Supporting information

Regiospecific linear assembly of Pd nanocubes for hydrogen gas sensing

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S1. Materials and methods

H_2PdCl_4 solution was made from a 1:1 molar ratio of HCl and $PdCl_2$ (Aldrich). PS (polystyrene, MW=280K Da), PEI (polyethyleneimine, MN=60 kDa, MW=750 kDa) and PAA (poly acrylic acid, MW=100 kDa) were purchased from Sigma-Aldrich. PGMA [poly(glycidylmethacrylate)], (MN=304 kDa, PDI=2.14) was synthesised using previosuly descriped procedure.[1] All ACS grade solvents were used in the current study.

Highly polished single-crystal silicon wafers of 100 orientation (Semiconductor Processing Co.) were used as a substrate. The wafers were cleaned in a piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 h, and then rinsed several times with MilliQ water.

S2. Fabrication of PDMS stamp

First, the metal layer in a blank CD was peeled off and the CD was washed with ethanol. The polycarbonate support (minus the metal layer) was used as master. Polymer base and curing agent from Sylgard® 184 (Dow Corning) silicone elastomer kit were thoroughly mixed together at ratio 10:1 by weight in a glass vial. In order to remove the trapped bubbles from mixing of the components, the vial was placed in a vacuum desiccator. Following vacuum treatment the elastomer was restored at atmospheric pressure slowly several times until it was free of bubbles. Finally PDMS mixture was cast onto the surface of the grooved side of CD and cured at 80 °C for 2 hours.

S3. Synthesis of Pd nanocubes [2]

0.5 mL of 10 mM H_2PdCl_4 solution was added to 12.5 mL of 10 mM CTAB (Cetyltrimethylammonium bromide) solution under stirring, the solution was stirred for at least 15 mins before heated to 90 ºC for 5 min prior to the addition of 80 μL of a freshly prepared 100 mM ascorbic acid solution. The reaction was allowed to proceed for 30 min. The whole reaction mixture was then left at room temperature for 3 h before washing. Figure S1 shows the morphology of as-prepared Pd nanocubes.

S4. The typical procedure of fabricating palladium nano-array

First, silica wafer was modified with a monolayer of PGMA which contains epoxy functional groups. Silica wafer was dip-coated in PGMA (0.07% w/v in $CHCl_3$) and put into oven under vacuum at 120 °C for 20 min to anneal PGMA. The unreacted PGMA was removed using $CHCl_3$. Next, PS film was deposited by dip-coating to cover the PGMA layer. The PDMS (polydimethylsiloxane) stamp was placed over the PS film followed by heat treatment in an oven at 130ºC. The assembly was left aside to cool down to room temperature before the PDMS stamp was peeled off. The patterns of the PS can be tuned according to the initial concentration of PS: negative replica of stamp and doubled strips of stamp can be obtained by using 1% w/v and 0.6% w/v PS in toluene, respectively. The whole complex was dip-coated with PAA (1% w/v in methanol) and left at 38 ºC for at least for two hours to allow PAA to graft onto PGMA. After the grafting was complete, excess PAA was removed by washing with an ethanol/water mixture. Pd nanocube solution was drop-casted onto the patterned silica wafer, followed by controllable evaporation to allow nanocubes to attach to PAA evenly. Finally the PS mask was removed using methyl ethyl ketone, leaving the

patterned Pd nanocubes on the surface.

S5. The procedure of hydrogen sensing test

Two silver epoxy electrodes were painted into two ends of the as-prepared Pd nano-arrays, and the whole integration was mounted into hydrogen gas sensing chamber subject to current-voltage (I-V) sweeps. The test procedure involved alternating nitrogen gas (10 min) and varying concentrations of hydrogen gas (5 or 2 min). The change of the current was monitored at the same time. The total flow rate of gas was 1000 mL min^{-1}. The voltage applied between electrodes was 100 mV dc.

S6. Characterisation by Ellipsometry, AFM, SEM and TEM

Ellipsometry was performed with a COMPEL automatic ellipsometer (InOmTech, Inc.) at an angle of incidence of 70°. For testing the thickness of PS film, a four-layer model (silicon substrate + silicon oxide layer + PGMA anchoring layer + PS layer) was used to simulate experimental data. The refractive indices used to calculate the thickness of silicon oxide, PGMA and PS layers were 1.457, 1.5 and 1.5, respectively. Topographical and phase images were obtained using a VEECO Dimension 3100 AFM with Nanoscope IIIa controller and Ver5.30r3sr3 software in ambient air. The height (topography) and phase images were both captured using a frequency of 1.0 Hz and 256 scan lines per image. The size and morphology of the Pd nanocubes were determined using transmission electron microscopy (TEM, JEOL 3000F) at 300 kV. Scanning electron microscope (SEM) images were recorded at a Zeiss 1555 VPSEM operating at an accelerating voltage of 10 kV.

