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Advanced selective optical sensors based on periodically organized mesoporous hybrid silica thin films†

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Mesoporous thin films functionalized with silylated β-diketone compounds with symmetry mesostructure dependent on the probe quantity were used as fast uranyl species sensors with high selectivity and sensitivity.

Continuous and increasing human activity is resulting in a significant release of pollutant compounds into the environment, threatening both the health of humans and the stability of natural ecosystems. Within this context, the detection of the metal cations classified by the Environmental Protection Agency as "*drinking water contaminants*" (*i.e.* Cd, Cr, Co, Pb, Hg, Ni, U) is of particular relevance. Sol–gel glasses are commonly used as supports in the development of optical sensor devices because they are transparent, chemically inert, thermally and mechanically robust, photostable, easily processed and they allow the embedding/grafting of molecular probes. However, the poorly ordered microporosity of such materials is sometimes a limiting factor to the homogeneous and fast diffusion of analytes inside the sensing matrix. On the other hand, mesostructured mesoporous thin films with their larger open porosity and their high surface area should improve analyte diffusion[1] and accessibility towards supported probes. Moreover, both their monomodal narrow pore size distribution and their controlled porous connectivity should make them much more resistant to the huge capillary stresses usually due to their instability and the collapsing of mesoporous xerogels during successive water dipping and drying sensing cycles.

Here, we demonstrate the possibility to realise *via* Evaporation Induced Self Assembly (EISA)[2,3] the one-pot preparation of ordered mesoporous functionalized silica thin films with controlled mesostructure,[4] optical quality and excellent cycling reproducibility, which are very promising materials for optical sensor applications. This method offers several advantages compared to post-grafting: (i) functionalization and structuration of films take place at the same time, (ii) it induces a homogeneous distribution of organic probes within the network and (iii) the stoichiometry of the thin film is perfectly controlled and is equal to the composition of the initial solution. Moreover, for a fixed [CTAB]/[Si] ratio (CTAB = cetyltrimethylammonium bromide), the mesostructure type can be adjusted by selecting the proper [probe]/[Si] ratio to obtain, for example, a mechanically more resistant cubic phase or the cylindrical pores of the 2D hexagonal phase in which the difference in the capillary stress between wetting and drying of thin films is minimal.

Focusing on the selective chelating properties of dibenzoylmethane (DBM) for metallic cations, we synthesised triethoxydibenzoylmethane (SDBM) for the "one-pot" sensor preparation. A pre-hydrolysed solution containing TEOS, deionised water and HCl (1 TEOS : 3 EtOH : 5×10^{-5} HCl : 1 H$_2$O, molar ratio) was prepared as detailed previously.[5] A second solution obtained by dissolution of CTAB in a mixture of ethanol and tetrahydrofuran was then added to the pre-hydrolysed solution with an additional amount of water and HCl. The replacement of a part of ethanol by a solvent, THF (which solubilises SDBM more efficiently than ethanol without altering the formation of the mesostructure), is crucial for the incorporation of SDBM into thin films. The final solution with a molar composition of 1 TEOS : 6 EtOH : 9 THF : 5 H$_2$O : 0.004 HCl : 0.14 CTAB was aged at room temperature for 5 days prior to the addition of SDBM. Thin films were prepared by dip coating silicon wafers and quartz substrates. In order to obtain both cubic structure, optical homogeneity and transparency, we kept the relative humidity at 40% for the first 30 s and at 70% for next 5 minutes.[5] Films were heat treated at 140 °C for 2 days and then washed with alcohol in order to remove surfactants (confirmed by FTIR experiments). This thermal treatment enabled stiffening of the silica network without decomposition of molecular probes. Mesostructures of thin films were determined by 2D-GISAXS experiments performed with synchrotron radiations (SAXS beam line ELETTRA, Trieste, Italy) (Fig. 1).

