Joining self-assembly techniques: A route to hierarchical nanopores

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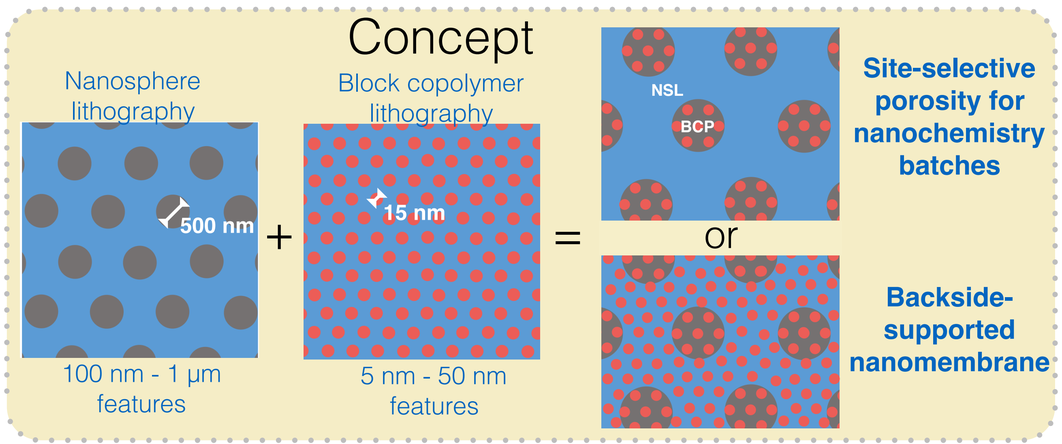
Self-assembly techniques

- Self-assembly process allows for easy and fast large-area surface patterning at the nanoscale.
- Nanosphere lithography (NSL) with plasma- treated polymer sphere monolayers is used for the preparation of patterns with tailored feature size and shape.
- Block copolymer (BCP) lithography is an emerging technique for surface patterning with sub 20-nm features.

Review: R. A. Puglisi, Hindawi J. Nanomaterials, Art. ID 586458 (2015).

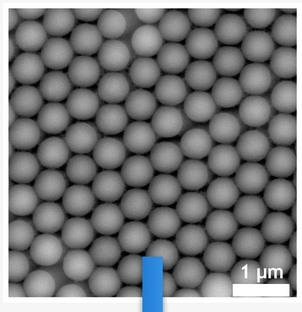
Concept



Hierarchical nano architectures

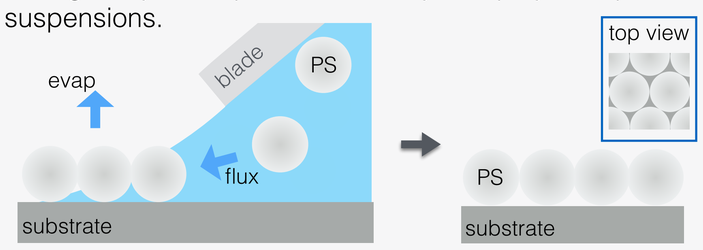
- Hierarchical surface patterning allows for the tailored creation of new functionalities in hybrid architectures.
- Different materials in different shapes on different size scales can be combined resulting in new material properties.
- We combine BCP lithography and NSL lithography, which act on different size scales, for the creation of hierarchical nanopores.

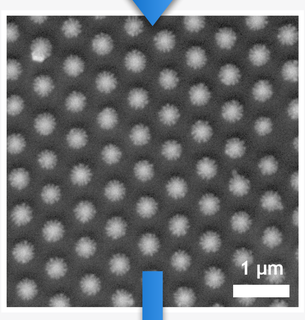
Antidot patterns by nanosphere lithography (NSL)



Step A: Polymer sphere monolayer

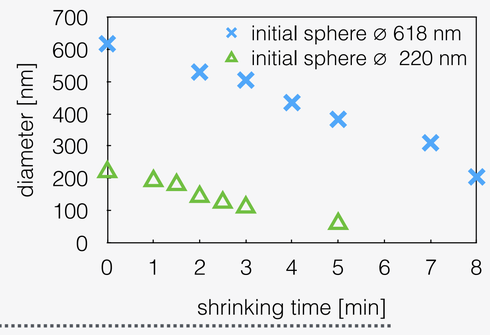
Convective self-assembly at a three-phase boundary results in the formation of a hexagonally close packed monolayer of polymer spheres from colloidal suspensions.





