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INVITED REVIEW

Porphyrin-doped mesoporous silica films for rapid TNT detection

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Abstract Two kinds of porphyrin-doped silica films with mesoporous structures were fabricated using evaporation-introduced self-assembly approach and examined for chemosensor applications to detect explosive compounds such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and nitrobenzene (NB). All synthesized silica films showed high fluorescence quenching sensitivity toward the vapors of TNT, DNT, and NB but is strongly dependent on pore structure. The silica film with three dimensional pore structure exhibits the highest quenching efficiency close to the quenching efficiency reported for emissive conjugated polymers, indicating these kinds of mesostructured composites are potentially useful chemosensory materials for rapidly detecting trace explosives. The preparation conditions, the structures of the resulting films, their sensing performances, and the fluorescence quenching mechanism were discussed in this paper.

Keywords Porphyrin · Sol–gel chemistry · Mesoporous silica films · TNT detection

Introduction

Functionalization of ordered mesoporous silica by covalent coupling of useful organic moieties on or within silica walls has significantly expended the application scopes of the original, pure mesoporous silica materials M41S [1–17]. In this context, due to large surface areas, fast molecule/ion transport kinetics within mesoporous silica channels and their inherent thermal and mechanical stability, these features make mesoporous silica very suitable and attractive for the development of robust sensors with high selectivity and rapid responsiveness by incorporating chemical sensing units into silica films. In this respect, Fan et al. [11] introduced a pH-sensitive dye, fluorescein, into the pore channel network of a cubic silica mesophase by postsynthetic grafting and successfully constructed a patterned pH-sensitive microfluidic system. Almost simultaneously, Wirnsberger et al. [12] also covalently anchored fluorescein moieties within optically transparent thin mesoporous silica films and demonstrated the preparation of pH sensors. More recently, high-performance uranyl species and NO gas sensors were also fabricated by using hexagonal or cubic mesoporous silica films [15, 16].

The development of efficient and cost-effective method for 2,4,6-trinitrotoluene (TNT) detection is highly desirable, as there are considerable environmental and security needs, especially with the surge of international terrorism and the increased use of explosives in terrorist attacks [18–25]. At present, besides trained dogs, several physical detection methods for explosives have been developed including high performance liquid chromatography, gas chromatography, cyclic voltammetry, surface-enhanced Raman spectroscopy, surface acoustic wave, and electron capture detection, etc. [18]. Although these techniques are highly selective, some are expensive and others are not easily portable. Recently, based on conjugated polymers, a highly sensitive sensor prototype was developed by Yang and Swager [19, 20]. Through an amplification mechanism, these special polymers display high fluorescence quenching (FQ) response to the vapors of nitroaromatic explosives. However, these conjugated polymers are not readily accessible, and the corresponding monomers require multistep syntheses [19–23].

