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ARTICLE TYPE

Mixed anionic surfactants-templated mesoporous silica nanoparticles for fluorescent detection of Fe^{3+}

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This work demonstrated a novel method for synthesis of large pore mesoporous silica nanoparticles (MSNs) with pore diameter of 10.3 nm and particle diameter of ~50 nm based on the incorporation of mixed anionic surfactant sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulphate (SDS) as template in the synthesis process. The dispersity, morphology, pore structure and size of mesoporous nanoparticles was adjusted by changing the molar ratio of two anionic surfactants, the concentration of co-structure-directing agent (3-aminopropyltrimethoxylsilane) and the reaction temperature. The results of synthesis experiments suggested that the formation of large pore MSNs was nucleation and growth process. MSNs were post-grafted with a Schiff based moiety for fluorescent sensing of Fe^{3+} in water. The applicability of functionalized MSNs was demonstrated by selective fluorescent detection of Fe^{3+} in aqueous media.

Introduction

Mesoporous silica nanoparticles (MSNs) have attracted increasing attentions because of their unique and tuneable pore structures, which potentially could be applied as drug carriers, catalyst supports and adsorbents in biomedical and industry fields.[1, 2] Various templating approaches have been developed in the past decades to synthesize mesoporous silica nanoparticles with well-defined topology and morphology using different surfactants as soft-templates.[3-7] For example, Zhao and co-workers synthesized biodegradable MSNs with tuneable pore size by cetyltrimethylammonium chloride (CTAC) as a cationic surfactant template.[8] Mou and co-workers designed and synthesized a series of cationic surfactant-templated MSNs for intracellular drug delivery and bio-imaging.[9-11] Yu and co-workers presented the synthesis of silica ellipsoids with hexagonal mesostructure via an organic-inorganic cooperative assembly process by using amphiphilic copolymers P123 as a template.[12] Che and co-workers introduced co-structure directing agents to synthesize anionic surfactants-templated silica nanoparticles with highly ordered structures.[13-15] Besides these, by designing and synthesizing of surfactants,[3, 16-21] different pore structures[22-26] and MSNs morphologies[27-30] have been proposed.

Particularly, it is important to synthesize MSNs with large mesopores, which offer superior mass transfer characteristics for nucleic acids and gene delivery for medical applications.[31] There are two major pathways to synthesize large pore MSNs. One is to expand the mesopores with swelling agents such as toluene, 1,3,5-trimethylbenzene (TMB) and octanoic acid.[32-35] Second is to utilize nonionic surfactants or surfactants with long hydrophobic chains as soft template.[36, 37] For instance, a series of large-pore ordered mesoporous materials have been prepared by surfactant paired with a micelle swelling agent. The single-micelle-templated organosilica and silica nanospheres can reach to large interiors (up to~18.5 nm in diameter) using this approach.[21, 38-40]

Although cationic and amphiphilic surfactants are typically used to synthesize large pore MSNs,[31] the reports on the use of anionic surfactants to synthesize large pore MSNs are scarce. Chen and co-workers prepared core-shell hollow mesoporous nanoparticles with amino-functionalized channels by using *N*-lauroylsarcosine sodium as anionic surfactant.[41] The pore diameters of the core-shell MSNs were about 3nm. Che and co-workers designed and synthesized a series of anionic surfactant-templated nanoparticles by introducing co-structured directing agent.[13, 15, 16] In their work, ordered mesoporous and chiral mesoporous silica were prepared and anionic surfactant-templated mesoporous silica displayed highly ordered 2D-hexagonal *p6mm* mesoporous structure with pore diameters tuned to 6.2 nm. Despite of the progress, it is still a challenge today to prepare larger pore MSNs by anionic surfactants without swelling agent or polymer micelle.