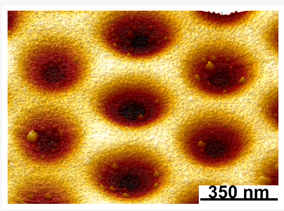
Step B: Sphere shrinking

By reactive ion etching in Ar/ O_2 plasma polymer spheres shrink and form a regular array of disconnected dots (SEM image, left). The feature diameter can be set by adjusting the time of plasma treatment (plot, right).



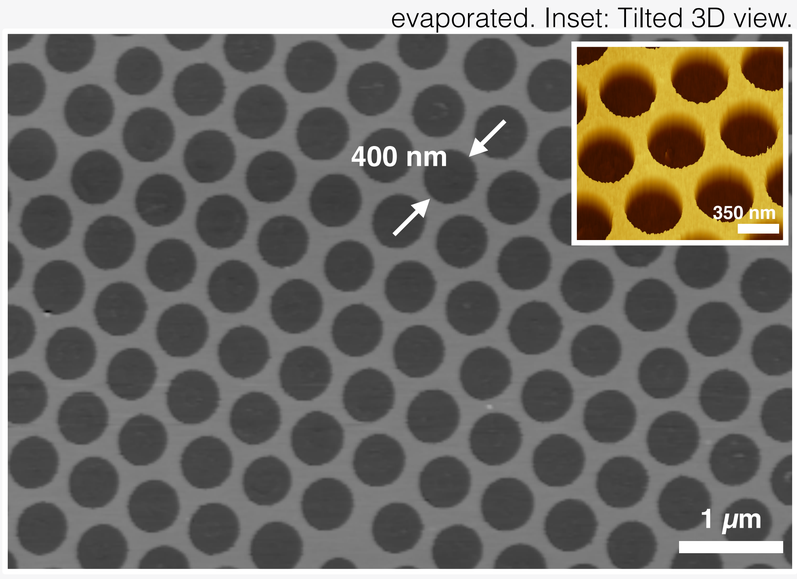
Step C: Antidot preparation

Dots act as shadow mask during sputter deposition or electron beam evaporation. After sphere removal antidot patterns consisting of regularly arranged cylindrical holes in a thin film on the substrate are achieved.



