

Highly Ordered Gold Nanotubes Using Thiols at a Cleavable Block Copolymer Interface

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Preparation of nanoporous surfaces through self-assembly of block copolymers (BCPs) has attracted considerable attention due to possibilities in surface patterning, nanoscopic templates, separation membranes, catalysis, and sensing.^{1,2} The repertoire of nanoporous materials will be significantly enhanced, if we were able to decorate the pore walls with reactive functional groups,³ since this will provide the opportunity to further manipulate the nanopores. A variety of BCPs have been explored to generate nanopores by removing the minor block components via ozonolysis, UV degradation, thermal treatment, and chemical etching.^{4–6} However, these techniques are quite limited, because of the rather harsh etching conditions used and due to the fact that these conditions are inherently suitable only to a few classes of polymers. In particular, chemical functionalization inside pores in a nanoporous thin film with a high degree of lateral order is considerably limited. One can envision the introduction of a cleavable group between the two blocks of a diblock copolymer assembly, which can be broken under mild conditions and leave behind a chemically active functional group. These functional moieties are then capable of providing facile access to a variety of functional nanostructures. We envisaged two necessary conditions for our method to be effective: (i) the cleavage reaction conditions should be mild so that the nanoporous structure does not collapse; and (ii) the functional group in nanopores should be reactive under gentle conditions as not to affect the matrix polymer morphology. Recently, it was reported that a nanoporous film was developed from an acid-catalyzed cleavable block copolymer with a similar concept.⁷ However, a limitation here was that the functional group after cleavage is a tertiary alcohol and thus not very reactive.

by a redox stimulus such as D,L-dithiothreitol (DTT), which produces two free thiols from disulfide linked BCP *via* hydrogen exchange and intramolecular cyclization of two thiol moieties in DTT.⁸ We demonstrate here that we can generate nanoporous thin films by simply immersing PS-ss-PEO thin films in a DTT-containing ethanol solution. The cleaved PEO block is soluble in ethanol and thus washed away, while the PS block remains on the surface without any morphological change. This process leaves behind thiol-coated nanopores. We then demonstrate that this thiol-functionalized nanoporous film can be a scaffold for developing highly ordered polymer-gold complex arrays (Figure 1).

We have previously reported a synthetic methodology for obtaining disulfide-linked block copolymers.⁸ We had to modify the method to obtain our target block copolymer here. The diblock copolymer, PS-ss-PEO, was synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene using a PEO-based macroinitiator containing a disulfide bond (Scheme 1). The macroinitiator was synthesized by treating a monomethylated PEO with thioglycolic acid to obtain **2**, which was then attached to the RAFT initiator using the thiol functionality to obtain the macroinitiator **4** (Scheme 1). Polymerization of styrene using **4** provided the polymer ($M_n^{\text{PS-ss-PEO}} = 17.1 \text{ kg mol}^{-1}$; $M_n^{\text{PS}} = 12.1 \text{ kg mol}^{-1}$; $M_n^{\text{PEO}} = 5.0 \text{ kg mol}^{-1}$) with a polydispersity of 1.07. To test the cleavage of the disulfide bond under redox stimuli, the PS-ss-PEO BCP was treated with DTT in DMF. GPC analysis of the reaction mixture confirmed the clean cleavage of the block copolymer.⁹

Scheme 1. Synthesis of PS-ss-PEO Block Copolymer

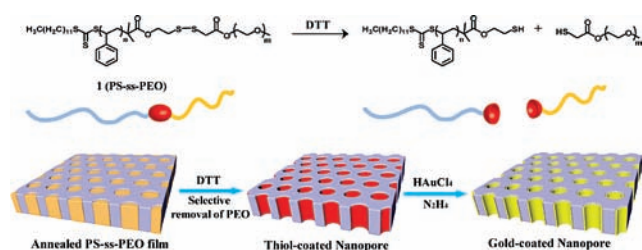
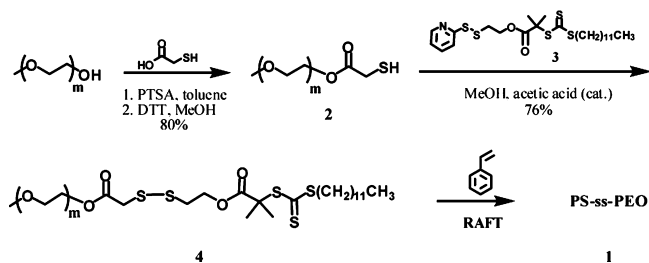


Figure 1. Structure of the polymer and schematic representation of the preparation of nanoporous thin film and gold-coated nanopore.

