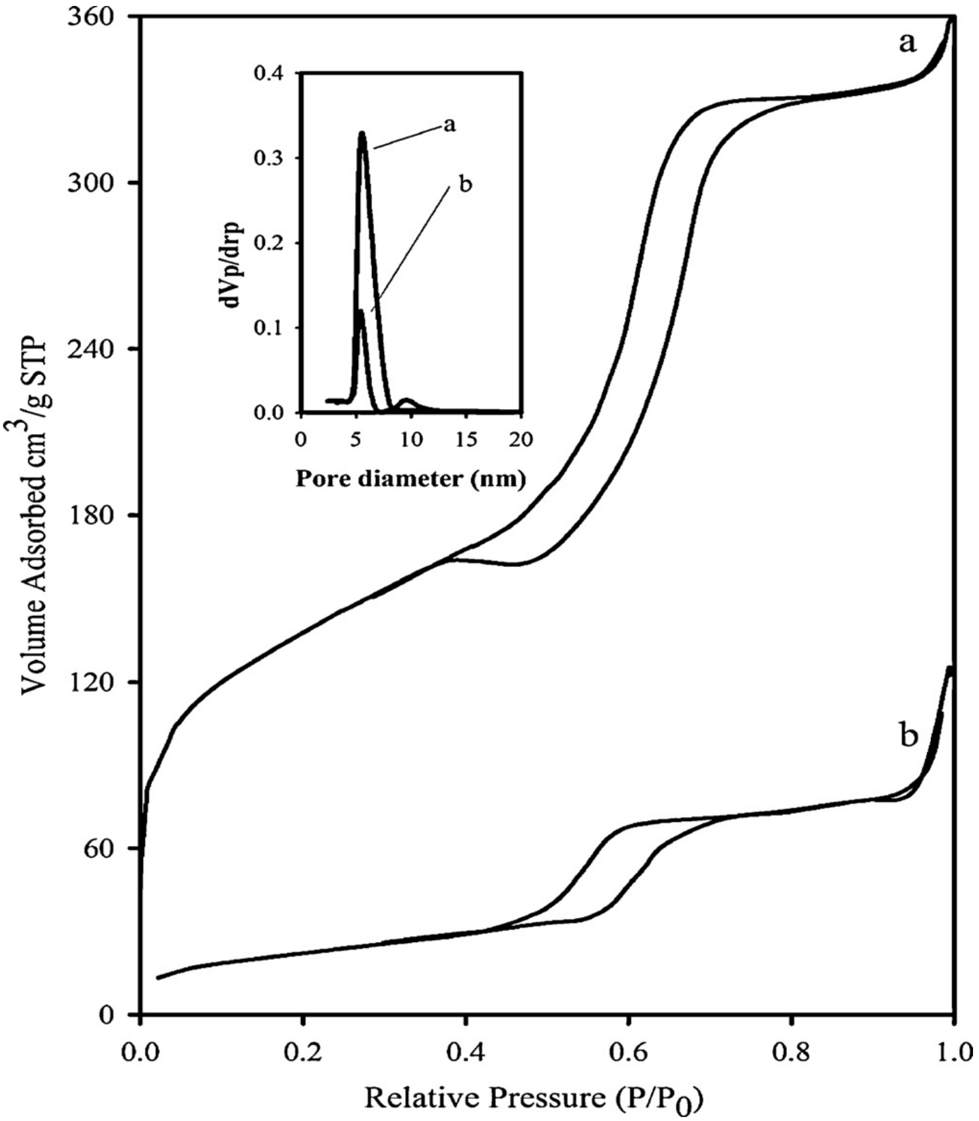


Fig. 2. N_2 adsorption–desorption isotherms of (a) SBA-15, (b) SBA-SPS-AlQ (inset: BJH pore size distribution curves of (a) SBA-15, (b) SBA-SPS-AlQ).

stepwise. Notably, titration of SBA-SPS-QAl against MnO_4^- led to a well-defined isosbestic point at 208 nm. Respectively, it was indicated that a stable complex having a certain stoichiometric ratio between the receptor L and MnO_4^- formed.

