

Cite this: *Chem. Commun.*, 2012, **48**, 1422–1424

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## Light-activated gating and permselectivity in interfacial architectures combining “caged” polymer brushes and mesoporous thin films†‡

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Received 21st July 2011, Accepted 22nd August 2011

DOI: 10.1039/c1cc14443j

**We demonstrate that “caged” macromolecular building blocks can endow mesoporous thin films with light responsiveness and lead to the creation of functional hybrid ensembles with photo-triggered permselective properties.**

The generation of interfaces discriminating the transport of ionic species through which the passage of ions can be triggered under the influence of an external stimulus has received increasing attention from the materials science community.<sup>1</sup> The efficiency by which biological membranes control the ionic transport using chemical and physical stimuli as triggers has been a source of inspiration for chemists to mimic such processes using functional hybrid assemblies.<sup>2</sup> Much of this interest arises from many important applications in nanoscience including nanofluidics, molecular separation, dosing and drug delivery.<sup>3</sup> Within this framework, the molecular design of nanostructured interfacial architectures combining addressable and/or switchable macromolecular entities and mesoporous inorganic materials (3D nanoscopic scaffoldings) has found incredible resonance in supramolecular materials science.<sup>4</sup> Among various types of stimuli that may be utilized to trigger actions, light-sensitivity is an attractive phenomenon for developing advanced hybrid materials capable of precise external modulation of chemical changes in mesoporous materials.<sup>5</sup> Light-driven chemical changes may therefore represent an appealing strategy; indeed, light can approach materials in a non-contacting manner also permitting various types of modulations in terms of intensity (flux) and energy (wavelength). In the case of photolabile “caged” compounds their chemical functionalities are blocked because of the presence of a covalently bound

chromophore.<sup>6</sup> Light irradiation removes the cage and activates the protected functional groups. This is a particularly flexible approach, since a good number of photoremovable groups are known that can be combined with the different organic functional groups and applied to generate materials displaying photo-tunable chemical states.<sup>7</sup> In recent years different light-responsive strategies have been applied as “triggers” for uncapping the pores and facilitating the molecular transport through mesoporous materials.<sup>5</sup> Despite these exciting developments, the majority of photoactive mesoporous materials today are exclusively based on an “ON/OFF” gating response without discriminating the passage of cationic and anionic species in the “ON” state, *i.e.* permselectivity. An ongoing challenge in supramolecular materials science relies on the construction of synthetic photoactive hybrid assemblies displaying not only light-triggered gating functions but also photo-stimulated charge selectivity properties that may ultimately lead to an exhaustive control over the transport of ionic species. Herein, we describe the integration of “caged” polymer brushes into mesoporous oxide thin films in order to create photoactive hybrid polymer–inorganic assemblies displaying light-activated gating and permselective transport of ionic species through 3D nanoscopic scaffoldings (Fig. 1).

Mesoporous amino-silica (0.2 amine: 1 Si) thin films were produced *via* a one-pot sol–gel method by dip-coating of glass and indium tin oxide (ITO) substrates, following previously reported procedures.<sup>8</sup> Mesoporous films with ~200 nm thickness were obtained, displaying organized pore arrays with high accessibility. X-Ray reflectivity (XRR) and grazing-incidence small-angle X-ray scattering (GISAXS) performed at D10A-XRD2 beamline of Laboratório Nacional de Luz Síncrotron (LNLS- Brazil) indicate that highly organized mesopore arrays with an interpore distance of ~12 nm were obtained. The pore symmetry is derived from an *Im3m* cubic mesophase, which suffered a uniaxial contraction after thermal treatment and template extraction. This mesophase is highly accessible due to the large interpore connections (3 nm diameter) between *ca.* 8 nm diameter mesopores (obtained by ellipso-porosimetry (EP), see Fig. 2), actually behaving as a “vertical pore” arrangement.

Modification of the mesoporous film with photolabile polymer brushes was accomplished by reacting the surface amino groups with 2-bromoisobutryl bromide in order to covalently anchor the polymerization initiators. Then, polymer brush growth took

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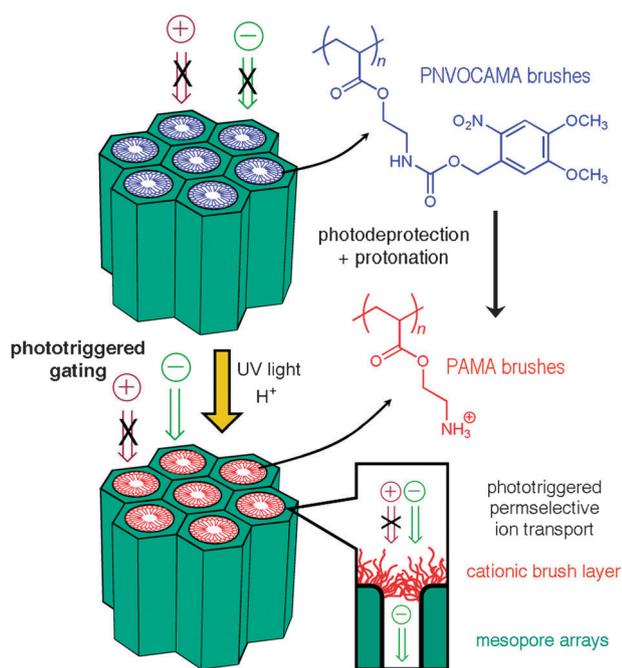
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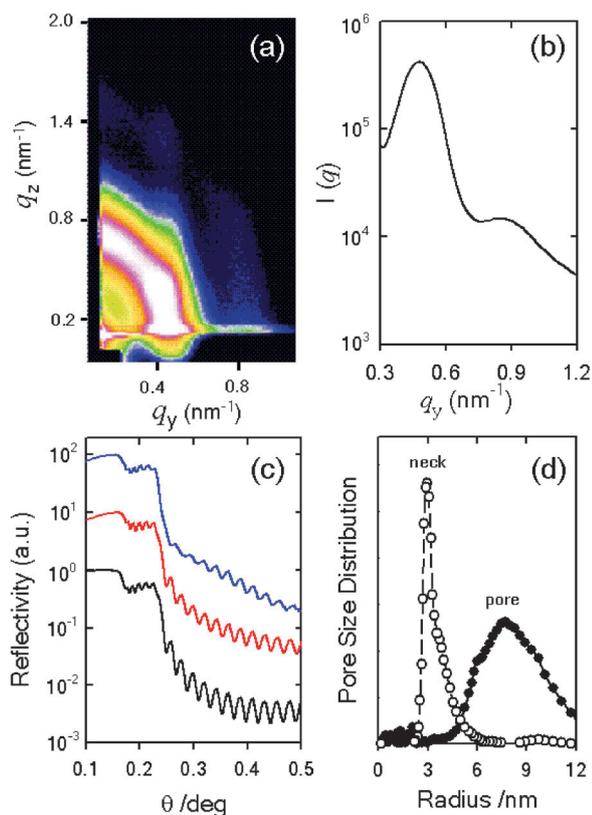
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† Electronic supplementary information (ESI) available: Experimental procedure of PNVOCA brush synthesis and details of XRR, GISAXS and ellipso-porosimetry characterization of the brush-modified mesoporous films. See DOI: 10.1039/c1cc14443j

‡ This article is part of the *ChemComm* ‘Emerging Investigators 2012’ themed issue.



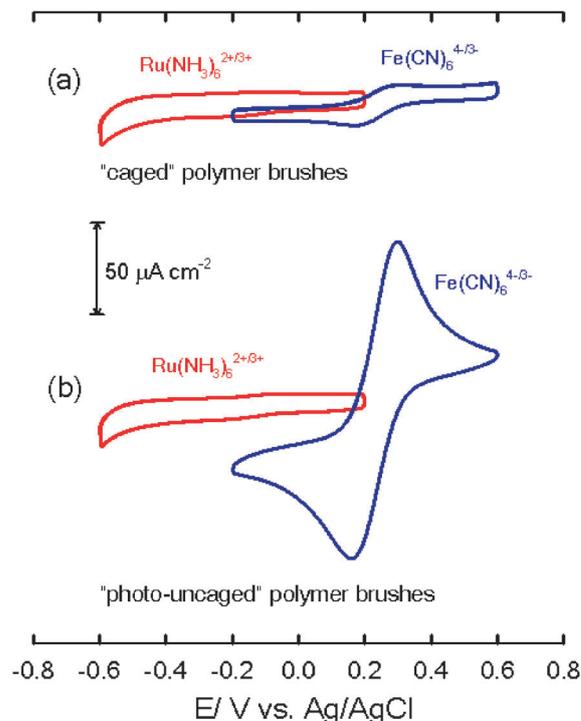
**Fig. 1** Schematic representation describing the modification of mesoporous silica films with photolabile polymer brushes and their subsequent “uncaging” to build up a permselective polycationic barrier in the outer region of the film.



**Fig. 2** (a) GISAXS pattern, (b) intensity vs. lateral momentum transfer vector,  $q_y$ , plot (c) X-ray reflectograms of aminosilica (black trace), “caged” PNVOCAMA-modified (red trace) and “uncaged” PAMA-modified mesoporous film (blue trace), and (d) ellipso-porosimetric estimation of the pore size distribution of a bare mesoporous thin film.

place *via* surface-initiated atom transfer radical polymerization<sup>9</sup> of 2-[(4,5-dimethoxy-2-nitrobenzoyl) aminoethyl methacrylate (NVOCAMA) monomers in the presence of the adequate solvent and catalyst (see ESI† for details). This process led to the surface modification of the mesoporous film with covalently anchored PNVOCAMA brushes (Fig. 1). After polymerization EP<sup>10</sup> revealed only slight changes in pore and neck sizes thus indicating that brush growth did not proceed to a large extent into the mesopores. However, XRR<sup>11</sup> (Fig. 2c) confirmed the presence of a thin brush layer (6 nm) grown atop the mesoporous film (see ESI† for details). We hypothesize that the selective growth of the photolabile brush atop the mesoporous film originates from the hydrophobic and bulky nature of the monomers that precludes the free diffusion into the hydrophilic inner environment of the nanoporous framework. This fact ultimately leads to the selective tailoring of the “outer” chemistry of the hybrid mesostructured assembly<sup>12</sup> (Fig. 1).

