

A general method for controlled nanopatterning of oxide dots: microphase separated block copolymer platform

Tandra Ghoshal,¹ Matthew T. Shaw,² Ciara T. Bolger,¹ Justin D. Holmes,^{1,3} Michael A. Morris^{1,3*}

¹Materials Research Group, Department of Chemistry and Tyndall National Institute, University College Cork, Cork, Ireland

²Intel Ireland Ltd., Collinstown Industrial Estate, Co. Kildare, Ireland

³Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin, Ireland

Supporting information:

Surface analysis by FTIR. FTIR spectra shown in Fig. S1 provides additional information of the film surface at different experimental conditions. The non-ethanol treated film shows distinct features typical of the PS and PEO blocks (Fig. S1(a)). Peaks at between 763 cm^{-1} (benzene bending) and 1602 cm^{-1} , 1494 cm^{-1} and 1452 cm^{-1} (benzene ring stretching), weak overtone and combination bands in the range of $1655\text{--}2000\text{ cm}^{-1}$ as well as features at $3000\text{--}3100\text{ cm}^{-1}$ (C-H stretching in benzene) can all be attributed to polystyrene.¹ The features at 1102 cm^{-1} (C-O-C stretch), 924 cm^{-1} (CH_2 PEO rocking modes), and 1749 cm^{-1} and 1720 cm^{-1} (C=O stretches of the ester and keto group respectively) as well as peaks at 2925 cm^{-1} and 2854 cm^{-1} (CH_2 PEO stretching modes) can all be assigned to the PEO block.² It is apparent that on ethanol activation, the PS derived features decrease in relative intensity compared to those of PEO (Fig. S1(b)). FTIR data of copper oxide nanodots after UV/Ozone treatment and further annealing are shown in Figs. S1(c) and S1(d) which confirms the removal of polymer content. Two features can be seen at 1084 and 1010 cm^{-1} which can be assigned to transverse optical phonon mode in $-\text{Si-O-Si}-$ ³ and the Si-O-Cu phonon mode⁴.

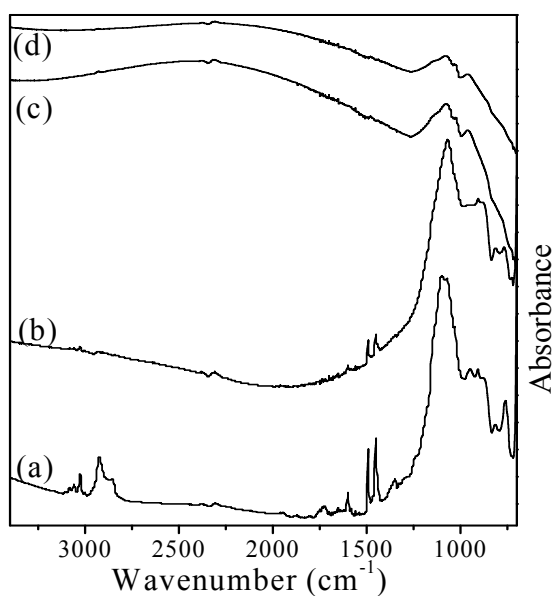


Fig. S1. FTIR spectra of (a) PS-PEO hexagonal dot patterns after solvent annealing, (b) nanoporous PS template after ethanol treatment (c) copper oxide nanodots after UV/Ozone treatment and (d) copper oxide nanodots after UV/ozone along with annealing.

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(3) C. T. Kirk, *Physical Review B* 1988, **38**, 1255-1273.

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Surface analysis by XPS. In order to further explore the surface composition, XPS analyses were performed for PS-PEO film before and after ethanol treatment. The C1s peak of PS-PEO before and after ethanol treatment can be curve-fitted to reveal four components as illustrated in Figs. S2a and S2b. They are attributed to carbon from the aromatic ring of PS ($\text{C}-(\text{C,H})_{\text{arom}}$) at 284.9 eV, carbon from the aliphatic backbone of PS ($\text{C}-(\text{C,H})_{\text{aliph}}$) at 285.2 eV, carbon involved in an ether link (C-O-C) from PEO at about 286.5 eV and, finally, a shake-up satellite peak associated with the aromatic ring of PS ($\text{C}_{\text{sh up}}$) at about 291.5 eV. Since the C-O-C component only comes from the PEO block and the rest of the carbon components are solely attributed to the PS block, it can be concluded that the PEO block is less present at the outermost surface for the PS-PEO film in comparison with its proportion for the ethanol treated film. Quantification of peak areas suggests that the relative concentration of PEO block increases from 14% to 19% during the ethanol treatment of PS-PEO film. The corresponding survey spectra shown in the inset of Figs. S2a and b also illustrate an increase in the oxygen peak intensity for the ethanol treated film. This again confirms much of the PEO is still present in the film and its surface contribution is enhanced (as suggested by the FTIR and TEM data). No silicon was detected by the survey spectra that mean the thickness of the film is sufficient to mask the substrate.

Fig. S2. (a, b) C1s core level spectrum of PS-PEO before and after ethanol treatment respectively. In sets of (a, b) shows the corresponding survey spectra.