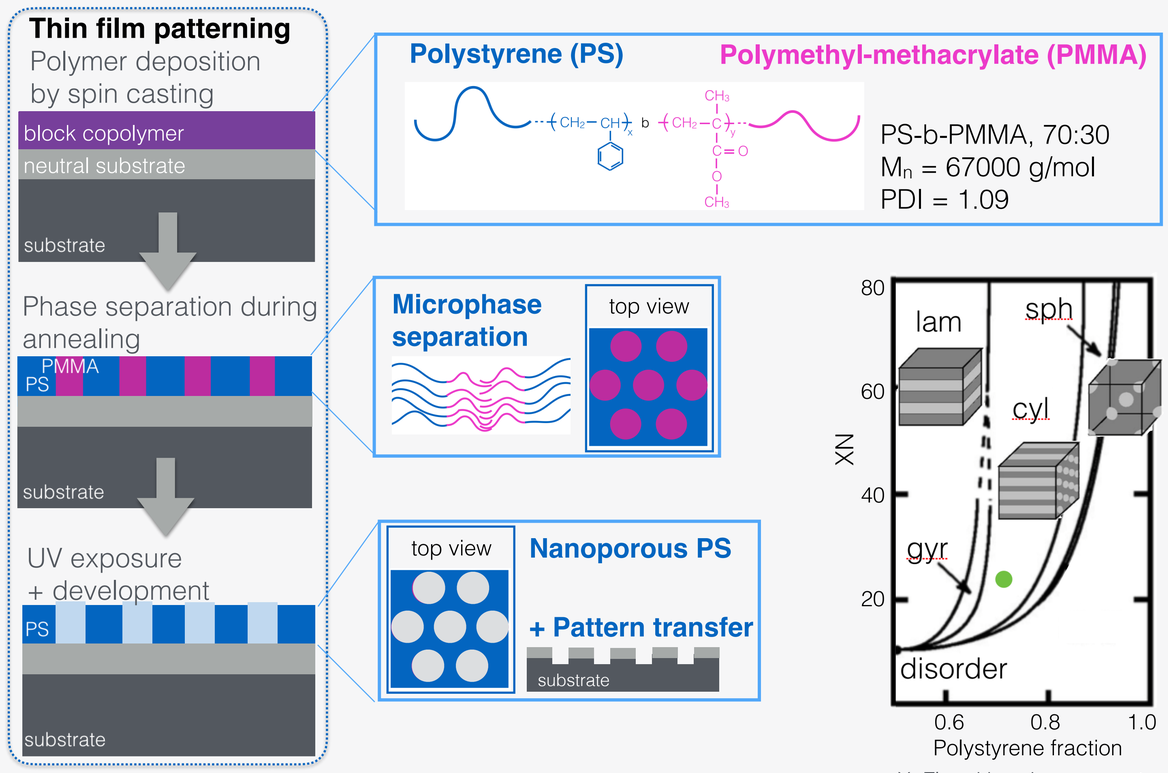
Tilted 3D view AFM image of the antidot geometry obtained by sputter deposition of 10 nm Pt. Note the flat side walls.

AFM image of antidot-patterned Au/ Ti thin film on a SiO_2 substrate. 2 nm Ti and 30 nm Au were electron beam evaporated. Inset: Tilted 3D view.



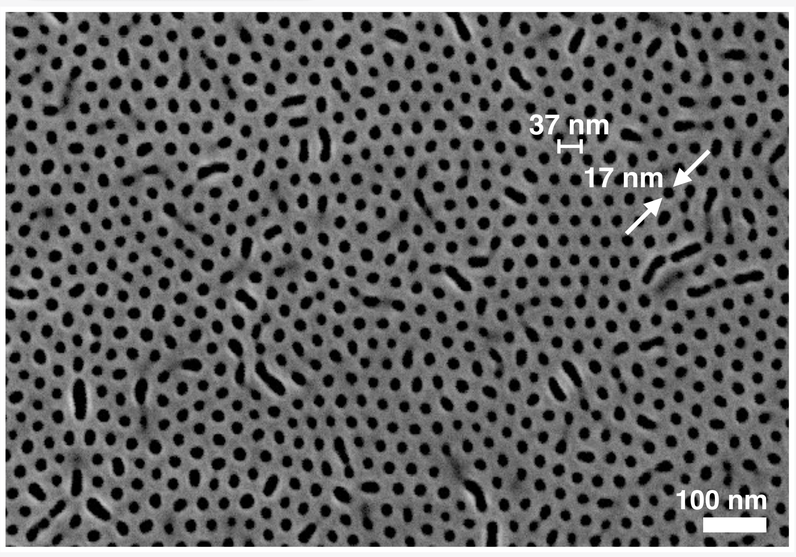
Block copolymer (BCP) lithography for sub-20 nm pores

Polymer thin films are patterned by microphase separation of BCP into self-assembled hexagonal PMMA cylinders in PS matrix. By selective PMMA removal, nanopores with 17 nm diameter are created.



