Electronic Supplementary Information (ESI)

Self-aligned Nanolithography by Selective Polymer Dissolution

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Upon application of an electrical bias to the electrodes, it was discovered that dissolution of large areas of the polymeric film occurred in MIBK/IPA mixtures in a fast and uncontrollable manner leading to large exposed areas opening around the electrodes within a short period of time (60 s) (Fig. 1Sa). It was observed that the PMMA film remained intact far away from the electrodes, as would have been expected due to the slow dissolution rate. The large irregular dissolved area can be attributed to the presence of an electric field. Experiments were carried out to confirm this. A probe with an applied voltage was used to create an electric field at the surface of the PMMA layer as illustrated in Fig. 1Sb, and was found to accelerate the dissolution rate in its vicinity. The resulting pattern dissolved at a bias of 2 V for 100 s is shown in Fig. 1Sc.

Fig. 1S. a) Optical image of PMMA dissolved in MIBK:IPA (1:3) in the presence of an electric field; b) Schematic of electric-field induced dissolution experiment; c) Optical image of PMMA pattern obtained. Large area dissolution occurred within a short time (100 s). Scale bar: 400 μm.

AFM images of the device upon selective dissolution are shown in Fig. 2S. Figs. 2Sa and 2Sc are topographic images with the height profile inset, while Figs. 2Sb and 2Sd show 3-D perspectives, respectively. As observed, the sidewall of the trench is sloped as the polymer dissolved from the top surface and hence the polymer at the bottom was exposed for less time in the solvent, resulting less amount of polymer dissolved. The polymer near the nanowire at the bottom surface is expected to be cleared (given the height and width exposed); however, the AFM tip (PhotoniTech, Singapore;
Tapping300Al, Al coating 30 nm in thickness) has a cone-shape (semi cone-angle ~20-25°) with a finite tip dimension of 40nm and hence has difficulty to probe into the bottom of the trench.

To exclude the possibility of non-specific binding of gold nanoparticles to the gold surface, control experiments were carried out on fresh bare gold surface and the exposed nanowire in the nanotrench after selective dissolution, and the results are shown in Fig. 3S. The sample shown in a and c is the gold surface without any DNA modification and it is observed that non-specific binding of gold nanoparticles was very limited, while the sample shown in b and d was modified with capture DNA strands and gold nanoparticles were assembled upon DNA hybridization. Note that for c and d, SEM images were taken after stripping the PMMA by low power oxygen plasma.

Fig. 2S. a) AFM image of the nanowire with the self-aligned trench after selective dissolution. b) 3D rendition of a). c) Magnified AFM scan of a). The inset is the height profile of the dotted line across the trench to show the sloped sidewall. d) 3D rendition of c).
Fig. 3S. SEM images of gold surfaces without DNA modification (a, c) and with capture DNA strands (b, d) after gold nanoparticle assembly, respectively. Scale bars: 200 nm.