The permselectivity properties of the mesostructured hybrid interface were characterized using redox probes that diffuse across the mesoporous film deposited on a conductive ITO substrate.<sup>13</sup> Fig. 3a displays the cyclic voltammograms of PNVOCAMA-modified mesoporous films supported on ITO in the presence of 1 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  at pH 3, respectively. It is observed that the electrochemical response of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$  ions is strongly inhibited. Considering that EP confirmed that mesopores are not occluded with “caged” brushes, it is reasonable to ascribe the absence of well-defined electrochemical signals to the presence of hydrophobic PNVOCAMA brushes grown atop the mesoporous film.



**Fig. 3** Cyclic voltammograms corresponding to: (a) “caged” PNVOCAMA-modified mesoporous silica thin film, (b) “uncaged” PAMA-modified mesoporous silica film in the presence of 1 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  (red trace) and 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  (blue trace), respectively. Scan rate:  $100 \text{ mV s}^{-1}$ . Supporting electrolyte: 0.1 M KCl (pH 3).

The marked hydrophobic nature of the outermost PNVOCAMA layer precludes hydrated ions from entering into the nanoscopic channels and diffusing across the interfacial architecture. This scenario leads to the “hydrophobic gating” or “capping” of the mesopores that hinders the transport of solvated ionic species through the nanostructured interface. It is worth mentioning that gating mechanisms based on hydrophobic forces operate in a number of biological ion channels and this concept has been recently extended to artificial nanoporous systems.<sup>14,15</sup>

In order to manipulate the chemical characteristics of the mesoporous hybrid assembly we irradiated the “caged” polymer brushes with UV light (365 nm, 4.7 mW cm<sup>-2</sup>). Light exposure cleaves the chromophore from the brush structure and generates poly(2-aminoethyl methacrylate) (PAMA) brushes in the mesoporous film. After careful rinsing with DMF to remove the chromophores, EP confirmed that the pore environment remained unaltered whilst XRR revealed that the photolabile brush layer grown atop the mesoporous film decreased its thickness from 6 to 4 nm. Voltammetric measurements were carried out under slightly acidic conditions in order to study the transport properties of the photodeprotected hybrid film. In principle, the presence of NH<sub>3</sub><sup>+</sup> groups in the film would introduce permselective properties to the interfacial architecture. Fig. 3b displays the cyclic voltammograms of PAMA-modified mesoporous films supported on ITO in the presence of 1 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> at pH 3, respectively. A well-defined electrochemical response of Fe(CN)<sub>6</sub><sup>3-</sup> ions is observed whereas that corresponding to the Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> species is not detectable. This implies that the mesoporous film displaying “uncaged” polymer brushes atop the pores is acting as a very efficient permselective nanostructured barrier inhibiting the transport of cationic species. It is evident that the photodeprotection of the PNVOCAMA brush introduces drastic changes in the transport properties of the mesoporous film owing to the electrostatic nature of the outermost cationic PAMA layer bearing –NH<sub>3</sub><sup>+</sup> groups. In stark contrast to that observed in PNVOCAMA-modified films, the “uncapped” mesoporous films repel the transport of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> but facilitate the free diffusion of Fe(CN)<sub>6</sub><sup>3-</sup> ions across the inner environment of the mesoporous film. Protonation of “uncaged” amino-bearing brushes located at the entrance of the pores generates an electrostatic barrier that determines the nature of the ionic species to be shuttled across the film, *i.e.* “gate-keeping” effect.

To the best of our knowledge, this is the first experimental report on light-activated permselectivity in mesoporous films using photoactive polymer brushes. The permselective ion transport is triggered when (upon irradiation) mesopores are “uncapped” and polymer brushes are massively switched between a “collapsed” hydrophobic state in which hydrated ions cannot enter the mesopores and a “swollen” hydrophilic state in which the cationic nature of the outer layer governs the transport through the vertically-oriented nanochannels.

In summary, in this work we described the integration of photolabile polymer brushes atop mesoporous silica films in order to create hybrid interfacial architectures displaying light-activated gating and permselective transport of ionic species through self-organized oriented nanochannels. We believe that these results will further broaden the range of possibilities to design heterosupramolecular films<sup>16</sup> in which the rich interplay between

nanostructural order and spatial distribution of chemical groups may govern the function and utility of the interfacial assembly.

Financial support from CONICET, ANPCyT (PICT #1848; PICT-PRH 163/08, PAE 2004 22711 for a postdoctoral grant to AB), Centro Interdisciplinario de Nanociencia y Nanotecnología, the Max Planck Society (O.A.) the Alexander von Humboldt Stiftung (O.A.) and Laboratório Nacional de Luz Síncrotron (LNLS, Brazil) (XRD2—11639/10736) is gratefully acknowledged. M.C., G.J.A.S.-I. and O.A. are CONICET fellows.

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