Anionic surfactants such as alkyl carboxylic acid, phosphoric acid, sulfonic acid and their corresponding sodium salts are consumed in a variety of fields because of their low cost, environmental friendliness and low toxicity.[13] In addition, the feasibility of using different surfactants or catalysts has been explored,[42] few effects of using mixed short carbon chained surfactants have been studied to synthesize large pore MSNs.[43] By adjusting the ratio of mixed cationic surfactants and temperature of reaction, Qiao and co-workers proposed and discussed stellate mesopores nanoparticles with large pores for intracellular drug delivery.[43]

In this study, by using mixed anionic surfactants of sodium

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dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulphate (SDS) as template, large pore MSNs have been synthesized without using swelling agent or polymer micelle. The morphology, structure and monodispersity of nanoparticles were tuned by the concentration of SDBS and APTS (3-aminopropyltrimethoxylsilane). Nucleation-growth process have been proposed and discussed in the formation of mesoporous silica nanoparticles. The diameter of mesoporores of silica nanoparticles was measured by transmission electron microscopy (TEM) and N_2 adsorption after extraction and calcination process. Because the MSNs are functionalized with amino group, various proteins and organic moieties can be post grafted on the surface of MSNs. We have grafted nanoparticles with Schiff base and reported Fe^{3+} fluorescent sensing in aqueous media.

Experimental Section

Materials

Tetraethylorthosilicate (TEOS) and (3-aminopropyl)-triethoxysilane (APTS) were purchased from Sigma-Aldrich. Sodium dodecyl benzene sulfonate (SDBS) and sodium dodecyl sulphate (SDS) were purchased from Aladdin Industrial Inc. Acetic acid (CH_3COOH, ⩾99.5 %), 4-benzhydrylbenzaldehyde (TPA), hydrochloric acid (HCl, fuming, ⩾ 37%), anhydrous Ferricchloride ($FeCl_3$, ⩾97%) was purchased from Alfa Aesar. All reagents and solvents were used without further purification. Deionised water was used in the experiment (Resistivity ≥ 18.2 MΩ).

Synthesis of MSNs

MSNs were synthesized using TEOS and APTS as the silica precursors, hydrochloric acid (HCl, fuming, ⩾37%) as acidic catalyst, SDBS and/or SDS as the anionic surfactants. In fact, APTS not only worked as co-condensation silica precursor to introduce amino group, but also as co-structure directing agent (CSDA) to form the morphology of nanoparticles and mesopores. All types of MSNs were formed under acidic conditions; synthesis system contained 0.1M HCl. By tuning the cocentration of SDBS and APTES and the temperature of the synthesis processes, products with different shapes and dispersities have been observed by TEM. The synthesis conditions and the physical parameters of samples have been summarized respectively in Table 1.

In a typical synthesis of MSNs, a given amount of SDS (0.06g) /SDBS (0.014g) and HCl (0.1M, 0.5g) was first dissolved in 8.75 mL DI water to form a clear micelle solution at a reaction temperature of 40 °C. After stirring the solution for 0.5 h, 0.375 mL of TEOS and 0.04 mL of APTS were quickly added to the solution. After an additional 4h of stirring, the as-synthesized products were separated by centrifugation at 10000 rpm for 8 min or filtration. The separated white powder was washed with DI water and ethanol to remove surfactant on the surface of MSNs. After that, MSNs were dried in an oven at 60 °C for 24h.

The anionic surfactant templates were removed by both extraction from reflux and washing by EtOH and HCl with molar ratio 1:1 and calcination at 600 °C for 5 h with a ramp rate of 1°C / min in air.

Characterization

Transmission electron microscopy (TEM) was carried out using FEI Tecnal G2 F20 s-twin D573 operated at 200 kV. The specimens for TEM were prepared by directly placing a small drop of the nanoparticles suspension on a carbon-coated TEM grid. Hitachi S-4800 field-emission scanning electron (FE-SEM) have been used in the test of morphologies.The IR spectra were obtained with a Bruker IFS 66v/S FTIR spectrometer. The adsorption-desorption isotherms of nitrogen were obtained at 77K using a Micrometeritics TriStar 3000 system. Adsorption isotherms of N_2 at 77K were used to calculate the pore size distributions based on the BJH model. The fluorescence emission spectra of the samples were recorded on a HORIBA Instrument FluoroMax - Compact spectrofluorometer.

