Facile molecular design of hybrid functional assemblies with controllable transport properties: mesoporous films meet polyelectrolyte brushes†

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We showed for the first time how to tailor the permselectivity of mesoporous thin films by changing the electrostatic environment of the nanopores through the covalent functionalization with polyelectrolyte brushes.

The rational design of robust platforms enabling the selective transport of ionic species has received considerable attention during the last decade.[1] This interest stems from the wide variety of technological applications relying on "gated" transport processes, such as ultrafiltration or controlled delivery.[2] The generation of interfaces discriminating the transport of cationic and anionic species, *i.e.*: permselectivity, is an intrinsic mechanism of nature, as can be observed in human skin[3] or cornea[4] which exploit fixed charges in the membrane to generate differential permeabilities.

When dealing with synthetic materials, manipulating chemistry and topology down to the nanoscale is essential to achieve this goal and, as such, represents one of the ongoing challenges in materials science. Different approaches with varied degree of versatility emerged during recent years. The use of surface-functionalized nanoporous substrates, such as silica opals,[5] glass nanoporous electrodes[6] or mesoporous films,[7] has been demonstrated to be a valuable alternative to build-up membrane-like platforms with outstanding physico-chemical properties. Ordered mesoporous films result particularly attractive due to well-established sol–gel protocols enable the facile generation of robust layers on almost any substrate, thus resulting in supported interfacial architectures of controllable thickness with high porosity and tunable pore sizes.[8]

To date, the manipulation of the permselective properties of mesoporous films has been exclusively relying on the use of monolayer assemblies and involving a very limited number of chemical functionalities. As discussed in detail by Bohn *et al.* the magnitude and polarity of the surface charges in the inner environment of the nanoporous film has a large impact on its molecular transport properties.[9] Within this framework, the development of new strategies to manipulate the chemical functionalities inside the mesoporous films is of critical importance to further broaden the reach of mesoporous films as highly functional platforms required in different areas of materials science. In this work, we describe for the first time the use of polyelectrolyte brushes as building blocks to manipulate the permselective properties of mesoporous films. We demonstrate that the convergence of mesoporous thin films and polyelectrolyte brushes provides a unique avenue to the facile creation of highly functional hybrid materials with tailor-made permselective properties.

Mesoporous amino-silica (0.2 amine: 1 Si) thin films were produced *via* a one-pot sol–gel method by dip-coating of silicon and indium tin oxide (ITO) substrates using a sol containing the oxide precursor (tetraethoxysilane), the amino precursor (aminopropyltriethoxysilane) and a non-ionic block-copolymer template (Pluronic-F127). This experimental protocol led to the formation of thin mesoporous displaying highly organized pore arrays (Fig. 1(a)) with cubic-derived mesostructure (*Im3m*) and pore openings in the range 6–9 nm,[10] as indicated by transmission electron microscopy (TEM) and small angle X-ray scattering with two-dimensional detection (SAXS-2D).

Thereafter, the surface chemical composition of the mesoporous films was monitored by X-ray photoelectron spectroscopy (XPS). It is worth mentioning that under our experimental conditions XPS probes the film surface, pore openings and film walls up to a thickness of ~ 9 nm, which is nearly the depth corresponding to two pore layers.[10] Fig. 2 shows the XP spectra of amino-silica films corroborating the presence of N in the samples. Deconvolution of the XPS signal reveals the presence of two contributions corresponding to $-NH_3^+$ at 401.7 eV and $-NH_2$ at 400.1 eV. The presence of NH_3^+ groups in the film would introduce, in principle, permselective properties to the interfacial architecture. The transport of ionic species through mesoporous films was electrochemically probed using charged electroactive species diffusing across the mesoporous film deposited on conductive ITO subtrates.[7a,c] Fig. 3(a) displays the cyclic voltammograms of amino-silica mesoporous films supported on ITO in the presence of 1 mM $Ru(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$ at pH 3.5, respectively. A well-defined electrochemical response of $Fe(CN)_6^{3-}$ ions is observed whereas the corresponding to