3.3. Fluorescence studies

All of the fluorescence titration experiments were performed in a suspended aqueous solution and the maximum excitation wavelength was selected to be 360 nm. As illustrated in Fig. 4C, SBA-SPS-QAl showed a typical emission band around 480 nm, which was considerably quenched in the presence of MnO_4^- and the fluorescence minimum was blue-shifted to 440 nm. The pH of the solution was 7. This phenomenon may occur because of a kind of anion coordination to the metal center of the chemosensor [31,32] and not according to Hofmeister series (i.e. hydrophobicities of the anions). When the concentration of MnO_4^- anions was increased up to 2.0×10^{-6} mol L^{-1}, more than 80% of the initial fluorescence of SBA-SPS-QAl was quenched (Fig. 4C). Both the excitation and emission intensities sharply decreased as a function of MnO_4^- concentration.

Fig. 5A indicates the steady-state emission Stern–Volmer analysis for different anions in the aqueous solution, plotted as in Eq. (1).

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \tag{1}$$

where F_0 and F are the steady represent fluorescence intensities in the absence and presence of quencher, respectively; K_{sv} is the Stern–Volmer quenching constant and [Q] is the concentration of the quencher. As it can be seen from Fig. 5A, in case of MnO_4^- a very strong quenching in the solution of SBA-SPS-QAl is observed. A quantified fluorescence quenching ability (K_{sv}) of MnO_4^- ion to the solutions of SBA-SPS-QAl was obtained from the Stern–Volmer quenching curves, which was calculated to be $(3.45 \pm 0.02)10^5$ mol^{-1} L by the Stern–Volmer equation. It suggested that the MnO_4^- has a strong ability to bind with the fluorophore SBA-SPS-QAl.

Furthermore, the detection limit of SBA-SPS-QAl as a fluorescent sensor for the analysis of MnO_4^- was studied by the plot of the fluorescence intensity as a function of the concentration of added anions. It was found that SBA-SPS-QAl as a fluorescent chemosensor

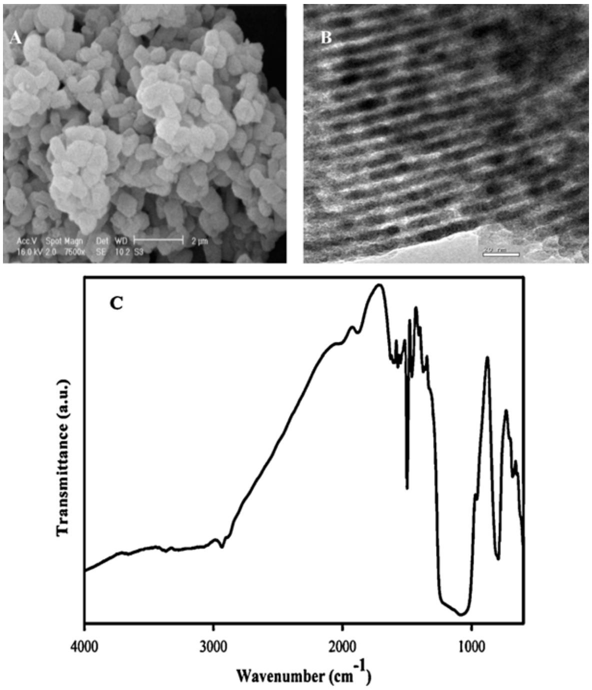


Fig. 3. (A) SEM image of SBA-SPS-AlQ; (B) TEM image of SBA-SPS- AlQ; (C) FT-IR spectra of SBA-SPS-AlQ.

has a detection limit of 1.4×10^{-7} mol L^{-1} for MnO_4^- anions with linear range of 0.16–4.6 µ mol L^{-1} [21].