The addition of increasing amounts of SDBM for a CTAB on silica molar ratio fixed at 0.14 in films induces mesostructural evolutions: from the cubic phase (Pm3n), a mixture of cubic (Pm3n) and 2D-hexagonal (p6m), the pure 2D-hexagonal phase to the lamellar phase. Such phase transitions are commonly observed when the [CTAB]/[SiO$_2$] ratio increases,[3] inducing a decrease in the curvature, but it is much more unusual in a one-pot grafting experiment at a fixed amount of CTAB.[4] Here, SDBM acts as a grafted co-surfactant since it solubilizes into the hydrophobic part of CTAB micelles, increasing the organic volume fraction.[4] The SDBM environment is confirmed by UV–visible analyses of the as-made films, showing that the keto–enol equilibrium of SDBM is shifted to the enol form, characteristic of the
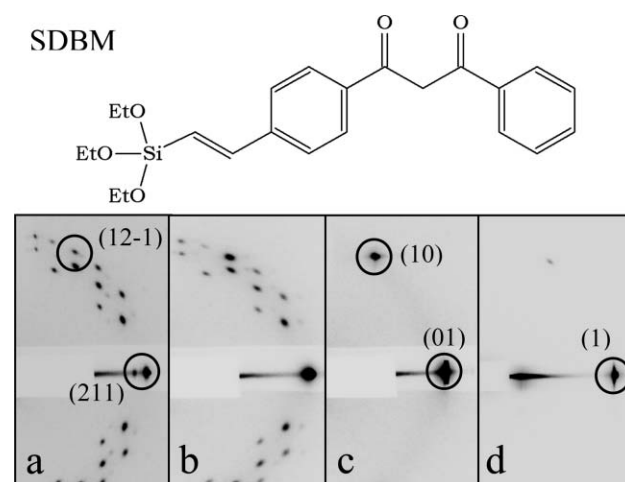

Fig. 1 SAXS patterns of sensing layers prepared with [SDBM]/[Si] ratio values of (a) 0–0.009, (b) 0.0095–0.014, (c) 0.027 and (d) 0.053–0.123 are typical of *Pn3m*, a *Pn3m*–*p6m* mixture, *p6m* and lamellar phases respectively.

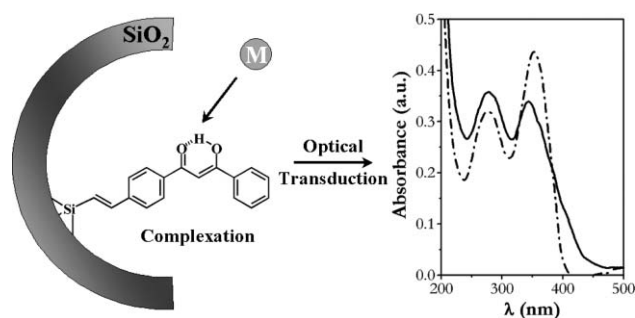† Electronic supplementary information (ESI) available: UV–vis and FTIR spectra of β-diketones. See http://www.rsc.org/suppdata/cc/b4/b408869g/

Fig. 2 UV–vis spectra of sensing layer before (dotted line) and after immersion in a 100 ppm uranyl aqueous solution (plain line). Cation detection may be efficiently performed at 355 nm or 400 nm.

Fig. 3 Complexation–regeneration cycles measured at 400 nm for a 2D-hexagonal mesostructured thin film. Complexation (●), regeneration (○) and variation (■) of the absorbance at 400 nm after a single cycle.

aprotic-apolar medium at the center of the micelles.[6,7] This unambiguous localisation of the DBM function implies all SDBM is directly available in the matrix as a probe when CTAB is removed.

After surfactant extraction, the spectral responses of functionalized thin films with [SDBM]/[Si] ratios of 2.7 and 5.3% (*p6m* and lamellar phases respectively) were studied in aqueous solutions with various metallic cation salts: Cd(II), Ce(III), Co(II), Cr(III), Eu(III), Ni(II), U(VI), Cu(II) and Fe(III). For a demonstration of their application as chemical sensors, films were soaked in the cation aqueous solutions under gentle stirring for 30 seconds, then washed with ethanol and dried. The *in situ* monitoring during these first 30 seconds shows that optical changes occur for three cations only (Cu(II), Fe(III) and U(VI)) in the UV domain and the formation of colored complexes for the two last cations only (orange with Fe(III) and yellow for U(VI)). The selectivity of films towards Cu(II), Fe(III) and U(VI) cations can be explained by a shorter complexation equilibrium time compared to other metallic cations. According to Stary[8] even if the DBM compound allows the extraction of many metals in solution, the extraction equilibrium time depends on the metallic cations (from a few minutes to several days). The selectivity observed with our thin films is thus due to the short time of our experiments (30 seconds) and not due to the intrinsic selectivity of the SDBM molecular probe.

Fig. 2 shows the evolution of thin films with a 2D hexagonal mesostructure containing a [SDBM]/[Si] ratio of 2.7% upon immersion in a 100 ppm uranyl nitrate solution. The immersion induces a hypsochromic shift of the enol peak at 360 nm, a decrease of enol/keto ratio (related to the strong intrinsic absorption of uranyl species below 350 nm) and the emergence of a new absorption band in the near-visible region. The absorption spectra after complexation is assigned to the superposition of SDBM, uranyl and the SDBM–U(VI) colored complex spectra. The complexation equilibrium is characterised by the presence of two isosbestic points observed at $\lambda = 330$ and 385 nm when the uranyl concentration increases. Therefore, a near-visible sensing range was selected for uranyl cation detection. The detection is optimal at 355 and 400 nm. As the intrinsic absorption of uranyl is weaker at 355 nm, the decrease of intensity was monitored at 400 nm. Complexation kinetics were observed to be dependent upon the concentration of U(VI), ranging from seconds at high concentrations (above 100 ppm) to minutes at low concentrations (below 100 ppm). The uranyl detection limit is attained for a 1 ppm solution, which is excellent for such a simple absorbance variation sensing method. Classical sol–gel functionalized thin films
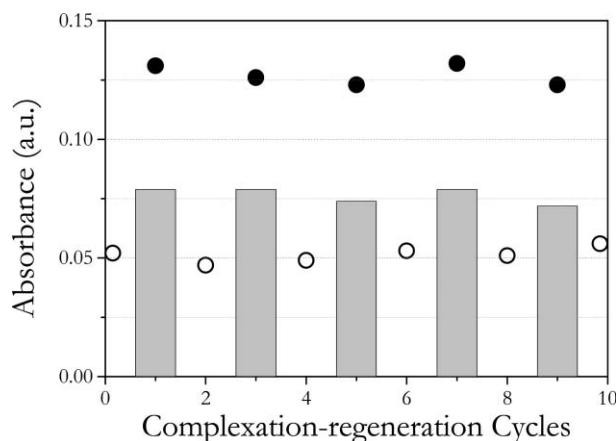
synthesized without surfactant showed similar UV–visible spectra but did not show detection of any tested metallic cations. We assume that this remarkable non-complexing property is due to both the confinement of SDBM and to stronger interactions between diketone functions and the acidic silica medium (*via* hydrogen bonding) rather than between SDBM and cations.

Finally, the reversibility and reproducibility of films which are crucial parameters were tested using repeated detection regeneration cycles. Here, a simple treatment in solution with acetylacetone permits regeneration of the films with good preservation of their sensing properties even after several complexation–regeneration cycles. For a 2D-hexagonal phase (Fig. 3) reproducibility was between $\pm$ 3% and, more surprisingly, between $\pm$ 7% for the lamellar structure. The stability of such a hybrid lamellar phase *versus* washing–complexation–regeneration cycles could be explained by the presence of π-stacking interactions between SDBM compounds located on the opposite sides of the silica layers. This study will be detailed in a future article.

In summary, the one-pot preparation of resistant selective hybrid SDBM–silica mesostructured optical sensors for uranyl cations was achieved. These homogeneous layers provided a high sensing stability as well as very good preparation reproducibility with a SDBM probe located inside the pores.

Notes and references

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