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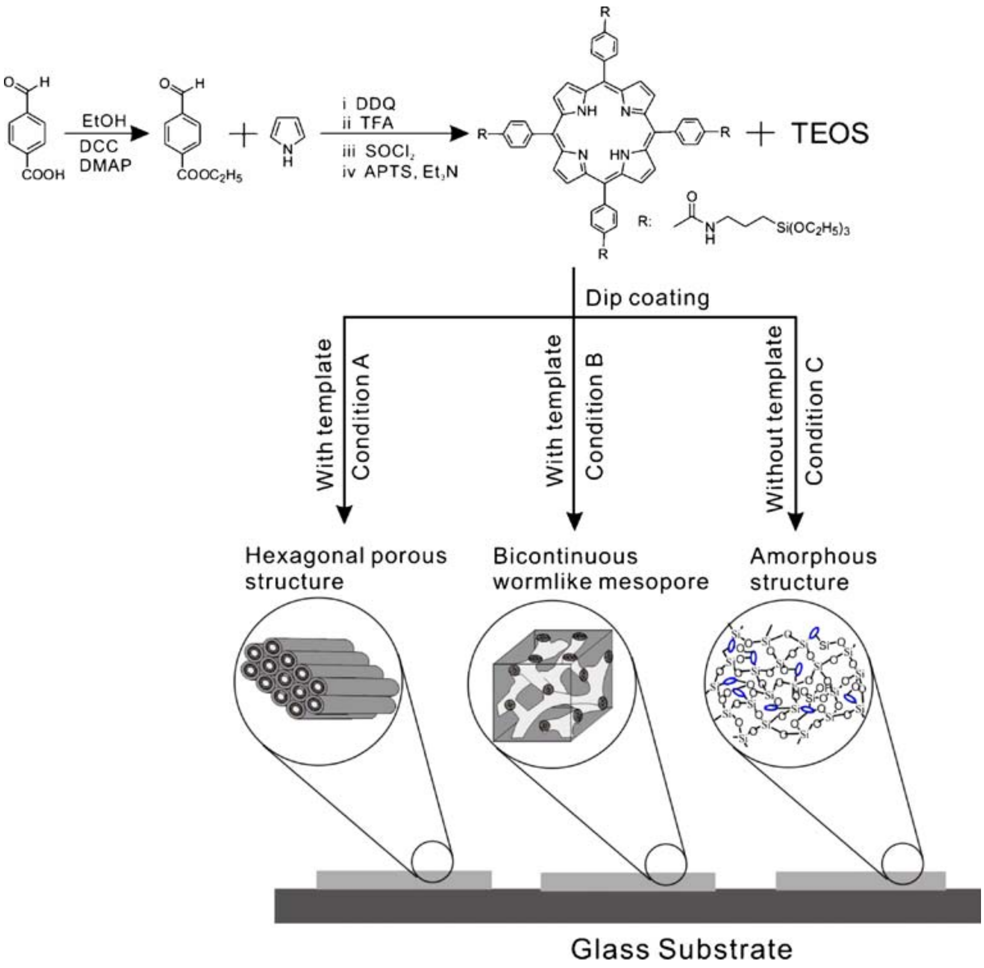
Bearing these considerations in mind, in this paper, we report two kinds of porphyrin-doped mesoporous silica films. It is found that these films show high FQ sensitivity toward the vapors of nitroaromatic compounds such as TNT. For example, silica film with wormlike pore structure exhibits a very fast response (expressed as a quenching of fluorescence intensity) upon exposing to TNT vapor (10 ppb), and after 10 s, the quenching percent reaches 27%. This result is very close to the quenching efficiency reported for most conjugated polymers [19–23], indicating that these mesostructured composites are potentially useful chemosensory materials for rapidly detecting explosives. Due to the ease of preparation, low processing cost, less expensive active materials, and easy incorporation into inexpensive and portable microelectronic devices, this explored new method could be a promising alternative of other developed explosive detection methods including spectroscopic, chromatographic, electrochemical, and conjugated polymer-based FQ methods [19–28].

Experimental section

Reagents

The 4-carboxybenzaldehyde (Fluka), 3-aminopropyltriethoxysilane (Fluka), and 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (Fluka) were used as received. Pyrrole (Py), tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), Thionyl chloride, 4-dimethylaminopyridine (DMAP), *N*, *N*′-dicyclohexylcarbodiimide, and triethylamine (Et_3N) were purchased from Beijing Chemical Reagents Company and used without further purification. The porphyrin dye bearing triethoxysilane groups (dye-silane) was easily synthesized according to the procedure shown in Scheme 1. All synthesized compounds were characterized using nuclear magnetic resonance (NMR) and mass spectrometry (MS). Anhydrous ethanol and deionized water were used in the preparation of silica sol. Glass slides (0.8×3 cm^2) were used as substrates for the deposition of thin silica films. Before using, glass slides were sonicated in ethanol and deionized water in turn for 15 min and dried under a stream of N_2.

Scheme 1 Illustration of the preparation of porphyrin-doped mesoporous silica films under three different conditions



Preparation of porphyrin-doped silica films

Silica film with hexagonal mesoporous structure Dye-silane, TEOS, anhydrous ethanol, water and HCl were mixed (mole ratios: 1×10^{-6}:1:3:8:5×10^{-5}) and refluxed at 60 °C for 90 min. Water and HCl were then added to give a HCl concentration of 7.34 mM. After stirring at room temperature (RT) for 15 min, the resulting sol was aged at 50 °C for 15 min and diluted with an ethanolic solution of CTAB, making Co=0.06 M (Co: concentration of CTAB) [24]. The obtained homogeneous precursor silica sol was employed for film deposition. In present work, transparent mesoporous silica films were prepared on glass slides by using dip-coating approach (8 cm/min) followed by solvent evaporation at room RT for 4 days. After further aging at 100 °C for 24 h and the extraction of surfactant template using HCl/EtOH (refluxed at 60 °C for 2 h), the desired mesoporous films deposited on glass slides were washed thoroughly with water and dried in air. The concentration of porphyrin incorporated in the films was determined by UV–Vis spectrometer.

Silica film with wormlike mesoporous structure An approach similar to that described above was employed for the preparation of wormlike silica film. Instead of Co= 0.06 M used for the preparation of hexagonal silica film, the final molar concentration of CTAB was adjusted to be 0.085 M in this case.