Table 1 Synthesis conditions of different mesoporous silica nanoparticles (MSNs)

	SDS(g)	SDBS(g)	H_2O(mL)	HCl(g)	TEOS(mL)	APTS(mL)	T(°C)
MSN-1	0.072	0	8.75	0.5	0.375	0.020	40
MSN-2	0.072	0	8.75	0.5	0.375	0.040	40
MSN-3	0.060	0.014	8.75	0.5	0.375	0.030	40
MSN-4	0.060	0.014	8.75	0.5	0.375	0.040	40
MSN-5	0.060	0.014	8.75	0.5	0.375	0.040	25

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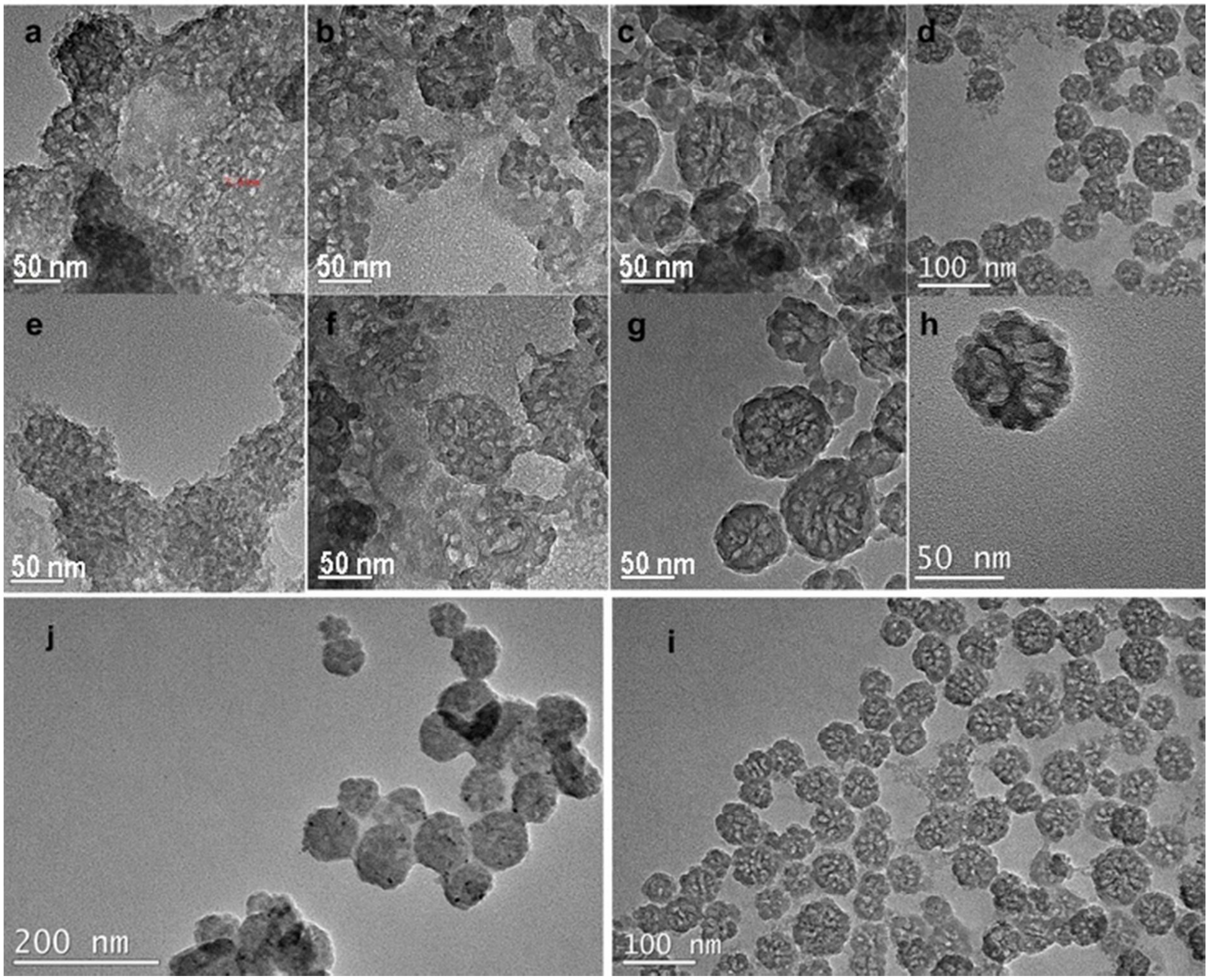

