Hybrid functional mesostructured thin films with photo-oxidative properties in the visible range†

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Hybrid mesostructured thin films functionalised with organic photosensitiser molecules demonstrated high efficiency for the decontamination of polluted atmosphere *via* singlet oxygen production.

Photoinduced generation of singlet oxygen in various materials (silica, zeolites, polymers, textiles, ...) is of great importance for oxidation purposes, in particular in the field of fine chemistry (mild oxidation of high added value molecules),[1] photodynamic therapy (PDT),[2] oxidation micro-reactors[3] and water sterilisation.[4] These materials are based on photosensitisers (PS) embedded or grafted on various matrices (polymers, cellulose or inorganic oxides). Silica-based materials processed *via* sol–gel chemistry are good candidates for photosensitisation because of their high transparency (especially in the UV-visible range), photostability,[5] mechanical strength[6] and chemical inertness. Silica-based monoliths containing different PS have already demonstrated a high selectivity and efficiency for the oxidation of nauseous sulfur compounds.[7] Singlet oxygen was shown to be efficiently generated in microporous silica monoliths,[8] with a lifetime significantly enhanced compared to those observed in water or alcoholic solvents.

Here, we propose to investigate the photo-oxidative properties of meso-organised hybrid matrices (recently shown to enhance optoelectronic or sensing properties of various matrices[9]) shaped as thin films functionalised with organic photosensitiser molecules and synthesised *via* the evaporation-induced self-assembly (EISA) method.[10] We demonstrate that such matrices, presenting large opened porosity, high surface area and important porous volume, improve molecular diffusion and accessibility to the organic functions grafted inside matrices. Moreover, the EISA approach which presents an impressive versatility in terms of processability (materials shaped as monoliths, particles, films, micro- and macropatterns obtained *via* a great variety of commercial deposition techniques[10,11]) could favour fast industrial development.

Two different sensitisers were tested: a laboratory made one, 9,14-dicyanobenzo[*b*]triphenylene-3-carboxylic acid (**PS-1**), and a silylated derivative of the commercial anthraquinone-2-carboxylic acid (**PS-2**) (Fig. 1). Both of them are known to react efficiently with oxygen to give reactive oxygen species (ROS) either by energy transfer with the formation of singlet oxygen $^1O_2$ or by electron transfer leading to radical intermediates.[12] Periodically organised mesoporous hybrid thin films (POMTF) functionalised with organic photosensitisers were synthesised *via* two routes depending on the nature of PS molecules (presence or absence of alkoxysilane functions).[13]

With **PS-2**, a "delayed" one-pot procedure was used. This approach, which notably limits the influence of functional organosilanes on the mesostructuration process, is based on a pre-hydrolysis-condensation step of inorganic precursors (TEOS) followed by the addition of functional organosilanes just prior the sol deposition. With **PS-1**, an approach combining the "one-pot" and post-functionalisation pathways was selected. It consists of "delayed" one-pot functionalisation of an organosilane bearing a reactive group (here an amino one) followed by post-modification (here a peptidic coupling reaction), after surfactant removal, of this reactive group with the desired organic molecule.

Briefly, a pre-hydrolysed solution containing TEOS, ethanol, deionised water and HCl was mixed with a solution of CTAB, ethanol and dilute HCl. The final solution (molar composition: 1TEOS : 22EtOH : $5H_2O$: 0.014HCl : 0.14CTAB) was then aged at room temperature for 3 days prior to the addition of functional organosilanes (APTS neutralised with concentrated HCl or **PS-2**, molar ratio: 1TEOS : 0.01APTS or 1TEOS : 0.02**PS-2**). Thin films were prepared by dip coating silicon wafers and quartz substrates. In order to obtain cubic *Pm*3*n* mesostructure, optical homogeneity and transparency, the relative humidity (RH) was kept at 40% for the first 30 s and at 70% for the next 5 minutes.[14] Films were heated at moderate temperature (130 °C for stiffening the silica network without decomposed grafted molecules) for 2 days and then washed with alcohol in order to remove surfactants.

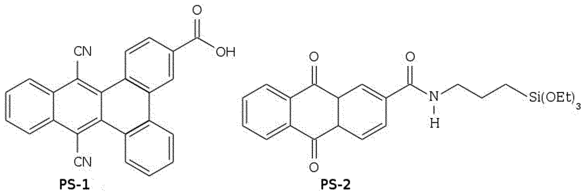

Fig. 1 Molecular structure of **PS-1** and **PS-2**.