Amorphous silica film For control experiments, the amorphous silica films were also produced. In this case, the same conditions used for the fabrication of hexagonal silica film were employed only without the addition of the surfactant CTAB.

Instruments and characterization

^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM–ECA300 at 300 and 75 MHz, respectively. MS data were obtained by means of a Finnigan MAT 112b and a Finnigan MAT 711. The UV–Vis absorption spectra were recorded using a Perkin-Elmer UV/VIS Lamda35 spectrometer. The infrared (IR) spectra were collected on a Nicolet 360 FT-IR spectrometer. The fluorescence emission measurements were carried out using a fluorescence spectrometer (Perkin-Elmer LS55). The glass slide coated with porphyrin-doped silica film was placed in a quartz cuvette. The emission data were collected in the region of 500 to 800 nm using excitation wavelength of 420 nm. X-ray diffraction (XRD) spectra were recorded on a D/max-RB (Japan, Rigaku) diffractometer with monchromatized Cu Kα radiation (λ=0.15418 nm), operating at 40 Kv and 120 mA. Data were obtained with a scanning rate of 1.0° min^{-1}. To get TEM images of the prepared silica films, silica samples were scratched off from the glass substrates and dispersed in ethanol by sonication for 15 min. A drop of the dispersed particles was then deposited onto a carbon-coated Cu grid and examined using Hitachi 800 microscope operating at 200 Kv.

Results and discussion

Fabrication of porphyrin-functionalized mesoporous silica films

Direct synthetic route involving the cocondensation of TEOS and dye-functionalized silane in the presence of the surfactant CTAB was used to covalently attach porphyrin molecules into the ordered silica mesophases (Scheme 1). To produce porphyrin-doped hexagonal and wormlike mesoporous silica films, a slightly modified synthetic procedure developed by Fan et al. was adopted [11, 28]. In our case, after the formation of precursor organo-silica sol prepared by a similar two-step process, transparent thin mesoporous films were deposited on glass slides by dip-coating at 8 cm min^{-1} followed by solvent evaporation (4 days at RT), and aged at 100 °C for 24 h. The mesostructure of the deposited silica film is strongly dependent on the mole ratio of TEOS, dye-silane, ethanol, water, and HCl. By properly adjusting the molar composition (TEOS: dye: ethanol: water: HCl) in precursor silica sol and the concentration of the used surfactant, different mesostructures were achieved (Scheme 1).

Enough aging time is necessary and determined for obtaining high-quality and ordered mesoporous silica films. In this work, after dip-coating, the resulting silica films were dried for about 4 days at RT and finally at 100 °C for 24 h [12]. This prolonged drying treatment ensures a sufficiently high roughness of the thin silica films before template extraction using HCl/EtOH at 60 °C for 2 h. Otherwise, the films exhibit severe cracking after extraction. In our case, when the aging time at 100 °C was shortened from 24 to 5 h, the formed silica channels were collapsed after the removal of CTAB. These resultant silica films with disordered pore structure were also used to check their sensitivity to TNT vapor for purpose of comparison. Additionally, for control experiments, amorphous silica films were produced without the addition of the surfactant CTAB.