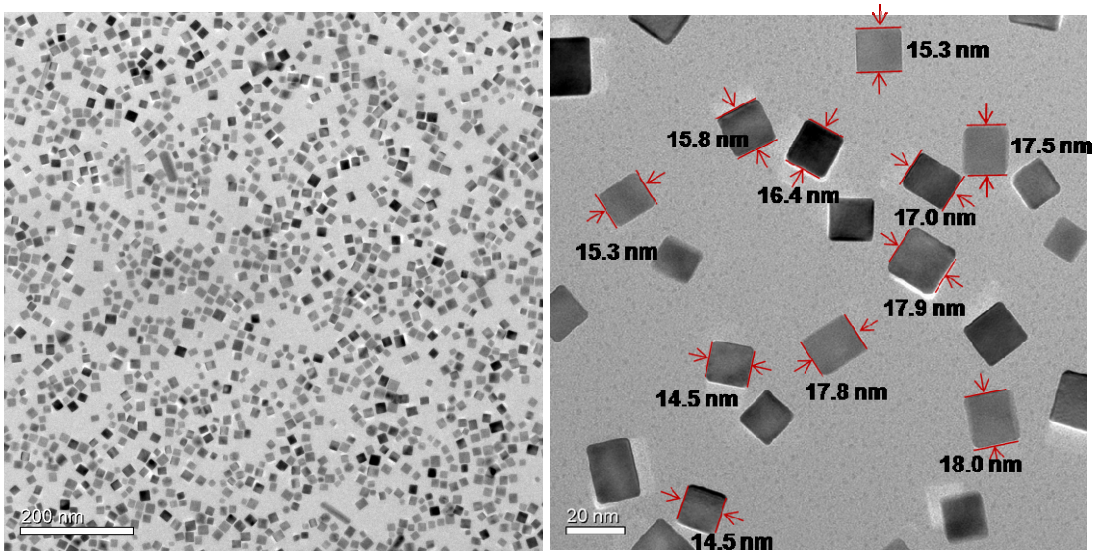

Figure S1. TEM images of Pd nanocubes.

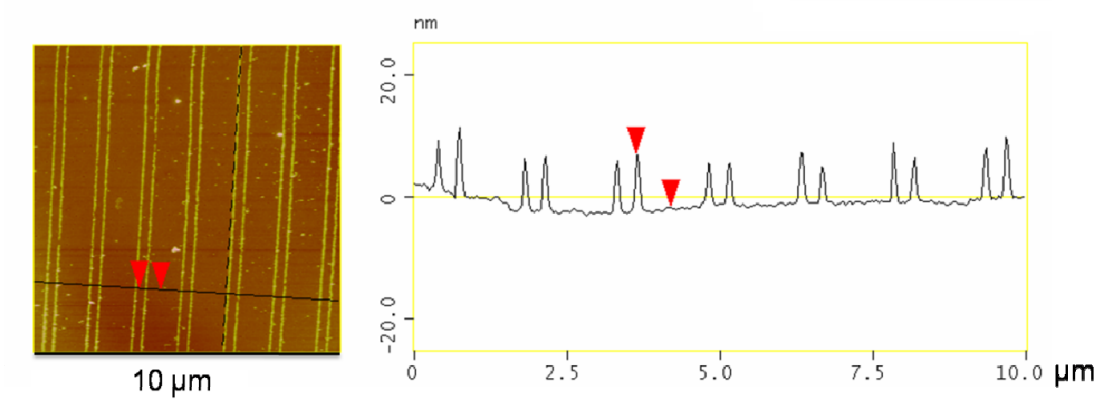

Figure S2. AFM image and line profile of PAA brush after removing PS by solvent, generated from the PS pattern shown in Figure 2b.