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For films functionalised with **PS-1** (namely **POMTF-1**), a further coupling step between the amino group grafted in thin films and the carboxylic function of **PS-1** was achieved with peptidic coupling reagents such as *N*-hydroxysuccinimide (NHS) and dicyclohexylcarbodiimide (DCC).[15] A solution of DMF containing **PS-1** (0.13 mmol), NHS (1.1 equivalent) and DCC (1.1 equivalent) was ultrasonicated for 10 minutes. Then films were soaked into the resulting solution and ultrasonicated for 15 more minutes. Films were rinsed in various solvents such as dichloromethane and cyclohexane to remove any adsorbed photosensitiser molecules. Absorption–emission spectra of **POMTF-1** confirm the presence of well-grafted **PS-1** inside thin films without a significant alteration of its photoluminescence properties and their high transparency and homogeneity (see ESI†). From the thickness of the film (about 270 nm, determined by ellipsometric experiments, see ESI†) and the molar absorption coefficient of **PS-1** and **PS-2** in several solvents (13 000 mol^{-1} L cm^{-1} at 418 nm and 6100 at 323 nm, respectively) the calculated concentration of the PS in **POMTF-1** is about 0.14 mol L^{-1} (corresponding to a coupling yield of around 80% of the amino functions available in the APTES-film), and 0.45 mol L^{-1} in **POMTF-2**.

The synthesis conditions (composition and RH) described above were carefully chosen in order to obtain thin films presenting a cubic *Pm*3*n* mesophase. In fact, it was reported that cubic *Pm*3*n* structure is highly mechanically stable and shows higher permeability compared to those of the other CTAB mesostructures (2D-hexagonal *p*6*m*, 3D-hexagonal, *P*6$_3$/*mmc*).[16] A typical XRD pattern and TEM image[17] of hybrid POMTFs synthesised in this study are given in Fig. 2. Water adsorption–desorption isotherms of thin films performed *via* environmental ellipsometric porosimetry technique are consistent with reported results for *Pm*3*n* POMTFs (Fig. 3).[18] Thin films present a mono-disperse pore size distribution and a porous volume of 35%. Due to the well-known unidirectional contraction of thin films perpendicular to substrate, pores are ellipsoidal with a dimension of 2.8 by 2.0 nm, which is in a good agreement with XRD and TEM results.

The photo-oxidative properties of the POMTFs were then investigated with the oxidation of two organic sulfide compounds: di-*n*-butylsulfide (DBS) and dimethyl sulfide (DMS). Two different experiments were carried out: in static closed reactors for gaseous DBS and in a "one-pass" gas flow reactor for more volatile DMS.

In the first set of experiments, three couples of POMTFs (2 × 1 cm) were placed in three different Pyrex tubes, prepared under identical conditions. One sealed tube contained two **POMTF-1**, the second one contained two **POMTF-2**, and the third tube contained two films without any PS (blank POMTF). Then 10 μL of DBS (4.4 × 10^{-5} mol) were added in each sealed tube through a rubber septum. Each tube was irradiated with 4 fluorescent lamps (λ = 420 nm, 4 mW cm^{-2}, see ESI†) for 16 hours. This experiment was duplicated by leaving a set of three identical sealed tubes in the dark. Finally a standard experiment was carried out with **Si-powder-1**, prepared from commercial silica gel functionalised with 3-aminopropyl moieties (Acros organics, particle size 40–63 μm, S_{BET} 330 m^2 g^{-1} determined by nitrogen adsorption–desorption volumetry, pore size 6–7 nm, grafted with **1** according to the previous procedure, ~4 × 10^{-7} mol mg^{-1} or 0.8 mol L^{-1} assuming silica density around 2, see ESI†). 5 mg of **Si-powder-1** deposited on a glass film were irradiated at 420 nm in another sealed tube containing 35 μL of DBS. The results are presented in Table 1.

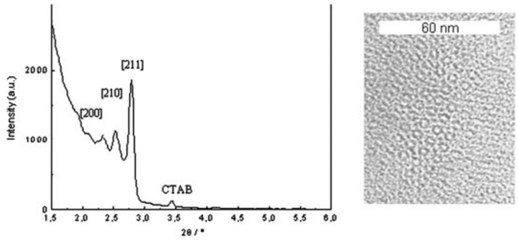

Fig. 2 XRD pattern (left) and TEM picture-[210] plane (right) of *Pm*3*n* hybrid POMTFs.[17]

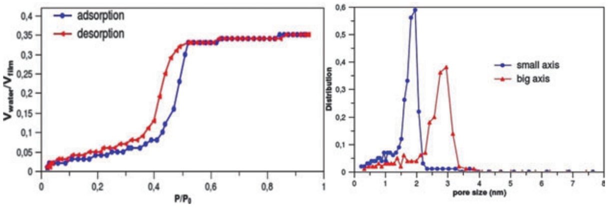

Fig. 3 Water isotherm (square: adsorption, triangle: desorption) of POMTFs and pore size distribution.