Characterization of porphyrin-functionalized silica films

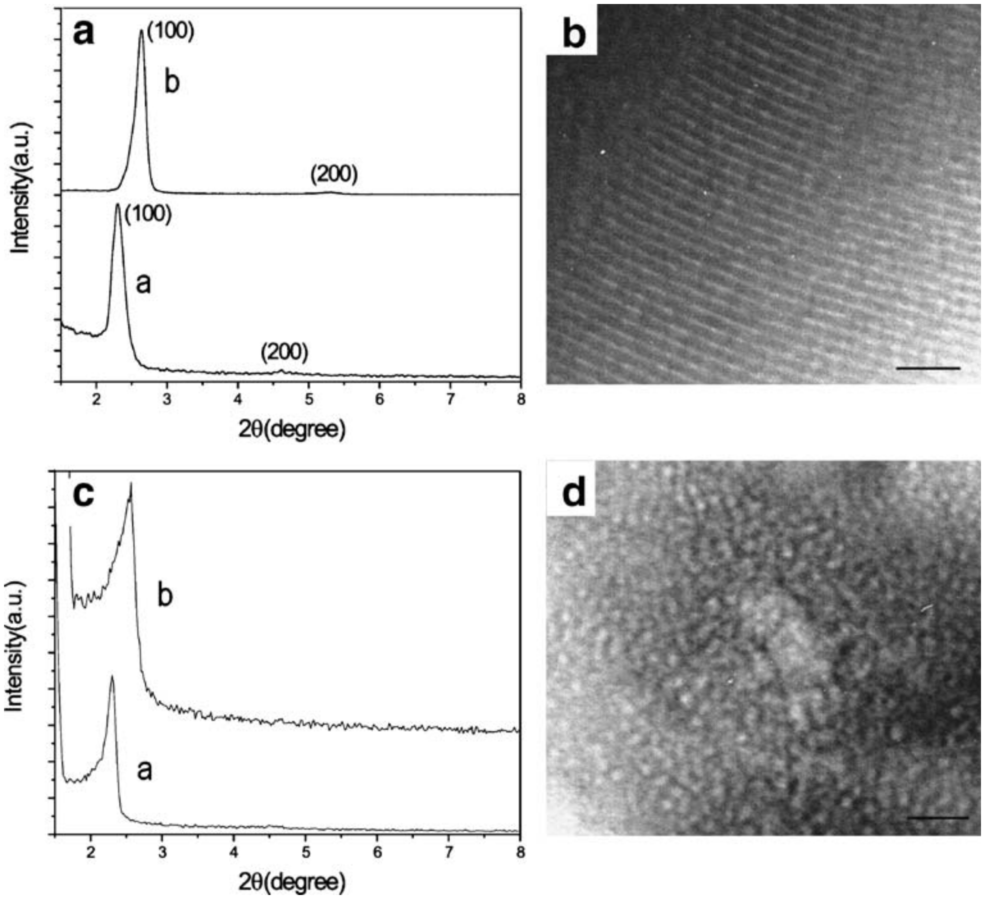
Although porphyrin has a larger molecular size (~4 nm^2), the cocondensation of the porphyrin-functionalized silane with TEOS can form ordered mesophases. The concentration of the used surfactant in the silica sol has a great influence on the resultant mesostructure. XRD of silica films fabricated with Co=0.06 M (Co: concentration of CTAB) shows the well-resolved pattern with an intense (100) reflection at low angle and one more weak intensity (200; Fig. 1a), corresponding to the reflections of a hexagonal mesophase with one-dimensional pore channels oriented parallel to the substrate surface [27, 28]. By comparison, only one intense diffraction peak at low *2θ* value was detected for the film prepared with Co=0.085 M, indicating the formation of silica film characterized by wormlike mesophase (Fig. 1b) [27, 28]. These results are consistent with the observations in the literature [29, 30]. As expected, without the use of surfactant template, only a broad reflection peak was observed, suggesting that the structure of the formed silica film under the condition C (Scheme 1) was substantially amorphous.

Complementary to the XRD investigations, the images of transmission electron microscopy (TEM) of both formed silica films display ordered hexagonal and wormlike mesoporous structures throughout the films, respectively. For comparison, the typical TEM images of the mesostructured films formed under condition A and B (Scheme 1) were depicted in Fig. 1c and d.

The employed aging conditions (4 days at RT followed by 24 h at 100 °C) render the prepared silica films sufficient stability. As shown in Fig. 1a,b, after template extraction at 60 °C, the XRD patterns of these films remained the same except of a small shift of diffraction peaks due to the shrinkage of pores, and the formed mesostructures were preserved. However, when the heating time was shortened from 24 to 5 h, the formed mesostructure was destroyed or collapsed through extraction process. Figure 2 displays this case. It is clearly seen that the CTAB extraction caused the structure collapse from one-dimensional hexagonal pore structure to disordered amorphous state. From the point of view of structure, this transformation is not desirable. However, this occurred collapse results in breakdown of silica walls between mesoporous channels, and consequently, the formation of three-dimensional (3D) interpenetrating pore structure. Although the film structure is 3D disordered, this state should be favorable for the permeation of gaseous molecules in silica film and also benefit the performance of it based chemosensors. This assumption was confirmed by experiment (*vide post*).

The correct incorporation of the used porphyrin dye into synthesized silica films was proven by Fourier transform infrared (FTIR), UV–Vis, and fluorescence measurements. Figure 3 shows the FTIR spectra of the synthesized

Fig. 1 XRD patterns and TEM micrograph of the silica films prepared under C_0=0.06 M (**a**, **b**) and C_0=0.085 M (**c**, **d**) before (*a*) and after (*b*) template extraction. The scale bar is 20 nm