We present here a chemically functionalized nanoporous film from polystyrene-*block*-poly(ethylene oxide) (PS-ss-PEO) connected by a disulfide bond (Figure 1). Disulfides can be readily cleaved



A 30 nm thick BCP thin film was prepared from spin-coating 0.7 wt % of polymer **1** in benzene. Subsequently, the films were annealed in a benzene/water vapor environment to orient the PEO cylindrical microdomains normal to the film surface and enhance the lateral ordering. Figure 2a shows an atomic force microscopy (AFM) image of highly ordered and oriented cylindrical microdomains normal to the film surface, and the corresponding Fourier transformation is shown in the inset, which is characteristic of long-range order as evidence of multiple order reflection peaks with a

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d-spacing of ~ 40 nm. To selectively remove the PEO block, the annealed PS-ss-PEO thin film was immersed into a 0.1 M solution of DTT in ethanol solution for 12 h and then washed with ethanol. Attenuated total reflection FTIR spectra (ATR-FTIR) showed that the peak at 1117 cm^{-1} , corresponding to a C–O stretching, disappeared after treating the DTT solution, indicative of the removal of PEO blocks from the thin film.⁹ The AFM image of this film did not change compared to the PS-ss-PEO film, which means that the PEO removal condition was mild enough to not affect the morphology of the thin film.⁹ We also confirmed this by transmission electron microscopy (TEM) experiments. The TEM image clearly highlights the nanoporous structure even without the need for any staining, due to the difference in electron density between the pore and the matrix regions (Figure 2b).¹⁰ An average center-to-center distance between the pores of ~ 40 nm and average pore diameter of ~ 20 nm were obtained. These results demonstrate that the simple and mild method, immersion of annealed PS-ss-PEO thin film in a DTT solution, directly results in a nanoporous thin film containing reactive functional groups at the interface.

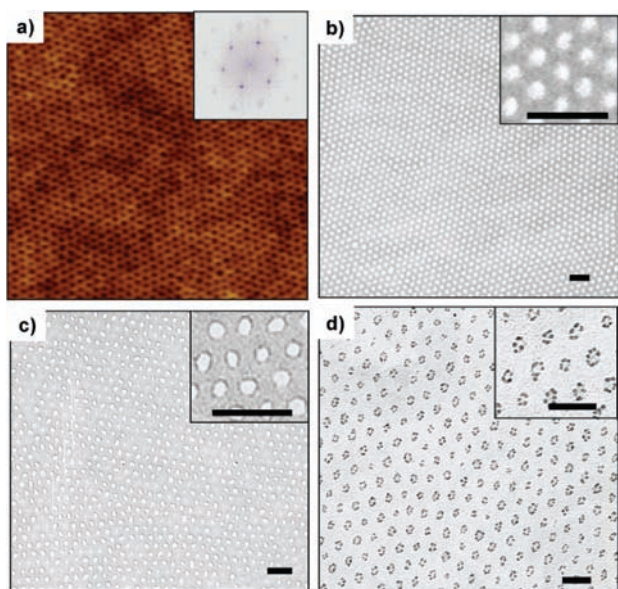


Figure 2. (a) Height mode AFM image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of PS-ss-PEO thin film after solvent-annealing for 4 h. The inset shows the corresponding Fourier transform. (b) TEM image after cleavage of PEO block. (c) Gold-loaded TEM image inside pore. (d) Gold growth inside pore by slow evaporation. Insets show magnified images (scale bar = 100 nm).

At this time, we were interested in demonstrating the availability of thiol functional groups by forming gold nanorings through thiol–gold interactions. For this, the nanoporous film was immersed into an ethanol solution of HAuCl_4 , and the gold ions anchored to the surface thiol groups were reduced by hydrazine (Figure 2c). To allow further growth of gold metal inside the nanopores, these were filled with a HAuCl_4 solution and were allowed to slowly evaporate. As shown in Figure 2d thicker gold nanoparticles are formed around the wall nanopores. These results suggest that a gold nanoring pattern with an extremely long-range order can be made from this approach. If the surface thiol groups are indeed the reason for our observations, silver ions should exhibit a lesser propensity to form these structures. Attempts to form silver rings resulted only in the formation of nanoparticles in the middle of the pores.⁹ Similarly, if thiols were needed, nanopores obtained from other polymeric architectures should not afford the gold structures. Therefore, PS-PMMA based PS-nanopores were subjected to this procedure, and no discernible gold-based features were observed.

The pore generation and gold loading were also investigated by grazing incidence small-angle X-ray scattering (GISAXS). The lattice constants of these three films from GISAXS and the intensity of the peaks were found to be consistent with the AFM and TEM results. To analyze if gold nanotubes can be isolated from these structures, we dissolved away the polymer component and analyzed the structures by TEM. Although we were unable to clearly isolate gold nanotubes presumably due to their small thickness and length, features consistent with the presence of gold nanostructures were seen in the TEM grid.⁹ Similarly, we were also interested in testing whether the process can accommodate variations in factors such as lattice distances. Accordingly, we synthesized a polymer with a higher PS molecular weight using the same macroinitiator **4**. In this case also, we were able to form porous structures, where the spacing between the pores are larger.⁹

In summary, we have demonstrated that the thiol-functionalized nanopores can be generated from cleavable block copolymers using a redox stimulus. The thiol functionalities present at the pore walls of these nanopores can then be used as handles to generate well-ordered polymer–gold composite nanostructures. The results described here represent a unique example of a mild etching process and pore functionalization using disulfide chemistry. The method described here opens up a broad range of possibilities, because thiol functionalities are reactive and thiols are commonly used as functional handles for manipulations in materials and biological chemistry.

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Supporting Information Available: Synthetic procedures, characterization, GPC, ATR-FTIR, AFM, TEM, and GISAXS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) See Supporting Information for details.
- (10) Note that it is difficult to see PEO cylindrical microdomains oriented normal to the film surface in PS-*b*-PEO film without staining in TEM because the electron density difference between these two blocks is quite small.

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