As expected, the *blank film* gave no oxidation product under irradiation. In the other experiments at 420 nm, after 16 hours of irradiation, the presence of sulfoxide (DBSO) and sulfone (DBSO$_2$) derivatives indicates the formation of singlet oxygen. Both **POMTF-1** and **POMTF-2** are photoactive, but the yield of oxidation product is much higher for the first one. The lower efficiency of **POMTF-2** may be explained by a lower molar absorption coefficient of the dye at 420 nm (50 mol^{-1} L cm^{-1}), as well as the weaker singlet oxygen quantum yield of anthraquinone.[7]

The enhanced efficiency of **POMTF-1** compared to **Si-powder-1** is obvious from the results of Table 1. The ratio of DBS to sensitiser is much higher with the films (3000 *vs.* 100) whereas the global yield of oxidation products are of the same order of magnitude. This may be the result of the high transparency of the films and less scattered light than in the powder. Moreover, compared to solution selectivity,‡ the noticeable disappearance of disulfide formation is observed with both catalysts, while the ratio of sulfone to sulfoxide is much higher with **POMTF-1** than with **Si-powder-1**. This increased selectivity for sulfone, already reported by Clennan *et al.* inside zeolites relative to acetonitrile homogeneous solutions, was assigned to a different environment of the key intermediate persulfoxide involved in the complex singlet oxygenation of sulfides, and was also shown to be sensitive to water content and sulfide loading inside zeolites.[19] The different selectivity of **POMTF-1** relative to **Si-powder-1** may be the result of either different porosity, water content or sulfide loading.

Another point of interest is the efficiency of **POMTF-1** under laboratory daylight (line 3, Table 1): oxidation products

Table 1 Products obtained under irradiation at 420 nm for 16 hours of gaseous DBS in the presence of POMTF or grafted silica powder (DBSO: di-*n*-butyl sulfoxide, $DBSO_2$: di-*n*-butyl sulfone

	[PS]/ mol L^{-1}	λ/nm	DBS (%)	DBSO (%)	$DBSO_2$ (%)	r^b
Blank film	0	420	100	0	0	0
POMTF-1	0.14	420	5	44	51	3000
POMTF-1	0.14	—[a]	75	25	0	3000
POMTF-2	0.45	420	74	26	Traces	850
Si-powder-1	0.8	420	11	67	22	100

[a] Laboratory daylight. [b] Molar ratio between DBS and sensitiser.

were also obtained, but in lower yield due to shorter irradiation time under visible (natural/artificial) light and lower light power.

The oxidation of another well-known volatile pollutant, DMS, was carried out in a one-pass gas-phase reactor. Six **POMTF-2** (2 × 1 cm) samples were placed in a thermo-regulated reactor (scheme in ESI†). Dry air containing DMS at a defined concentration (about 110 ppmv) was flowed over the films at a 20 mL min^{-1} flow rate. The reactor was irradiated with 16 lamps at 420 nm and the gas at the outlet of the reactor was analysed by GC-FID. A typical concentration curve with **POMTF-2** is given in Fig. 4.

After an equilibrium adsorption step in the dark, lamps were switched on. The DMS concentration sharply dropped, while disulfide concentration first increased and then smoothly dropped. After 5 hours irradiation, a photostationary state was reached: dimethyl sulfone ($DMSO_2$) and dimethyl sulfoxide (DMSO) appeared in the gas flow, while DMDS concentration decreased. 76 hours of irradiation were needed to recover the initial DMS concentration. In this case, the molar ratio between total introduced DMS and the sensitiser was about 1 : 1800.

This latter one-pass experiment allows to monitor the oxidation reaction *in situ* under continuous sulfide flow. It emphasises a favoured initial formation of disulfide inside the mesoporous films where sulfide was previously adsorbed. Once adsorbed sulfide first reacts to yield mainly disulfide, singlet oxygen addition to sulfide preferentially yields sulfoxide and sulfone along with disulfide. This result implies that at the beginning of the reaction oxygen slowly diffuses to the vicinity of the excited PS because of the presence of large amounts of pre-adsorbed DMS. Thus only sulfide is activated, most probably by electron transfer,[11] yielding disulfide as the main initial product.

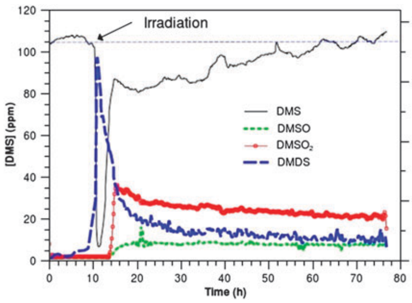

Fig. 4 DMS oxidation products detected during irradiation of **POMTF-2** at 420 nm (DMSO: dimethyl sulfoxide, $DMSO_2$: dimethyl sulfone, DMDS: dimethyl disulfide Me–S–S–Me).