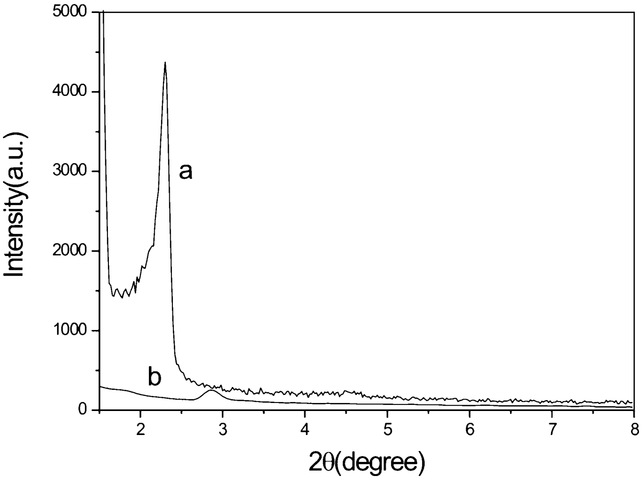


Fig. 2 XRD patterns of the silica films under C_0=0.06 M and aged at 100 °C for 5 h. *a*, before the removal of template; *b*, after the removal of template

porphyrin and the formed silica films. Obviously, besides the broad and strong absorptions from siloxane-$(SiO)_n$-groups in the range of 1,000 to 1,200 cm^{-1} [31], FTIR spectrum of the synthesized silica exhibits the characteristic absorptions of the porphyrin units at 2,971, 1,637, 1,471, and 945 cm^{-1} [32], comparable to those of porphyrin monomer (Fig. 3a,b). The concentration of the porphyrin dye incorporated in the formed film, determined by UV–Vis spectrometer, is about 3.9×10^{-7} M, indicating that ~40% of porphyrin molecules in pre-gel was incorporated in the films. The molar ratio of the dye-silane and TEOS in the prepared hybrid mesoporous is about $1{:}4\times10^{-7}$.

The silica films coated on glass slides has a strong scattering effect in UV–Vis region. Consistent with FTIR results, however, the characteristic Soret band absorption of porphyrin units is clearly to be seen in UV–Vis spectrum of silica film at 417 nm similar to that of the porphyrin dye in CH_2Cl_2 (Fig. 4a), also 2-week Q bands at 510 and 550 nm was observed as the characteristic absorptions of porphyrin

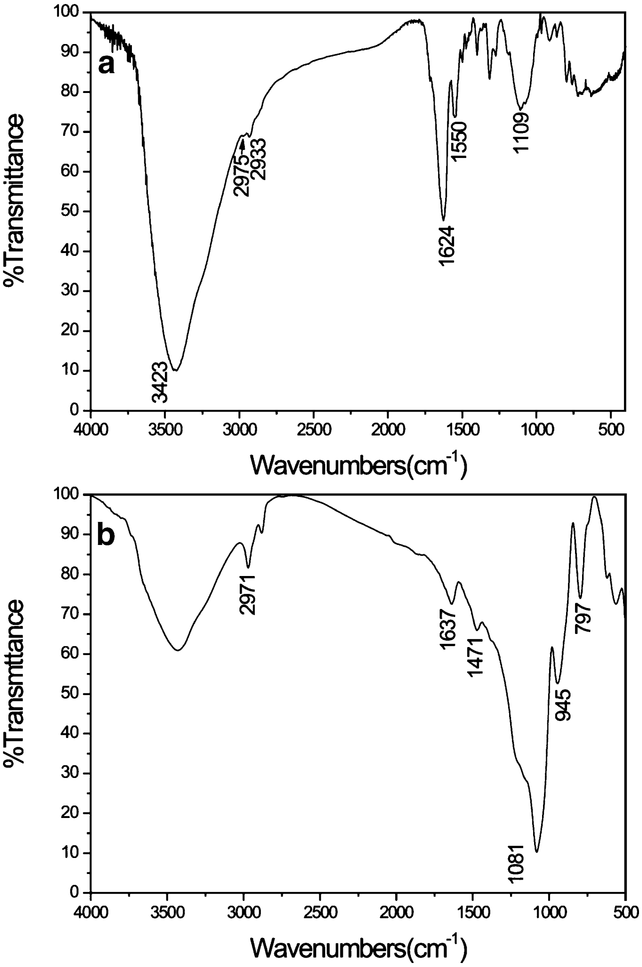


Fig. 3 FTIR spectra of the synthesized silane–porphyrin dye (**a**) and the formed silica film (**b**)

