Nanoparticle Organisation into Branched Morphologies Using Thin Films of Crystalline Polymers as Dynamic Templates

Mariela J. Pavan and Roy Shenhar*

The Institute of Chemistry and the Center for Nanoscience and Nanotechnology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904

E-mail: roys@chem.ch.huji.ac.il

Supporting Information

Fig. S1  Cooling curve recorded from 60 °C ($T_m$ of PEG) during the cooling process after heating at 250 °C for 12 hours. The cooling rate at 60 °C measured ca. 0.2 °C·min⁻¹.
Fig. S2  AFM images showing different patterns obtained under the same heating conditions (250 °C, 12 hrs) with different film thicknesses. a) 23 nm; b) 14 nm; c) 11 nm; d) 8 nm. Height contrast is 30 nm.
Fig. S3  AFM images showing different patterns obtained from a 23 nm film heated for 12 hrs to a) 250 °C; b) 150 °C. Height contrast is 30 nm.
**Fig. S4** SEM image of a sample after the deposition of 700 Au-cit NP \( \mu \text{m}^2 \) in total in one cycle, where the solvent was let to evaporate spontaneously in air at room temperature, evidencing the low selectivity obtained under these patterning conditions.

**Fig. S5** SEM images (at two magnifications) after deposition of 1.2 mg mL\(^{-1}\) Au-DT in hexane for 15 s, showing the considerably increased brightness of the channel edges. Although the limited SEM resolution hinders the observation of individual Au-DT NPs, the gray levels within the channels suggest that narrow sections of the channels get filled up with NPs while wider sections feature NPs accumulated only at the edges.
Fig. S6 (a) High magnification SEM images of samples after the deposition of 0.6 mg mL$^{-1}$ Au-DT in hexane for 1 s, showing individual NPs deposited at the edges of the channel. (b) and (c) show a
region that suffered beam damage during a magnification attempt, which increased the contrast both of NPs deposited at the channel edges and of NP cluster located on top of the crystalline domains.
**Fig. S7** High magnification SEM images of the extensive template degradation region after the deposition of 5600 Au-cit NP $\mu$m$^{-2}$ in total in 6 cycles (corresponding to Fig. 4d).

**Fig. S8** (a) High magnification SEM image of a sample after 2300 Au-cit NP $\mu$m$^{-2}$ in total in 6 cycles (corresponding to Fig. 4b), showing NPs deposited in the trails of partially degraded crystalline domains. (b) Atomic force microscopy (AFM) height image of a sample after the deposition of 5000 Au-cit NP $\mu$m$^{-2}$ in total in 10 cycles (corresponding to Fig. 4e), showing NPs deposited in the trails of fully eroded crystalline domains. Height scale: 40 nm. The color contrast in both images indicates that the NPs are lying on the same plane, leading to the conclusion that the crystalline domains were eroded.
Fig. S9 AFM images and representative cross-sections of a 20 nm thick PEG film before (a) and after (b) extended exposure (7 cycles) to the solvent. Image (b) represents the structure at a certain location in the film, where crystalline domain degradation is evident. In addition to the apparent increase in channel width, the average depth of the channels increased from 11 nm in (a) to 18 nm in (b), indicating dissolution and removal of polymeric material from the channels.