

Mesostructured SBA-3 silica containing Reichardt's dye as an optical ammonia sensor

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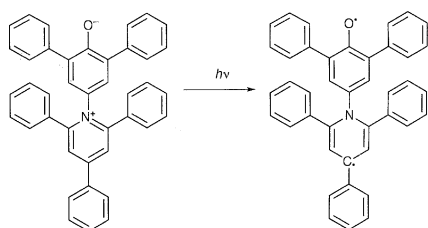
Mesostructured SBA-3 silica containing Reichardt's dye is shown to give a reversible optical response to gaseous ammonia, with a response time of a few seconds and an intensity proportional to the ammonia partial pressure, which are desirable properties for gas sensing.

Mesoporous materials have been recently proposed as hosts for chemo-sensing molecules.^{1,2} Materials free from surfactant are usually used: mesostructured systems still containing micelles of the templating agent may also be considered, because the micellar phase is permeable to guest molecules.^{3,4}

One advantage is that the surfactant removal step is avoided, a critical step in the production of sensing devices. The presence of the micellar phase also facilitates a homogeneous distribution of dye molecules^{5,6} and may allow tailoring of sensor properties.⁷

The present paper reports on ammonia optical sensing by using Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)-phenolate, embedded in the micellar phase (CTABr) of SBA-3 mesostructured silica, the hexagonal phase formed in acidic synthesis gels. Reichardt's dye (RD) is a solvatochromic compound⁸ which has been already immobilized in polymeric substrates,⁹ silica,¹⁰ and glasses,⁹ to obtain opto-chemical sensors for various vapours. RD has a charge-transfer (CT) transition in the visible region (depicted in Scheme 1) which is very medium-dependent, because polar solvents tend to stabilise the molecular electronic ground state, thus increasing the CT transition energy. Protonation of RD leads to the formation of a phenolic species, H-RD⁺, not showing the CT band in the visible region⁷ and hence colourless.

Synthesis of RD-containing SBA-3 mesostructured silica (RD-SBA-3) was accomplished following a standard recipe,¹¹ adding RD to the acidic synthesis solution before adding TEOS. The molar composition of the synthesis mixture was: 1 TEOS : 0.12 CTABr : 9.2 HCl : 130 H₂O, with TEOS : dye molar ratios of 1000 : 1 and 100 : 1. The mixture was stirred for 30 minutes and then the product was filtered. Both the powder and the filtered mother solution were colourless, because the RD was protonated by HCl. Absence of RD in the filtered solution was checked by adding NH₃ until a basic pH was reached. The solution remained colourless, thus suggesting complete incorporation of the dye into the solid mesophase. The powder was then washed with distilled water and air dried. No dye leaching occurred during washing



Scheme 1 Reichardt's dye charge-transfer transition.

(checked as above) thus confirming the incorporation of RD into the micelles.^{5,7}

Fig. 1 shows the X-ray diffraction patterns of RD-SBA-3 (TEOS : dye = 100 : 1) and dye-free SBA-3. Both samples show a hexagonal *p6mm* symmetry, characteristic of SBA-3 type mesostructures, suggesting that incorporation of dye molecules does not prevent formation of an ordered material. A smaller d_{100} is observed for the RD-containing sample; the corresponding decrease in the a parameter (from 46.8 to 44.4 Å) indicates that guest molecules bring about an increase of the distance between polar heads of the surfactant.

Interaction between RD-SBA-3 and gaseous ammonia was studied by using a suitable UV-visible cell connected to a vacuum line and gas dosing frame. Curve 1 in Fig. 2 is the diffuse reflectance (DR) visible spectrum of RD-SBA-3 (TEOS : dye = 1000 : 1). No light absorption is observed because the acidic synthesis conditions yield the dye in the H-RD⁺ phenolic form. Dosing with ammonia at an increasing pressure resulted in the development of an absorption band at 530 nm (Fig. 2), due to the dye CT transition. The H-RD⁺ species transfers a proton to ammonia, thus becoming coloured. This effect is immediate and fully reversible; the colour was found to disappear upon ammonia removal. Optical sensing tests carried out in NH₃ flow (500 ppm in air) show that the response time is 27 s.

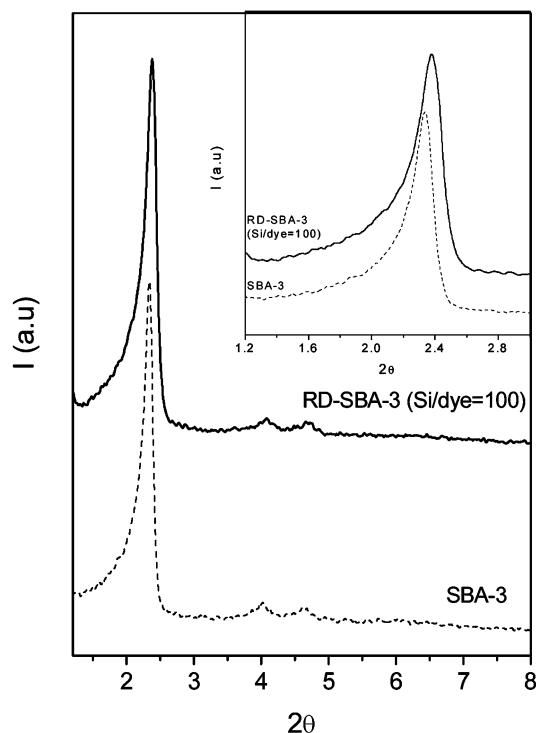


Fig. 1 XRD patterns (Cu K α radiation) of dye-free SBA-3 and RD-containing SBA-3.

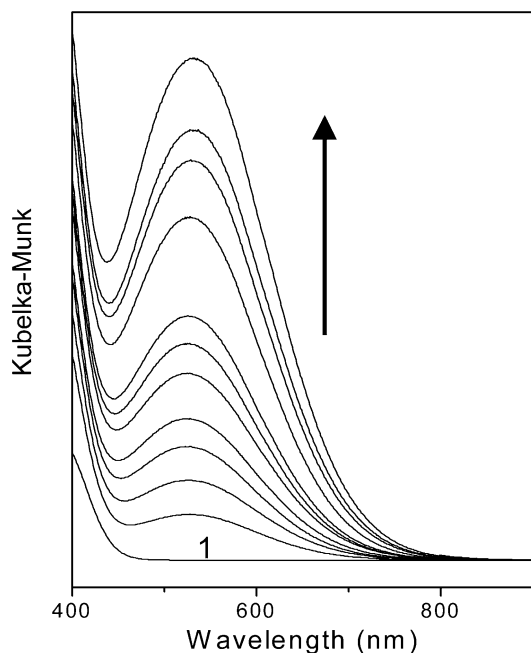
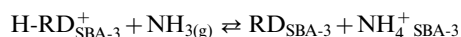


Fig. 2 DR-visible spectra of RD-SBA-3 (TEOS : dye = 1000 : 1) exposed to an increasing equilibrium pressure of ammonia gas (1–180 mbar).

The observed optical effect is due to the equilibrium reaction:



The corresponding equilibrium constant is:

$$K = ([\text{RD}_{\text{SBA-3}}][\text{NH}_4^+_{\text{SBA-3}}])/([\text{H-RD}_{\text{SBA-3}}]p_{\text{NH}_3}),$$

which can be written as:

$$\theta^2/(1 - \theta) = Kp_{\text{NH}_3} \quad (1)$$

where the concentration of deprotonated RD molecules, $\text{RD}_{\text{SBA-3}}$, and $\text{NH}_4^+_{\text{SBA-3}}$ species are both equal to θ , the extent of reaction, while $(1 - \theta)$ is the fraction of unreacted species, $\text{H-RD}_{\text{SBA-3}}$, and p_{NH_3} is the equilibrium pressure of ammonia. From the spectra in Fig. 2, θ can be calculated by dividing the integrated intensity at each coverage by the intensity at the maximum coverage (I/I_{max}). Fig. 3 reports $\theta^2/(1 - \theta)$ values as a function of ammonia equilibrium pressure. A straight line passing through the origin was obtained, in agreement with eqn. (1) above. The equilibrium constant resulted to be $K = 5 \times 10^{-3} \text{ mbar}^{-1}$.

Fig. 4 (curve 1) shows the DR visible spectra of RD-SBA-3 (TEOS : dye = 1000 : 1) and RD-SBA-3 (TEOS : dye = 100 : 1) (curve 2) exposed to the same ammonia equilibrium pressure (ca. 50 mbar). The absorption band of RD-SBA-3 (TEOS : dye = 100 : 1) is about ten times more intense than that of RD-SBA-3 (TEOS : dye = 1000 : 1), i.e. the optical signal approximately follows the amount of incorporated dye. It is thus seen that sensitivity of the system can be tailored by changing dye concentration.

In conclusion, mesostructured SBA-3 silica containing Reichardt's dye were shown to give a reversible optical response to ammonia. The response time is of the order of a few seconds, and the intensity is proportional to ammonia partial pressure; i.e., to concentration in a gas phase. The sensitivity of the system can easily be tailored by changing the dye content of the nanostructured mesophase. Reversibility and proportionality are desirable properties for chemosensors. The system is rather selective in that it does not respond to alcohols, thiols, and other proton-acceptor substances.

Further research is in progress to extend these studies to amine sensing which, along with ammonia sensing, is a subject of

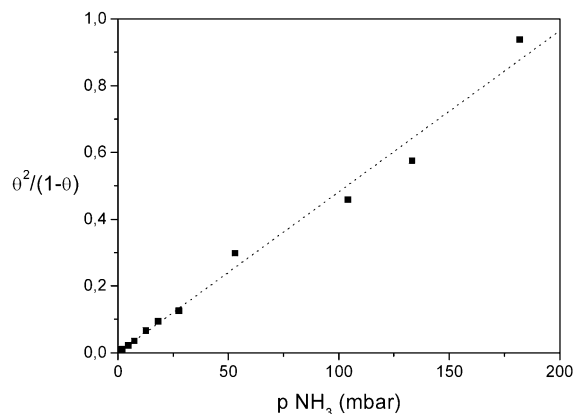


Fig. 3 Plot of $\theta^2/(1 - \theta)$ as a function of NH_3 equilibrium pressure.

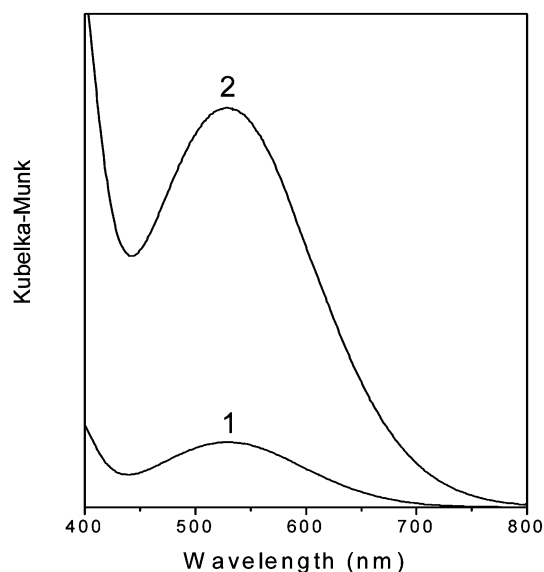


Fig. 4 DR-visible spectra of RD-SBA-3 (TEOS : dye = 1000 : 1) (curve 1) and RD-SBA-3 (TEOS : dye = 100 : 1) (curve 2) exposed to the same equilibrium pressures of ammonia (50 mbar).

potential interest to both biomedical applications and the food industry.

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