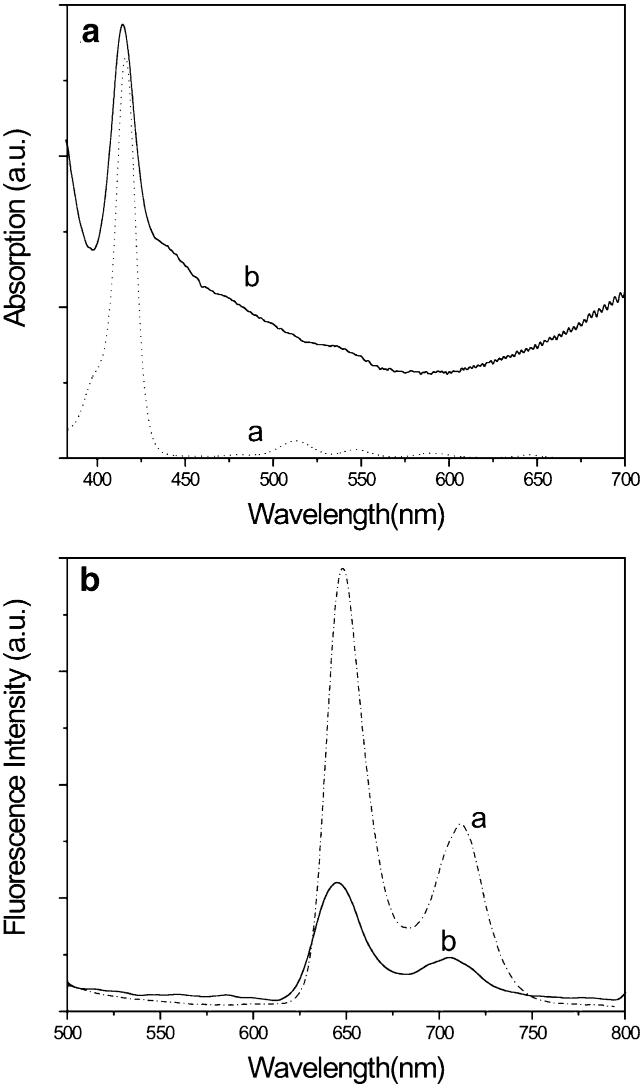


Fig. 4 UV–Vis spectra (**a**) and photoluminescence spectra (**b**) of the porphyrin molecules in the formed silica film or in CH_2Cl_2 solution. *a*, in CH_2Cl_2 solution; *b*, in silica thin film

molecule (Fig. 4a). Additionally, the emission spectra of this silica film have two emission peaks at 650 and 755 nm, respectively, which are also similar to those of the porphyrin dye in solution (Fig. 4b). These results clearly reveal that after the film preparation process, the properties of porphyrin moieties in silica matrix were maintained without loss.

Sensitivity of porphyrin-doped silica films toward the vapors of nitroaromatic

For the demonstration of TNT sensing, a series of 10-ml glass vials containing 1.5 g TNT solid and cotton gauze was used to prevent direct contact of film-coated glass slides from TNT powder and to maintain a constant vapor pressure (VP) of analyte. Exposure of a silica film to the vapor of analyte was performed by placing a silica film into a sealed vial at RT (25 °C). The saturation VP of TNT (10 ppb), DNT (180 ppb) or NB (3×10^5 ppb) is assumed to form in these sealed vials [19]. After exposing the silica film coated glass slide for a given period of time, the fluorescence spectra were measured immediately at excitation wavelength of 420 nm. Like TNT, the sensitivity of the pophyrin-doped silica films toward the vapor of 2, 4-dinitrotoluene (DNT) was also determined. For NB, however, we used a cotton ball imbued with liquid NB to give a stable VP in a vial for sensing measurements.

Photoluminescence quenching was observed for all three types of porphyrin-doped silica films (hexagonal, wormlike, or amorphous silica film) upon exposing to TNT vapor. As expected, the sensing property is strongly dependent on the pore structure of the fabricated silica films. Figure 5 illustrates the time-dependence of fluorescence intensity of three types of silica films upon exposing to trace TNT vapor (10 ppb). Clearly, due to its 3D pore structure and hence good gas accessibility, wormlike pore silica film exhibits the highest response (expressed as a quenching efficiency of fluorescence intensity) among these three different silica films, and after 10 s, the quenching percent reaches 27%, which is close to the quenching efficiency reported for most conjugated polymers [19–23]. As expected, smaller quenching can be seen for amorphous tightly cross-linked film (3% in 10 s). For the silica film with one-dimensional hexagonal mesostructure, however, a relative fast response to TNT (20% in 10 s) was also observed, probably due to the gas accessibility to the mesopores on the sides of film [16]. In all cases, after repeated puffing with nitrogen gas or washing with toluene, the quenched silica films can be recovered for further use.