The selectivity behavior, expressed as the relative response of the chemosensor to the primary ion over the other ions present in the solution, is obviously one of the most important characteristics of a selective chemosensor. Thus, the influence of a number of common anions on the fluorescence intensity of the proposed MnO_4^- chemosensor was investigated. The influence of the interfering anions such as N_3^-, NO_3^-, CN^-, HCO_3^-, Cl^-, F^-, $H_2PO_4^-$, SO_4^{2-}, $Cr_2O_7^{2-}$, IO_3^- and I^- ions on the fluorescence behavior of SBA-SPS-QAl are shown in Fig. 5B. No obvious changes in the fluorescence intensity were observed even exceed concentration of other anions were used. Also, since some cations could influence the fluorescence intensity of the quinoline ligands, the effect of the cations on the fluorescence intensity of the chemosensor was studied using nitrate solution of the tested cations (such as Na, K, Mg, Ca). No significant effect was seen.

To explore the practical applicability of SBA-SPS-QAl as a permanganate-selective fluorescent ionophore, competition experiments were also performed in the presence of MnO_4^- at 30 µmol L^{-1} mixed with 30 µmol L^{-1} background anions. The fluorescence intensity of the solutions containing background ion, other anions and MnO_4^- showed no obvious variation compared with those only containing MnO_4^-. Therefore, these anions cannot to interfere with the determination of MnO_4^-. Fig. 5B clearly reveals the extremely good selectivity of the sensor to MnO_4^- at low concentrations against all other anions tested here.

