Supporting Information

Multilayer polymer thin film for fabrication of ordered multifunctional polymer nanocomposites
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Experimental:
The block copolymer [PS-b-P4VP, PS (32900)-b-P4VP (8000) (PDI=1.06)] were purchased from polymer source Inc. The solvents used during experiments were purchased from Acros Organics and used as it is. Other reagents were purchased from Aldrich Sigma chemicals. Silicon wafers {100} and quartz slides were cleaned successively in an ultrasonic bath (dichloromethane) for 15 min and a “piranha” bath (30% H2O2, 70% of H2SO4, chemical hazard) for 90 min at 75 °C, and then thoroughly rinsed with Millipore water and dried under an argon flow.
The thickness of block copolymer layers on silicon substrate was measured by an SE 400 ellipsometer (SENTECH Instruments GmbH, Germany) with a 632.8 nm laser at a 70° incident angle. The thickness of each polymer layer is around 30 nm.

Fabrication of multilayer films. The block copolymer layers were fabricated on silicon wafer from filtered solutions of PS-b-P4VP of 1 wt. % concentration in 1,4-Dioxane. For the spin-assembled multilayer films, PS-b-P4VP solution was completely wetted on the silicon substrates and then rotated with a spinner at 2500 rpm for 20s. The BCP thin films were further annealed in vapours of appropriate solvent for the reorientation of the microdomains and for improving the long-range order. The solvent vapour treatment of the thin films was done in a crystallographic dish with a Petri dish containing the solvent. For stabilizing each block copolymer layer, the layers were further cross-linked using a photocross-linker 4,4’-Diazido-2,2’-stilbene disulfonic acid disodium salt tetrahydrate. The photocross-linking was done by irradiating the layer under UV radiation (λ = 254 nm, germicidal UV lamp, type G8T5, 2.5W, TecWest. Inc.,USA).
1 weight % filtered solution of the cross-linker in ethanol solution was completely wetted on the block copolymer layer for 3 minutes and then rotated with a spinner at 6000 rpm for 30s. After that the layer was exposed to UV radiation for ten minutes. The photo cross-linking mechanism of the cross-linker molecule is shown in Fig.S1. The cross-linking mechanism of this type of molecules having azide group is well known. In this case, UV irradiation of the azide group in the polymer backbone leads to the formation of highly reactive nitrene radicals, which undergo facile cross-linking reactions.

The cross-linking of the block copolymer layer was checked further by dipping the cross-linked layer in 1,4-Dioxane for 5 minutes. As shown from the Fig.S2c it is clear that large scale morphology of the block copolymer layer is intact after cross-linking and also exposing the cross-linked block copolymer layer in 1,4-Dioxane.

\[\text{Fig.S1 Schematic diagram for the photo crosslinking mechanism of 4,4'}^{\prime}\text{-Diazido-2,2'}\text{stilbene disulfonic acid disodium salt tetrahydrate under UV light.}\]

The thickness of the polymer films on silicon substrate was measured by an SE 400 ellipsometer (SENTECH Instruments GmbH, Germany) with a 632.8 nm laser at a 70° incident angle. The thickness of the films are around 30nm.

**Atomic Force Microscopy.** Atomic force microscopy (AFM) imaging was performed using a Dimension 3100 scanning force microscope (Digital Instruments, Inc., Santa Barbara, CA) and a CP microscope (Park Scientific Instrument, Inc.) in the tapping mode. The tip characteristics were spring constant 1.5-3.7 N m\(^{-1}\), resonant frequency 45-65 Hz, and tip radius about 10 nm. Analysis of the AFM images was performed with the WSxM software (Nanotec Electronica)\(^1\).

**FESEM Study.** The block copolymer double layer, deposited on silicon wafer which was used for AFM investigation was further used directly for FESEM study. FESEM images were obtained with field emission electron microscopy (Zeiss Ultra 55 Gemini with FIB) operating at 3 kV. The samples were investigated without staining, and the working distance was 3 mm.
**Transmission Electron Microscopy.**

For TEM sample preparation, the block copolymer double layer used for AFM and SEM measurement and was first transferred on TEM grid from silicon surface by etching the layer using 1M sodium hydroxide solution. The staining of the block copolymer layer was done by putting the TEM grid containing the block copolymer layer in Iodine chamber for 14 hours. TEM images were taken using transmission electron microscope (Libra 120) operating at 120 kV.
TEM image clearly indicate the hexagonally arranged perpendicular cylinder and parallel cylinder in same film.