Fig.1 TEM images of MSNs synthesized with different surfactant molar ratio of SDS and SDBS: (a) and (e) MSN-1, (b) and (f) MSN-2, (c) and (g) MSN-3, (d) and (h) MSN-4, (j) MSN-5, and (i) MSN-4. Scale bars are showed in each photo.

Results and discussion

In this study, our basic idea is to prepare large pore MSNs by using mixed anionic surfactants as template. By changing the concentration of SDBS, co-structure directing agent (APTS), reaction temperature, we investigated the formation process of large pore MSNs. After analysis of the relationship between the morphology and dispersity in different experimental conditions (summarized in Table 1), a nucleation-growth process for the MSNs formation have been elucidated. Finally, MSN-4 was post-grafted with triphenylamine and Schiff base moieties, which demonstrated good sensing ability of Fe^{3+}.

Effect of Mixed anionic surfactant and APTS

The morphology characterization by TEM (Fig. 1) of synthesized nanoparticles suggests that without SDBS, mesoporous silica nanoparticles can be synthesized using SDS and APTS (Fig.1a, e, b and f). When the concentration of SDS was 0.72g/ mL and the amount of APTS was 0.02 mL, as-synthesized MSN-1 displayed aggregated morphology and the synthesis product contained large fraction of mesoporous silica monoliths with the pore diameter of 5-6 nm approximately measured from TEM image. MSN-1 were nonuniform in size from 40nm to 100nm and different particle morphologies (Fig.1a and 1e). On further addition of APTS (0.03 or 0.04 mL) into the synthesis system, as shown in Fig. 1 b and f, the dispersity of nanoparticles (MSN-2) improved. However, MSN-2 showed different particle morphology and pore structure. In addition, we found that MSN-2 were frangible. The fragmented particles of MSN-2 are detected in Fig. 1b and 1f. Similar results and morphologies of MSN-1 and MSN-2 have been observed in SEM images (Fig. 2). In Fig. 2a, MSN-1show aggregation, spherical shape and smooth surface, while MSN-2 show broken spheres (Fig. 2c). The dispersity and the uniformity of SDS-templated mesoporsous silica nanoparticles were further tuned by adding an increasing amount of APTS as a co-structure directing agent (CSDA).

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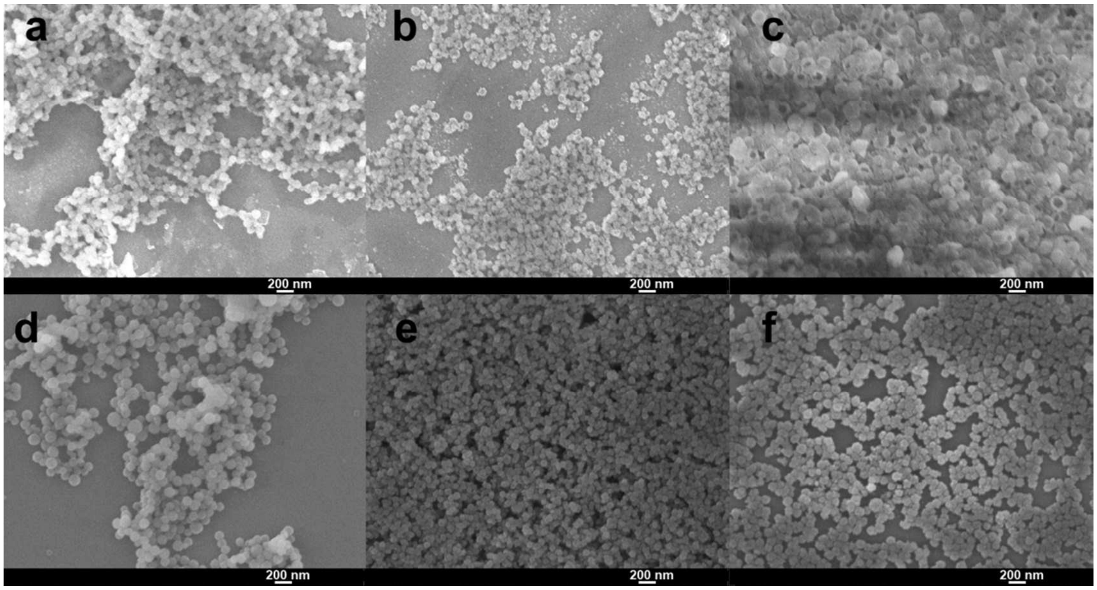


Fig.2 SEM images of MSNs synthesized with different surfactant ratio of SDS and SDBS: (a) MSN-1, (b) and (c) MSN-2, (d) MSN-3, (e) and (f) MSN-4

The synthesis was performed by using SDS alone without SDBS and APTS to evaluate the surfactant effect of SDS and the co-structure-directing effect of APTS. Large vesicles and their aggregates were formed, as shown in TEM images in Fig. S2 (a) and (b). The images indicate that without mixed surfactant and APTS, the formation of mesopores could not be realized. The same synthesis experiment was performed by using SDBS without SDS and APTS. The TEM images (Fig. S2 (c) and (d)) showed the formation of silica gel block without mesopores. These syntheses suggest that mesopores could not form by using SDS or SDBS alone. In other words, mixed anionic surfactants (SDS and SDBS) played an important part for the formation of mesopores via a CSDA method.

To construct more stable MSNs, we used SDBS mixed with SDS as mixed anionic surfactant template. We try to introduce SDBS for the morphology and the pore structure control of large pore MSNs. As shown in Fig. 1c and g, MSN-3 showed obvious improved dispersity than MSN-2 (Fig. 1b and f). The improved dispersity is attributed to the SDS replaced by SDBS in the mixed surfactant-templated synthesis system; the amount of free anion in the reaction process would become lower due to the stronger binding of tosylate over SDS.[42, 43] The tosylate moieties could be used to form large mesopores by an anion competition process, as discussed before,[42] where the tosylate anions compete with silicate oligomers during the particle formation.[42] From the observation of SEM image of MSN-3(Fig. 2d), we find that the nanoparticles size is not uniform. Similar results could be found in Fig.1c and g, which performed strong aggregation between particles. The particle sizes of MSN-3 (Fig.1c and g) ranges from 30 nm to 100 nm with larger aggregates. However, by adding an increasing amount of APTS (0.04g), the uniform and monodisperse MSN-4 formed with similar pore structures as that of MSN-3 (Fig.1d, 1h and Fig.2e, 2f). Rescently, the tosylate effects have been proposed by Zhang[42] and Qiao[43] in cationic surfactant-templated method, respectively.

From comparison of MSN-2 and MSN-4, we could find that by adding SDBS to form mixed surfactant template, the morphology and the pore structure considerably changed (Fig. 1). We could deduce that SDBS not only contributed to the formation of mixed template but also played an important role to control pore structure, particles size and morphology. The mixed surfactant template method proposed the significance of SDBS in formation of mesoporous silica nanoparticle with large pore, small size and good dispersity, all these kind of properties are different from the previous works.[44] Moreover, the SDS and SDBS are commercially used and short carbon chain surfactants, which result lower cost than the synthesized anionic surfactants. By comparison with previous strategy to synthesis large pore MSNs,[31, 44] our method is superior to avoid the usage of swelling agent and hydrophobic polymer micelle with long carbon chain.

Effect of reaction temperature

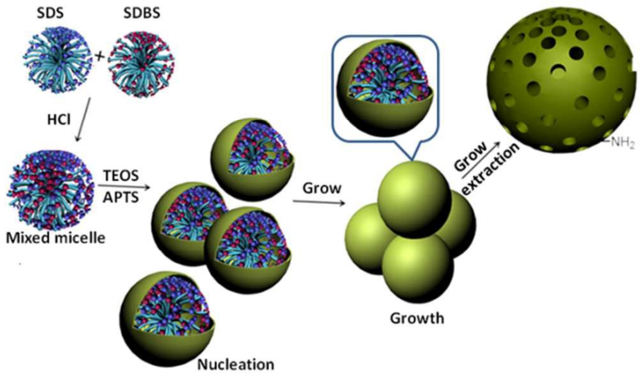
We compared the synthesis product of same molar ratio of reactants at 40°C (MSN-4) and 25°C (MSN-5), Table 1. The synthesis reaction at 25°C (MSN-5) resulted in particle aggregation, different particle morphologies and pore structures of the product (Fig. 1j and i). While the TEM image (Fig. 1i) of reaction product at 40°C (MSN-4) displayed better dispersity and uniform morphology of nanoparticles. It is convincing to state that the higher reaction temperature causes a higher rate of reaction during synthesis process.[43] Therefore, we deduce that the higher temperature would result in a proper rate for the assembly of silica precursor and mixed surfactant micelles to form large mesopores.

The temperature optimization results suggest that reaction kinetics plays an important role in the formation of large mesopores (Scheme 1). Compared with MSN-4, MSN-3 displayed non-uniform size when fewer amounts of APTS were used in synthesis process. In addition, we found that the nanoparticles had grown bigger by changing the stirring rate and the reactant concentration, shown in Fig. S1. These results were consistent with a nucleation and growth process similar to the growth process proposed by Zhang and co-workers.[43]

N_2 adsorption of MSN-4

By adjusting the molar ratio of SDBS in the mixed surfactant and the amount of APTS in synthesis system, we achieved proper synthesis conditions of MSN-4 with large mesopores. N_2 adsorption and desorption isotherms of MSN-4 in Fig. 3a show that there are two hysteresis loops at relative pressure of 0.6-0.8 and > 0.9. The hysteresis loop at $P/P_0 > 0.9$ suggests the existence of textural interparticle pores, while the hysteresis loop at P/P_0 from 0.6 to 0.8 is attributable to the framework porosity of MSN-4. The pore size distribution in Fig. 3b shows a narrow peak located at 10.3 nm and a broad peak at 30.7 nm. The broad peak may be related to the textural interparticle mesopores, which is in accord to the anion competition process.[42] The pore size of MSN-4 is larger than the mesoporous silica nanoparticles previously reported by only using one anionic surfactant as template,[15] suggesting that mixed anionic surfactant has played an important role in the formation of large pore.

The BET surface area of MSN-4 is 217 m²/g. The surface area is similar to previous report on mesoporous nanoparticles (245 m²/g) synthesized by mixed surfactant template.[43] Moreover, BET surface area is in accord to surfactant-templated large mesoporous silica reported previously.[31, 45-47] We measured the pore size of MSNs in TEM image and found that the pore diameter of MSN-4 is larger than the pore of MSN-1. To specifically illustrate the pore size of MSN-4, we have marked the pore with red line in TEM image. (Fig. S3)