X: Flory Huggins parameter
N: Degree of Polymerization

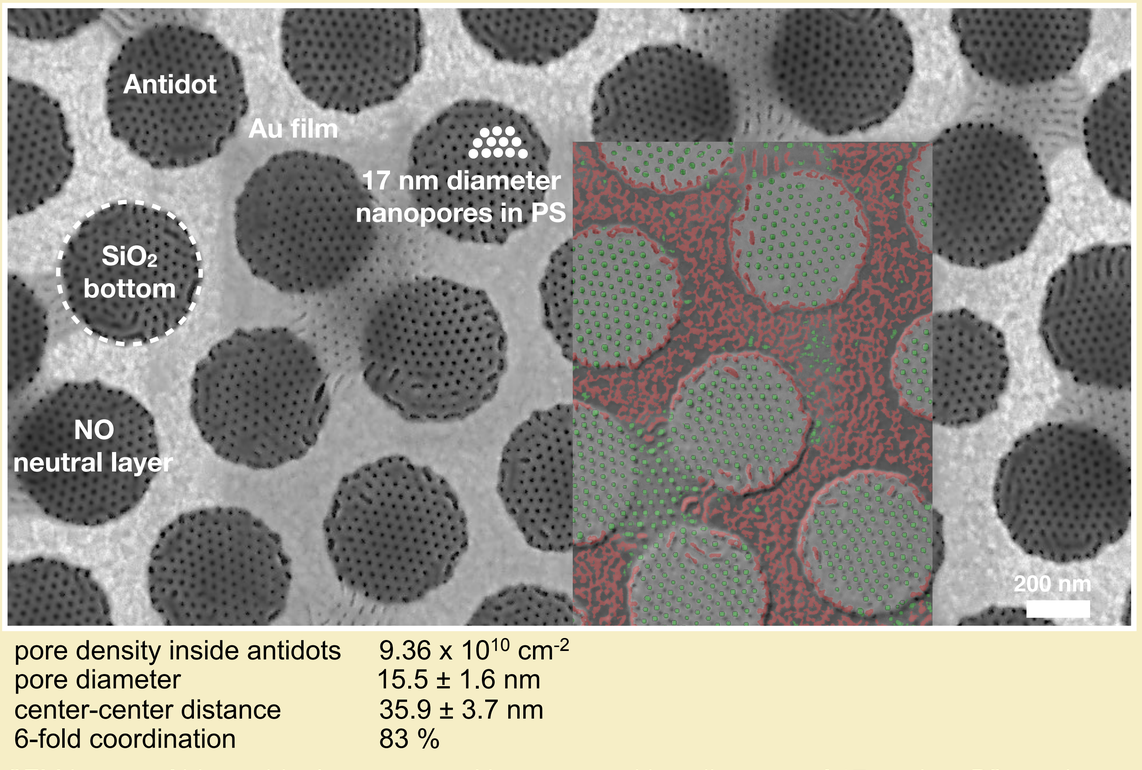
T. H. Andersen et al., J. Electron. Spectrosc. Relat. Phenom. 121, 93 (2001).



SEM image of nanopores in PS matrix after selective removal of PMMA cylinders. The hexagonally arranged nanopores have a diameter of 17 nm. The surface nanopatterning can be easily exploited on wafer scale.