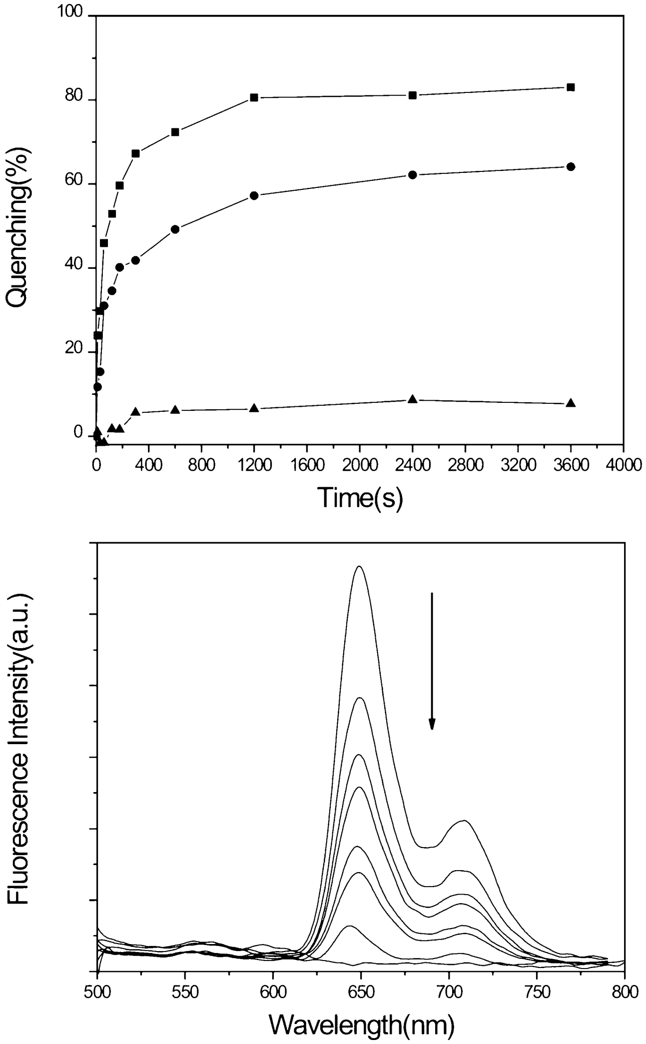


Fig. 5 Time-dependent fluorescence quenching of the prepared silica films upon exposing TNT vapour (10 ppb). *Filled square*, silica film with bicontinuous worm-like pore structure; *filled circle*, silica film with one-dimensional hexagonal pore structure; *filled triangle*, silica film prepared without the use of surfactant

Interestingly, it is found that the collapsed silica films (aged at RT for 4 days and at 100 °C for 5 h) also exhibit rather good sensitivity to the vapors of nitroaromatic compounds. Figure 6a displays the time-dependent fluorescence response of the collapsed silica films to TNT, DNT, and NB. It is seen that after 10 s, 10–40% of fluorescence was quenched. This quenching efficiency is close to that of silica film with wormlike mesoporous structure. In contrast, amorphous silica film without appropriate pore structure showed very low sensitivity (Fig. 6b). These results clearly indicate that a good permeability resulted from appropriate pore structure is one of the key factors, which determines the sensing performance of silica-based chemosensors.

The constructed nanocomposite film shows very high FQ sensitivity toward TNT vapor. The following reasons are believed to be principally responsible for the observed remarkable sensing performance. First, the unique porous structure provides a necessary condition for the facile diffusion of analytes to sensing elements, while the large

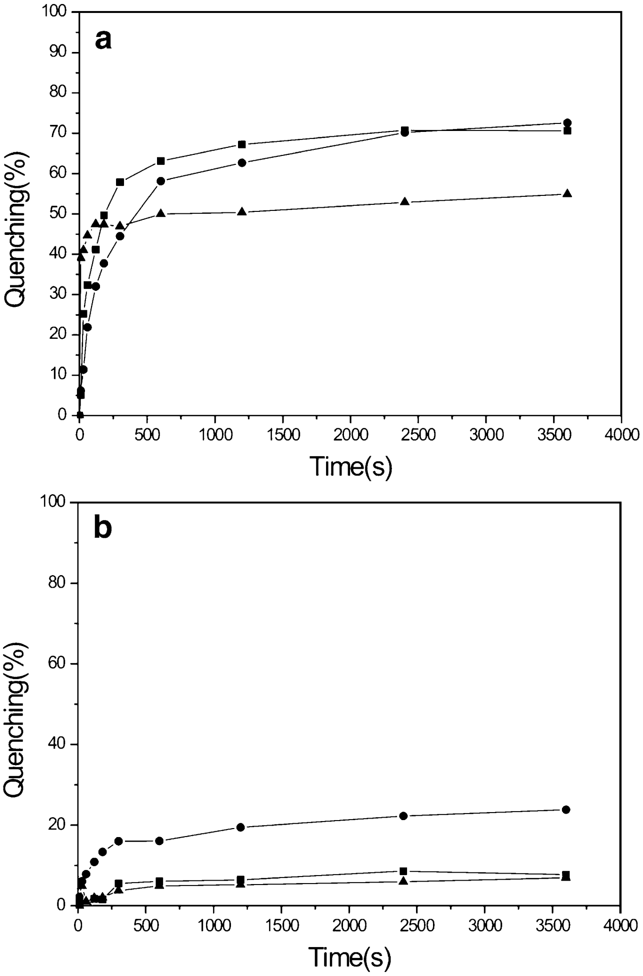


Fig. 6 Time-dependent fluorescence quenching of the collapsed silica film (**a**) and amorphous silica films (**b**) upon exposing TNT (*filled square*); DNT (*filled circle*) and NB (*filled triangle*) vapors

surface area (~1000 g/m^2) considerably enhances the interaction sites between analyte molecules and sensing elements, and thereby further improves the detection sensitivity [16, 19]. Second, besides the diffusion ability of analytes through films, theoretic studies show that the FQ per unit time is also affected by various other factors, including the VP of analyte, the exergonicity ($\Delta G°$) of electron transfer, and the binding strength (K_b) between sensing elements and analytes, as described by the following equation: $FQ \propto (VP)[\exp(-\Delta G°)^2](K_b)$ [22]. Obviously, for a given analyte like TNT, strong binding strength and energy level matching are essential for obtaining high TNT quenching efficiency. In fact, due to the well-known strong tendency to form hydrogen bonding between imino hydrogen of the used porphyrin molecule with nitro groups of nitroarmatic as well as π-stacking between porphyrin and nitroaromatics [33, 34], porphyrin units have relative large affinity for nitroaromatic molecule, which provides a strong driving force for fast FQ. Additionally, the adequate energy-level matching between nitroaromatics and porphyrin molecules makes the FQ very effective. The different FQ efficiencies of TNT, DNT, and NB, shown in Figs. 5 and 6, are probably due to their different VPs and different affinities to porphyrin molecule. In summary, good permeation kinetics of analyte, strong analyte-emissive component interaction, and comparable energy level of analyte and emissive component are the key factors for fast FQ. In our case, the constructed mesostructured films just meet the mentioned requirements. Figure 7 shows a schematic diagram of the electron-transfer mechanism for the quenching of photoluminescence of the porphyrin dye with analyte.

Conclusion

Two kinds of porphyrin-doped mesoporous silica films were successfully fabricated, which show a high FQ sensitivity toward trace vapors (10 ppb) of TNT and other explosive compounds. As the preparation procedure is very simple, the used materials are inexpensive, and the synthesized sensing films can be easily incorporated into portable electronic devices, these mesostructured composites are potentially useful chemosensory materials for rapidly detecting explosives. To the best of our knowledge, this is the first report about the preparation of porphyrin-doped silica films with ordered mesoporous structure and porphyrin dye as sensing element for detecting the vapors of explosive nitroaromatic. We believe this explored method should be a promising alternative of other developed explosive detection means.

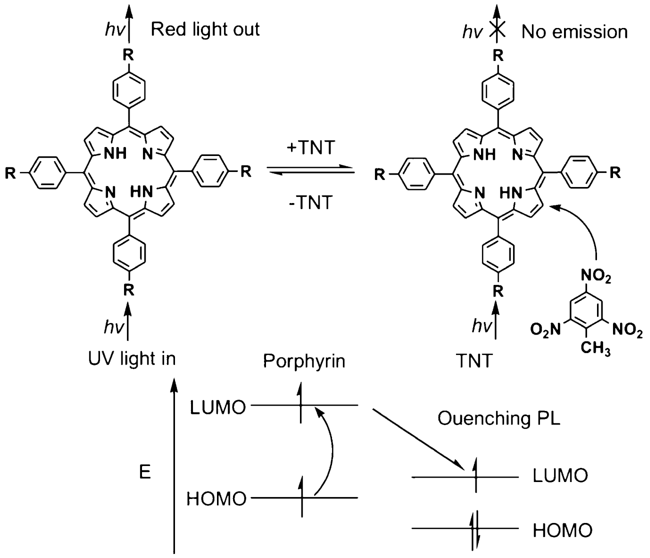


Fig. 7 Schematic diagram of electron-transfer mechanism for quenching the fluorescence of porphyrin by TNT molecule

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