Scheme 1 Synthesis and growth route of MSN-4

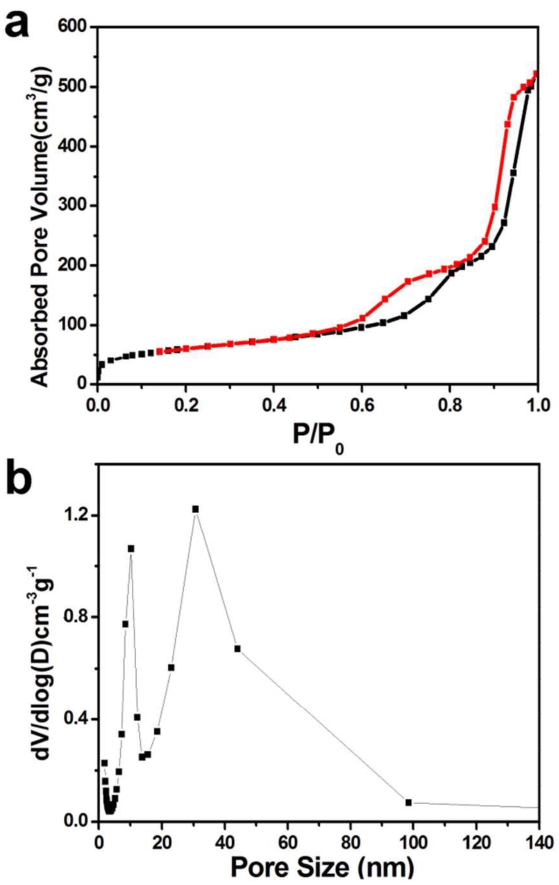


Fig.3 Nitrogen adsorption–desorption isotherms (a) and respective pore size distributions (b) of MSN-4

Schiff based-TPA functionalized MSN-4 and Fe^{3+} fluorescent sensing

To functionalize MSN-4 with Schiff based fluorescent moieties (Fig. 4a), we choose blue light emitting TPA moieties as organic group to conjugate with surface amino group on MSN-4 under acidic conditions. The white MSN-4 powder was dispersed in EtOH, after reflux for 3 hours under acid condition with TPA, centrifugation have been proposed to separate Schiff based-TPA functionalized MSN-4 with liquid. The Schiff based-TPA functionalized MSN-4 displayed yellow color, depicting a successful conjugated bonding between TPA and MSN-4. FT-IR spectrum in Fig. 4b is in accordance with the conjugated bonding product. As shown in Fig. 4b, the FT-IR spectrum of as-synthesized Schiff based-TPA functionalized MSN-4 display peaks corresponding to silica around 790 cm^{-1}, 956 cm^{-1} and 1040 cm^{-1}, which are attributed to the symmetric Si-O, Si-OH and asymmetric Si-O-Si vibrations. The characteristic band of C=N occurs around 1630-1690 cm^{-1}, which in good agreement with conjugated bond between TPA and MSN-4. All the data above suggest that Schiff base bond has been successfully formed, which gives Schiff based-TPA functionalized MSN-4. In our synthesis process of mixed anionic surfactant-templated mesoporous materials, APTS worked as CSDA agent to form mesopores and tune nanoparticles morphology with a grafting moiety for post-grafting.

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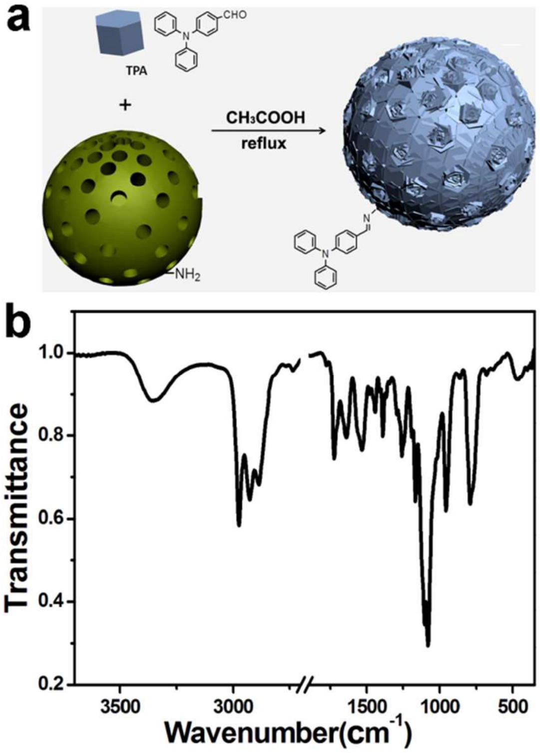

Fig.4 (a) MSN-4 functionalized with Schiff based-TPA and (b) FTIR spectra of MSN-4 functionalized with Schiff based-TPA

Schiff based TPA-functionalized MSN-4 featured excellent water dispersity and displayed blue fluorescence at 428 nm in water. With 2ppm of Fe^{3+} added each time, fluorescence intensity of Schiff based TPA-functionalized MSN-4 was gradually quenched, which could be ascribed to a PET (photo-induced energy transfer) mechanism and/or a paramagnetic quenching effect of Fe^{3+}.[48] Thus, Schiff based TPA-functionalized MSN-4 could be used as a fluorescent sensing material to detect Fe^{3+} in the water.