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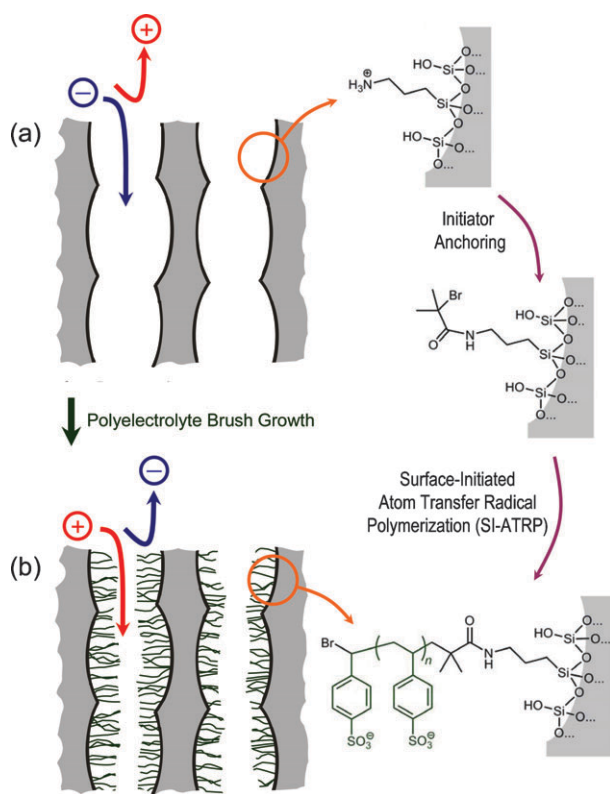
Fig. 1 Schematic depiction corresponding to the inner environment of the mesoporous amino-silica thin film prior to (a) and after (b) the surface-initiated atom transfer radical polymerization of poly(styrene sulfonate) brushes. In the figure are also described the different chemical entities present in the pore surface during the sequential modifications.
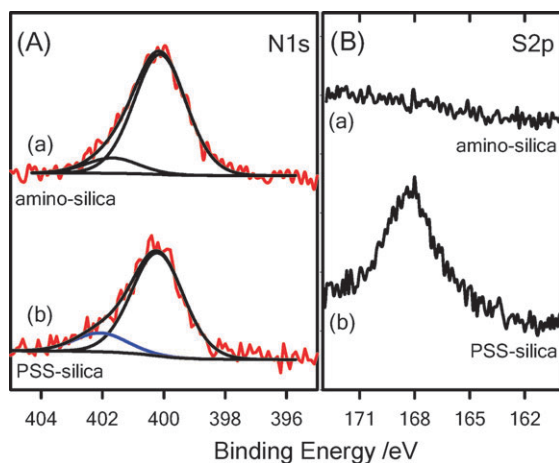

Fig. 2 (A) N 1s XP spectra corresponding to: (a) mesoporous amino-silica thin film, (b) PSS brush-modified mesoporous silica film obtained by the procedure described in Fig. 1. The red trace indicates the raw data whereas the blue trace describes the signal contribution originated from the amide bonds (BE = 402.1 eV) (B) S 2p XP spectra corresponding to: (a) mesoporous amino-silica thin film, (b) as for (a) after the surface-initiated polymerization of poly(styrene sulfonate) brushes.

the $Ru(NH_3)_6^{3+}$ species is not detectable. This implies that the amino-silica mesoporous film is acting as a very efficient permselective barrier precluding the transport of cationic
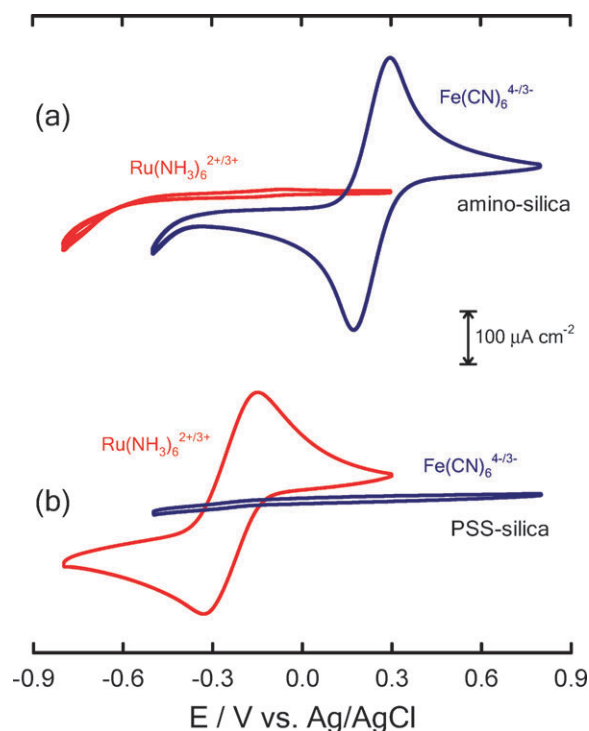

Fig. 3 Cyclic voltammograms corresponding to: (a) mesoporous amino-silica thin film, (b) PSS brush-modified mesoporous silica film obtained by SI-ATRP in the presence of 1 mM $Ru(NH_3)_6^{3+}$ (red trace) and 1 mM $Fe(CN)_6^{3-}$ (blue trace), respectively. Scan rate: 100 mV s^{-1}. Supporting electrolyte: 0.1 M KCl (pH 3.5).