Hierarchical nanopores

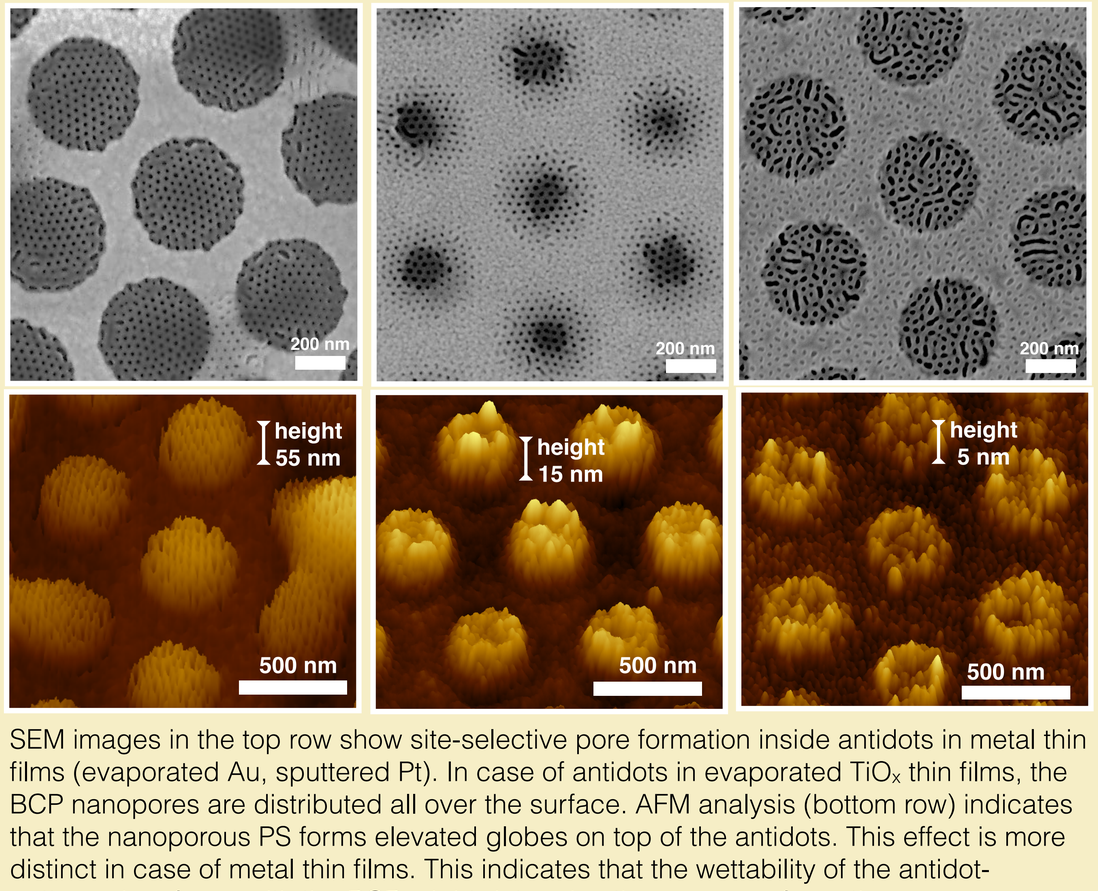
In a first step, antidot patterns in material thin films are created by NSL lithography. The BCP lithography is then performed in the second patterning process on the NSL pre-structured substrates.



pore density inside antidots	9.36 x 10^{10} cm^{-2}
pore diameter	15.5 ± 1.6 nm
center-center distance	35.9 ± 3.7 nm
6-fold coordination	83 %

SEM image of hierarchical nanopores: Nanopores with a diameter of 17 nm in a PS matrix are formed site-selectively inside 400 nm diameter antidots in a Au thin film. The image overlay shows the result of an automated image analysis. BCP nanopores are marked green. For comparison: pore density on a planar SiO_2 film with random copolymer film is 8.95x10^{10} cm^{-2}.

Depending on the materials choice of the antidot patterned thin film, BCP nanopores are either formed site-selectively inside the antidots or homogeneously all over the surface.



SEM images in the top row show site-selective pore formation inside antidots in metal thin films (evaporated Au, sputtered Pt). In case of antidots in evaporated TiO_x thin films, the BCP nanopores are distributed all over the surface. AFM analysis (bottom row) indicates that the nanoporous PS forms elevated globes on top of the antidots. This effect is more distinct in case of metal thin films. This indicates that the wettability of the antidot-patterned surfaces with the BCP might determine the nanopore formation.

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