We also tested the selective detection of Schiff based TPA-functionalized MSN-4 to other ions such as Fe^{2+}, Cu^{2+}, Na^{+}, Zn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Mg^{2+}, as is shown in Fig.5b. No significant shape change or intensity decrease during the other ions added by comparison with the addition of equivalent Fe^{3+}(the detailed experiment condition of Fe^{3+} sensing and the detection selectivity have been illustrated in supporting information) This result may attribute to that no PET of quenching process occurred by other ions influences. Thus, a selective Fe^{3+} detection materials have been successfully synthesized by introduce Schiff base TPA to the surface of MSN-4 by using a conjugated bond.

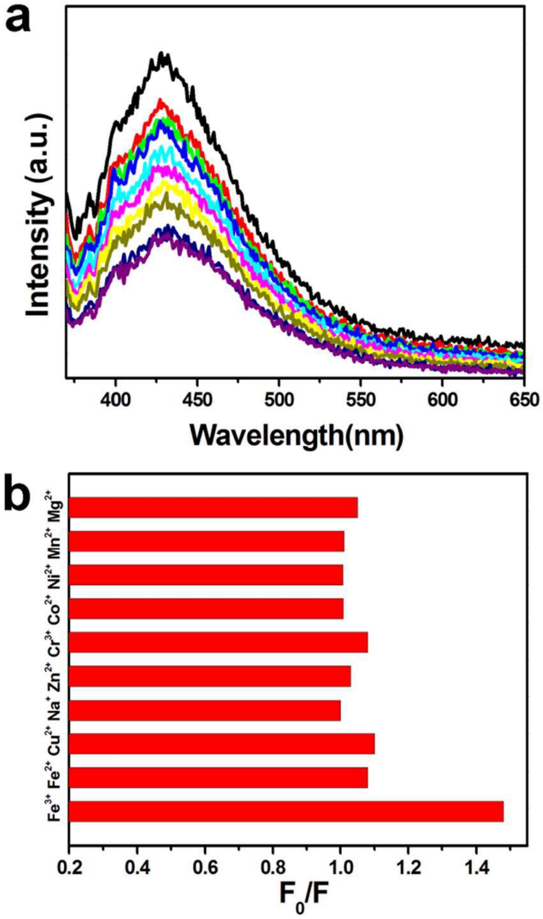

Fig.5 (a) Fluorescent emission spectra of Schiff based TPA-functionalized MSN-4 performed by adding an increasing amount of Fe^{3+} (excited at 350nm) and (b) selectivity of Fe^{3+}

Conclusions

In summary, this work demonstrated the synthesis of large pore mesoporous silica nanoparticles with uniform size by using mixed anionic surfactant as template without polymer micelle or swelling agent. The dispersity, mesopore structure and the morphology of mesoporous silica nanoperticles could be tailored by the concentration of anionic surfactants and the co-structure-directing agent. The formation process of MSNs was nucleation and growth. A post graft method has been used to introduce TPA on the surface of nanoparticles, which performed good selectivity detection of Fe^{3+} in aqueous media.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The TEM of MSN-4 synthesized and calcinated at different reactant concentrations and temperatures are shown in supporting information. See DOI: 10.1039/b000000x/

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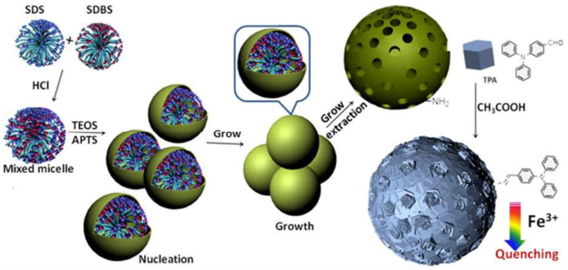
Graphical abstract



This work demonstrated that the design and synthesis of mesoporous silica nanoparticles with large pore using mixed anionic surfactant as soft template to favour nanoparticles with more amino group and graft TPA on the surface for high selective determination of Fe^{3+} in aqueous media.

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