In summary, mesoporous organised thin films containing two different sensitisers have been prepared. Hybrid POMTFs are efficient in both static and dynamic mode under visible light. The photo-oxidative properties of these highly transparent films at the gas–solid interface over sulfide pollutants were shown to be enhanced compared to more light-scattering silica powders. Mesoporosity is not only responsible for the high transparency of the films, but also for different selectivity, probably arising from the different environments of sulfides inside the pores.

Notes and references

‡ Irradiation at 420 nm of an acetonitrile solution of DBS (2.5×10^{-2} M) containing **1** (8.2×10^{-5} M) leads to the following product distribution, sulfoxide : sulfone : disulfide 65 : 19 : 10.

1 M. Oelgemoller, C. Jung and J. Mattay, *Pure Appl. Chem.*, 2006, **79**, 1939–1947.

2 M. I. Burguete, F. Galindo, R. Gavara, S. V. Luis, M. Moreno, P. Thomas and D. A. Russell, *Photochem. Photobiol. Sci.*, 2009, **8**, 37–44; S. H. Cheng, C. H. Lee, C. S. Yang, F. G. Tseng, C. Y. Mou and L. W. Lo, *J. Mater. Chem.*, 2009, **19**, 1252–1257.

3 E. E. Coyle and M. Oelgemoller, *Photochem. Photobiol. Sci.*, 2008, **7**, 1313–1322.

4 N. A. Kuznetsova, D. A. Makarov, O. L. Kaliya and G. N. Vorozhtsov, *J. Hazard. Mater.*, 2006, **146**, 487–491.

5 C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Adv. Mater.*, 2003, **15**, 1969–1994.

6 F. Mammeri, E. Le Bourhis, L. Rozes and C. Sanchez, *J. Mater. Chem.*, 2005, **15**, 3787–3811.

7 C. Cantau, T. Pigot, R. Brown, P. Mocho, M. T. Maurette, E. Benoit-Marque and S. Lacombe, *Appl. Catal., B*, 2006, **65**, 77–85.

8 C. Cantau, T. Pigot, N. Manoi, E. Oliveros and S. Lacombe, *ChemPhysChem*, 2007, **8**, 2344–2353.

9 D. Chandra, S. Mridha, D. Basak and A. Bhaumik, *Chem. Commun.*, 2009, 2384–2386; K. A. Killian, T. Böcking and J. J. Gooding, *Chem. Commun.*, 2009, 630–640.

10 C. J. Brinker, Y. Lu, A. Sellinger and H. Fan, *Adv. Mater.*, 1999, **11**, 579–585.

11 H. Y. Fan, Y. F. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, L. V. Perez, G. P. Lopez and C. J. Brinker, *Nature*, 2000, **405**, 56–60; P. Innocenzi, T. Kidchob, P. Falcaro and M. Takahashi, *Chem. Mater.*, 2008, **20**, 607–614; Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker and C. J. Brinker, *Nature*, 1999, **398**, 223–226; J. B. Pang, J. N. Stuecker, Y. B. Jiang, A. J. Bhakta, E. D. Branson, P. Li, J. Cesarano, D. Sutton, P. Calvert and C. J. Brinker, *Small*, 2008, **4**, 982–989.

12 V. Latour, T. Pigot, M. Simon, H. Cardy and S. Lacombe, *Photochem. Photobiol. Sci.*, 2005, **4**, 221–229.

13 C. Sanchez, C. Boissiere, D. Grosso, C. Laberty and L. Nicole, *Chem. Mater.*, 2008, **20**, 682–737.

14 F. Cagnol, D. Grosso, G. J. A. A. Soler-Illia, E. L. Crepaldi, F. Babonneau, H. Amenitsch and C. Sanchez, *J. Mater. Chem.*, 2003, **13**, 61–66.

15 T. Berthelot, J. C. Talbot, G. Lain, G. Deleris and L. Latxague, *J. Pept. Sci.*, 2005, **11**, 153–160.

16 M. Etienne, A. Quach, D. Grosso, L. Nicole, C. Sanchez and A. Walcarius, *Chem. Mater.*, 2007, **19**, 844–856.

17 D. Y. Zhao, P. D. Yang, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Commun.*, 1998, 2499–2500.

18 C. Boissière, D. Grosso, S. Lepoutre, L. Nicole, A. Brunet-Bruneau and C. Sanchez, *Langmuir*, 2005, **21**, 12362–12371.

19 E. L. Clennan, W. Zhou and J. Chan, *J. Org. Chem.*, 2002, **67**, 9368–9378.