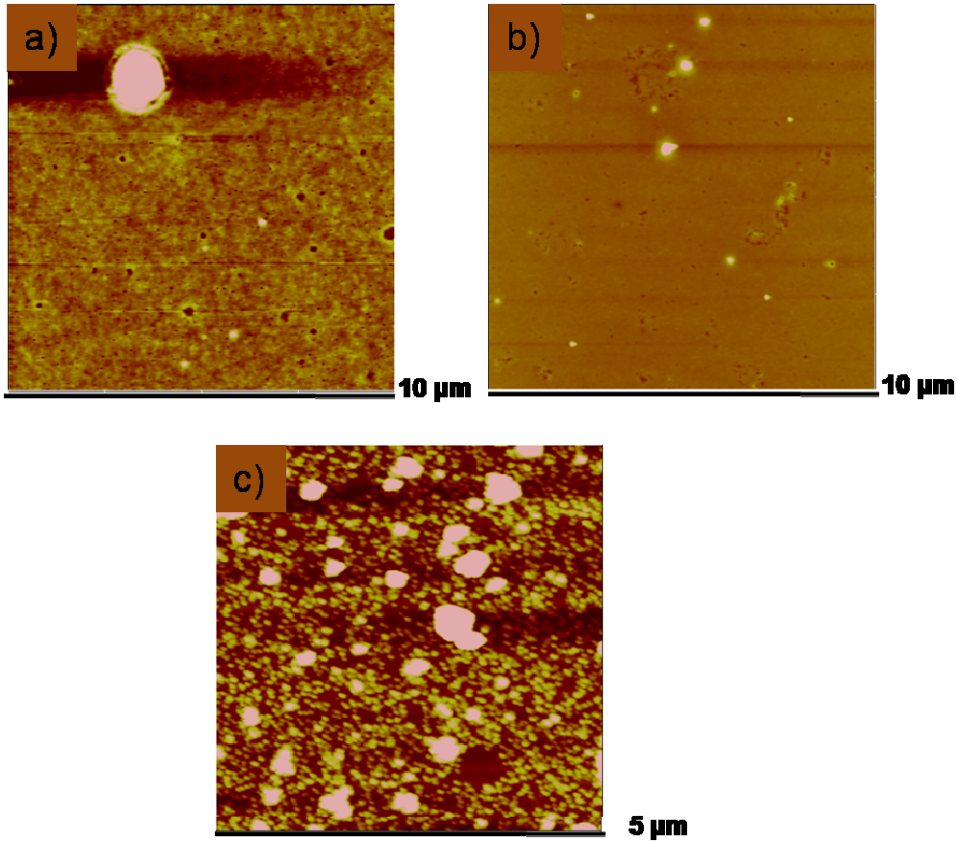

Figure S3. AFM images of a) Pd attached to P2VP, b) Pd attached to PEI, and c) Pd attached to PAA.

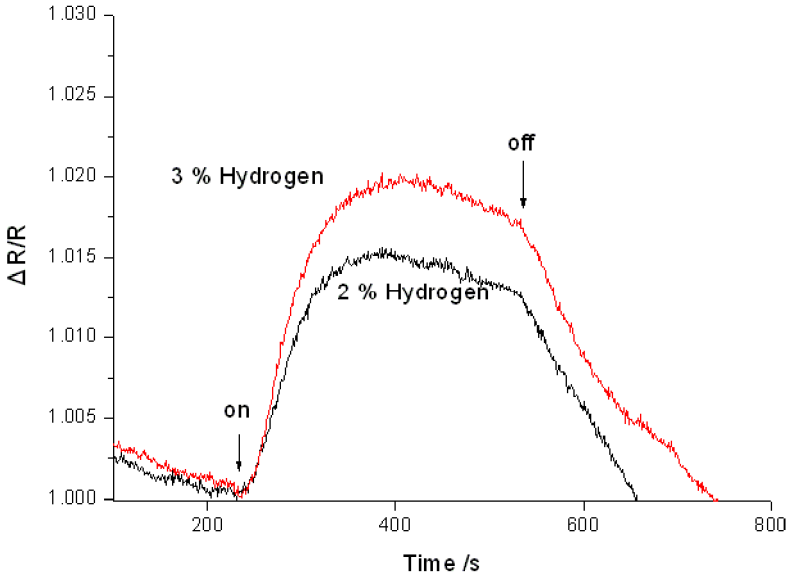

Figure S4. The responses to 2% and 3% hydrogen gas (5min hydrogen gas followed by 10 min nitrogen gas).

Reference:

(1) Iyer, K. S.; Zdyrko, B.; Malz, H.; Pionteck, J.; Luzinov, I. *Macromolecules* **2003**, *36*, 6519-6526.

(2) Niu, W. X.; Li, Z. Y.; Shi, L. H.; Liu, X. Q.; Li, H. J.; Han, S.; Chen, J.; Xu, G. B. *Cryst. Growth Des.* **2008**, *8*, 4440-4444.