species which originates from the electrostatic nature of the pore walls that are positively charged with the $-NH_3^+$ groups. In order to manipulate its permselective properties, *i.e.*: pore surface charge, we proceeded to grow an anionic poly-electrolyte brush constituted of poly(styrene sulfonate) in the sodium salt form. This was accomplished by reacting the surface amino groups with 2-bromoisobutyryl bromide in order to covalently anchor the polymerization initiators (Fig. 1). Then, the surface-initiated atom transfer radical polymerization[11–13] of the styrene sulfonate monomers in the presence of the adequate solvent and catalyst (see ESI† for details) was accomplished.[14] This process led to the surface modification of the mesoporous film with covalently anchored poly(styrene sulfonate) brushes (Fig. 1(b)). The presence of the sulfonate groups was confirmed by XPS as indicated by the content of S in the sample (S 2p, 168.2 eV) (Fig. 2B) and corroborated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (see ESI†). A detailed analysis of N 1s spectra (Fig. 2A(b), blue trace) revealed that the N intensity remains constant in line with the surface chemical reaction and that the surface amino groups reacted with 2-bromoisobutyryl bromide to give the amide bonds corresponding to the surface-confined ATRP initiators (Fig. 1). Having corroborated the chemical functionalization, we proceeded to the permselectivity studies using the diffusing redox probes. Fig. 3(b) describes the voltammograms of PSS brush-modified mesoporous film in contact with electrolyte solutions containing $Fe(CN)_6^{3-}$ and $Ru(NH_3)_6^{3+}$, respectively. It is evident that the presence of the PSS brush introduces drastic changes in the permselective

characteristics of the mesoporous film. In stark contrast to that observed in amino-silica films, the PSS brush electrostatically repels the free diffusion of $Fe(CN)_6^{3-}$ ions across the inner environment of the mesoporous film and, consequently, no redox reaction is detected at the ITO surface. Conversely, a similar voltammetric experiment in the presence of $Ru(NH_3)_6^{3+}$ described a completely different scenario in which the cationic redox probe was able to diffuse across the hybrid mesoporous film to finally reach the ITO interface. The negatively charged environment of the mesoporous film provides the pathways for the transport of $Ru(NH_3)_6^{3+}$ ions in which the attractive electrostatic interactions are the driving force for incorporating the electroactive cations in the mesoporous film. In this regard, we have to note that the supporting electrolyte used in the permselectivity experiments was 0.1 M KCl. Recent work by White and co-workers, using nanoporous opal films (tortuous cavities ~35 nm) modified with monolayer assemblies, revealed that the presence of high ionic strength environments could significantly affect the permselective properties of the film.[15] In particular, these authors reported that varying the supporting electrolyte from very low concentrations to 0.05 M KCl has an impact on the Debye screening length in such a way that an ~50% decrease in the blocking of diffusion is observed. This means that the film is not acting as an efficient permselective barrier in 0.05 M KCl. In contrast, the PSS brush-modified mesoporous films display outstanding permselective properties even at higher ionic strengths, 0.1 M KCl. This could be ascribed to the nanoconfinement provided by the nanoporous channels with dimensions comparable to the Debye length which renders the nanoenvironment highly permselective regardless of the ionic strength. The set of electrochemical experiments also demonstrate that the pore functionalization is not restricted to the outermost layers but proceeds in the inner environment of the film close to the ITO interface as well. The presence of unreacted $-NH_3^+$ groups in the innermost layers of the film would electrostatically repel the flux of $Ru(NH_3)_6^{3+}$ species towards the ITO surface and, consequently, the voltammetric response would be seriously affected. As can be seen in Fig. 3(b), this is not the case of PSS brush-modified samples.

These electrochemical experiments further corroborate the versatility of SI-ATRP as a chemical methodology to manipulate the inner environment of the mesoporous film.

In summary, in this work we showed for the first time the use of polyelectrolyte brushes as building blocks enabling the facile manipulation of the permselective properties of mesoporous thin films. Considering the chemical versatility of atom transfer radical polymerization these proof-of-principle experiments using poly(styrene sulfonate) brushes could be easily extended to a wide variety of monomer units. These results introduce an interesting example of molecular design of a functional interface using tools from two well-established research areas, *i.e.*: mesoporous films and polymer brushes. We envision that this approach combining elements from macromolecular and sol–gel chemistry will pave the way to the rational design and facile creation of highly functional interfacial architectures.

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