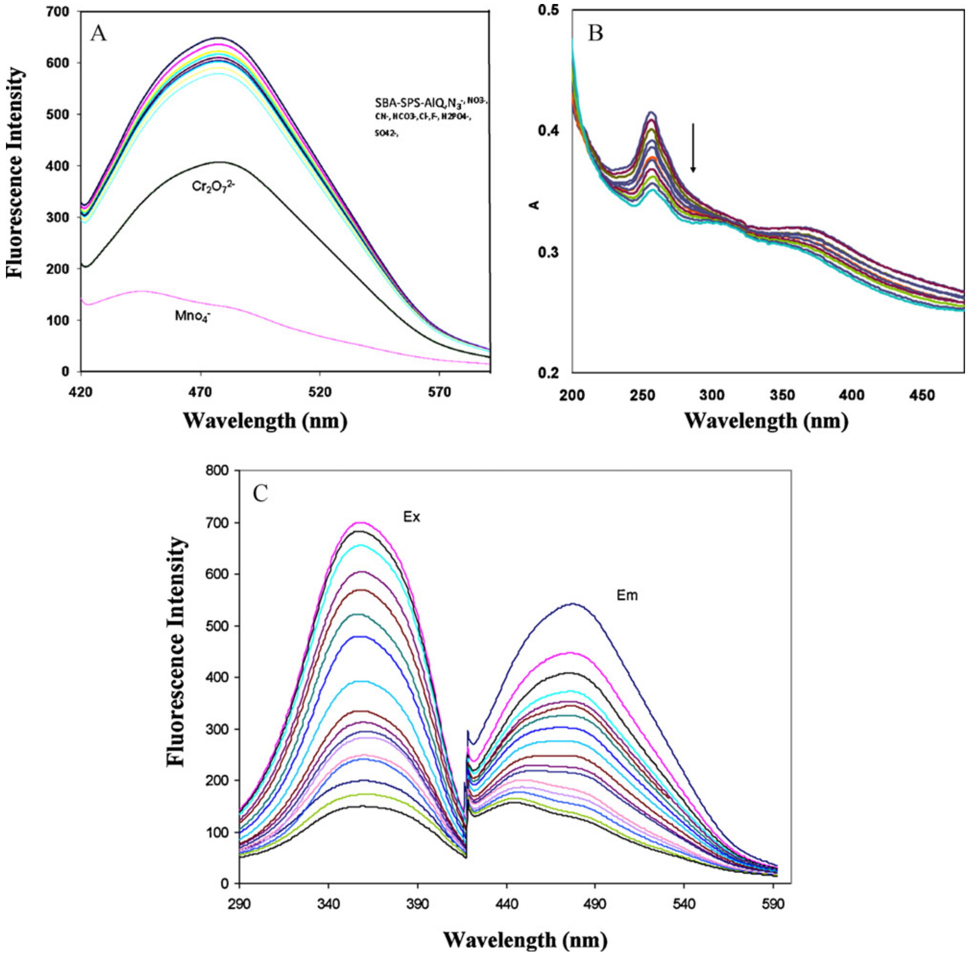


Fig. 4. (A) Fluorescence response of SBA-SPS-AlQ (3 mL 0.04 g L^{-1}) upon addition of different anions (1.0×10^{-4} mol L^{-1}) in aqueous solution (λ_{ex} = 360 nm); (B) UV–vis spectra change of SBA-SPS-AlQ (0.03 g L^{-1}) upon addition of MnO_4^- in aqueous solution; (C) excitation and Emission spectra of the proposed chemosensor in the presence of varying concentration of MnO_4^- anion.

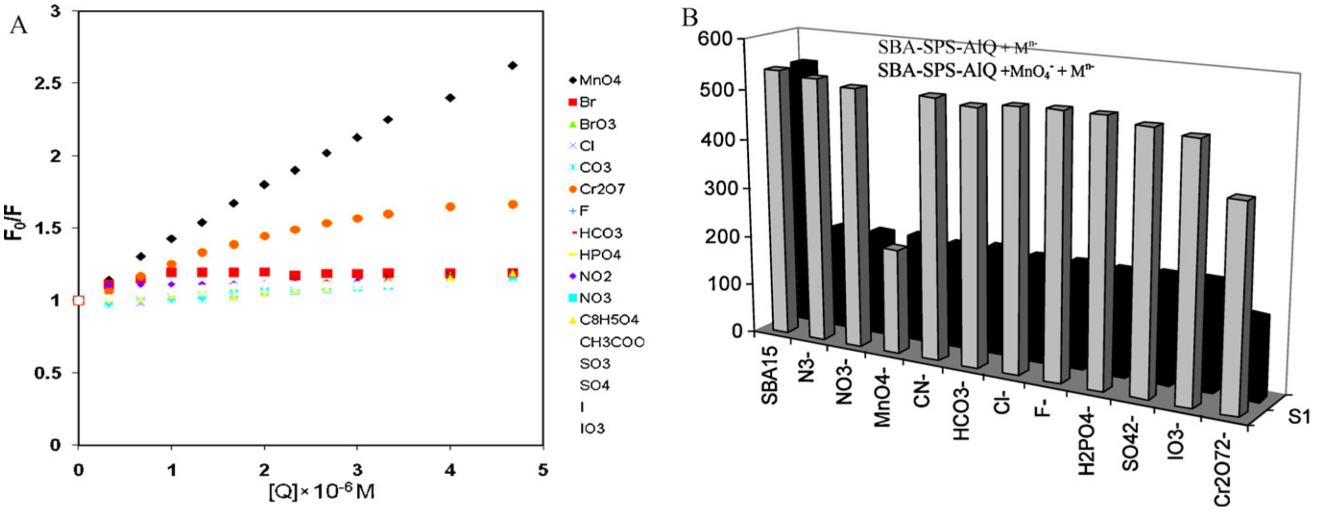


Fig. 5. (A) Stern–Volmer plots for the quenching of SBA-SPS-AlQ 0.04 g L^{-1} by anions; (B) (a) fluorescence responses of SBA-SPS-AlQ (0.04 g L^{-1}) upon addition of various anions (λ_{ex}: 360 nm) and (b) fluorescence responses of SBA-SPS-AlQ (0.04 g L^{-1}) containing 30 m mol L^{-1} MnO_4^- and the background anions (30 mmol L^{-1}) (λ_{ex}: 360 nm).

4. Conclusion

Consequently, it was concluded that the new hybrid material of SBA-SPS-QAl can be used as a nano-chemosensor for the detection of different concentrations of MnO_4^- ion with high selectivity. A remarkable fluorescent quenching of SBA-SPS-QAl was attributed to the effect of MnO_4^- anion. The linear detecting range of the hybrid mesoporous chemosensor for MnO_4^- anion is 0.16–4.6 μmol L^{-1} and the lowest detection limit is 0.2 ng mL^{-1} in the aqueous solution. The ordered porous structure of SBA-15 is still retained on the hybrid chemosensor material.

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