Fig.S3 SEM image (a) bottom layer after solvent annealing and surface reconstruction (b) double layer after surface reconstruction.
**Fabrication of the double layer nanocomposite films:** Before the fabrication of the multilayer nanocomposite thin films, the stability of the nanomaterial deposited block copolymer layer after cross-linking was further checked by dipping the layer (after nanomaterial deposition and cross-linking) in 1,4-Dioxane for five minute. Fig.S5a shows the AFM image of Co deposited block copolymer layer. Whereas Fig.S5b shows the cobalt deposited block copolymer layer after cross-linking and dipped in 1,4-Dioxane. From the AFM image it is clear that the large scale morphology of the block copolymer layer after cross-linking and directly exposed in solvent remains intact. Now the second layer, which will be further functionalized, can be deposited over the first layer using block copolymer solution in 1,4-Dioxane.

![AFM images](image.png)

Fig.S5 AFM height images of (a) block copolymer layer after cobalt deposition (b) cobalt deposited block copolymer layer after cross-linking and dipping in 1,4 Dioxane respectively. The color code with each AFM image shows the scale bar for the height in the image.

**Fabrication of double layer multifunctional nanocomposite containing arrays of gold nanowires in lower layer and hexagonal arrays of cobalt nanodots in the top layer**

A block copolymer layer of around 30 nm thickness was first deposited on cleaned silicon substrate. Ordering of the microdomains was further done by solvent annealing in chloroform. Then the solvent annealed thin film was immersed in the aqueous metal salt solution (consisting of 10 mL of 0.01 M HAuCl₄ and 10 mL of 0.01M HCl) for 20 min. After metal salt deposition, the sample was thoroughly washed with water to remove the loosely absorbed salt on the block...
copolymer layer surface and dried under argon stream. The block copolymer layer was then dipped into freshly prepared sodium borohydride (NaBH₄) solution in water for the reduction of HAuCl₄. The deposition of gold was confirmed from AFM, SEM and UV-vis study. After gold deposition, the block copolymer layer was photocross-linked and a second layer was deposited on the cross-linked layer from spin coating in 1,4-Dioxane solution. The block copolymer layer was further annealed in 1,4-Dioxane. Then the solvent annealed block copolymer was further immersed in the ethanolic Cobalt salt solution (consisting of 0.01CoCl₂ and 10 mL of 1m HCl) for 20 min. After Cobalt salt deposition, the sample was thoroughly washed with ethanol to remove the excess salt absorbed on the block copolymer template surface and dried under argon stream. Then the block copolymer template was dipped into freshly prepared sodium borohydride (NaBH₄) solution in ethanol for the reduction. The deposition of the cobalt nanoparticles was further confirmed from AFM and SEM study.
Fabrication of double layer multifunctional nanocomposite containing arrays of gold nanowires in lower layer and arrays of CdS nanodots in the top layer

The deposition of the gold is already described in the earlier section. After fabricating a block copolymer layer having arrays of gold nanowires, was further cross-linked and a second layer of hexagonally arranged cylinder was deposited. In the second layer CdS was deposited by the following method. For CdS deposition, the block copolymer was dipped into 0.1 M cadmium acetate solution for 2 h. Then the block copolymer layer was transferred from cadmium acetate solution to an aquas solution of thioacetamide, which acts as a source of sulfide ion (S\(^{2-}\)). The AFM images confirm the deposition of CdS. Same way we can fabricate a block copolymer double layer nanocomposite films having lower layer arrays of gold nanodots and top layer arrays of CdS nanowires.
Fig. S10 AFM image of a block copolymer layer after CdS deposition (a) perpendicular morphology (b) parallel cylinder morphology. The color code with each AFM image shows the scale bar for the height in the image.

References: