

Structural Transformation by Electrodeposition on Patterned Substrates (STEPS): A New Versatile Nanofabrication Method

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EXPERIMENTAL DETAILS

Silicon masters of the micropost arrays were fabricated using the Bosch process as described elsewhere.^{S1} Polymer-based replicas of this master structure were prepared by creating a negative mold using PDMS, then molding a commercial UV-curable one component epoxy resin, UVO114 (Epoxy Technology, Billerica, MA). Gold electrodes were deposited using a bench top sputter coater (208HR, Cressington, Watford, UK) or using an electron-beam evaporator (Explorer, Denton Vacuum LLC, Moorestown, NJ). The gold-coated sample was cleaned by 100 W oxygen plasma (Femto, Diener GmbH, Nagold, Germany) for 10 seconds, then subject to subsequent depositions of polypyrrole.

Pyrrole (Sigma-Aldrich, Milwaukee, WI) was purified by an alumina column prior to use. An aqueous solution of 0.1M pyrrole and 0.1 M sodium dodecylbenzene sulfonate (Sigma-Aldrich, Milwaukee, WI) was prepared and purged by dry nitrogen for 10 minutes. Into this solution, a gold-coated parent substrate, acting as a working electrode, was placed; then the polypyrrole films were

electrochemically deposited using a standard three electrode configuration. An anodic potential of +0.55 V – 0.65 V vs. Ag/AgCl (saturated with NaCl) was applied under a potentiostatic condition and a platinum mesh was used as a counter electrode. A gradient of the thickness of the deposited polypyrrole film was created by withdrawing the sample at a constant rate from the solution over a total deposition time. Freshly deposited polypyrrole layer was washed with deionized water and dried by either blowing air or critical point drying. For the concentric double ring fabrication, the outer gold layer was deposited on the polypyrrole layer and the sample was embedded in an epoxy. Thin sections were generated by microtoming the embedded sample and transferred to a substrate for imaging.

Pseudomonas aeruginosa (strain PA14), a rod-like gram-negative bacterium, was incubated in LB medium for 12 hours at 37°C for the preculture. UVO114 epoxy replicas of test surfaces were placed individually in six-well plates, submerged by 3 mL of TB medium, and inoculated at 1% initial concentration with the PA14 preculture. The samples were incubated on a rocker at room temperature for 22 h. The surface-adherent bacteria were then fixed, labeled with SYTOX green nucleic acid stain, and imaged by fluorescence microscopy.

Mechanical testing of UVO114 epoxy replicas of parent and STEPS-reinforced structures was performed on an Agilent G200 nanoindentation system equipped with a Berkovich tip.

S1. McAuley, S. A.; Ashraf, H.; Atabo, L.; Chambers, A.; Hall, S.; Hopkins, J.; Nicholls, G. *Journal of Physics D: Applied Physics* **2001**, 34, 2769-2774

SUPPORTING FIGURES

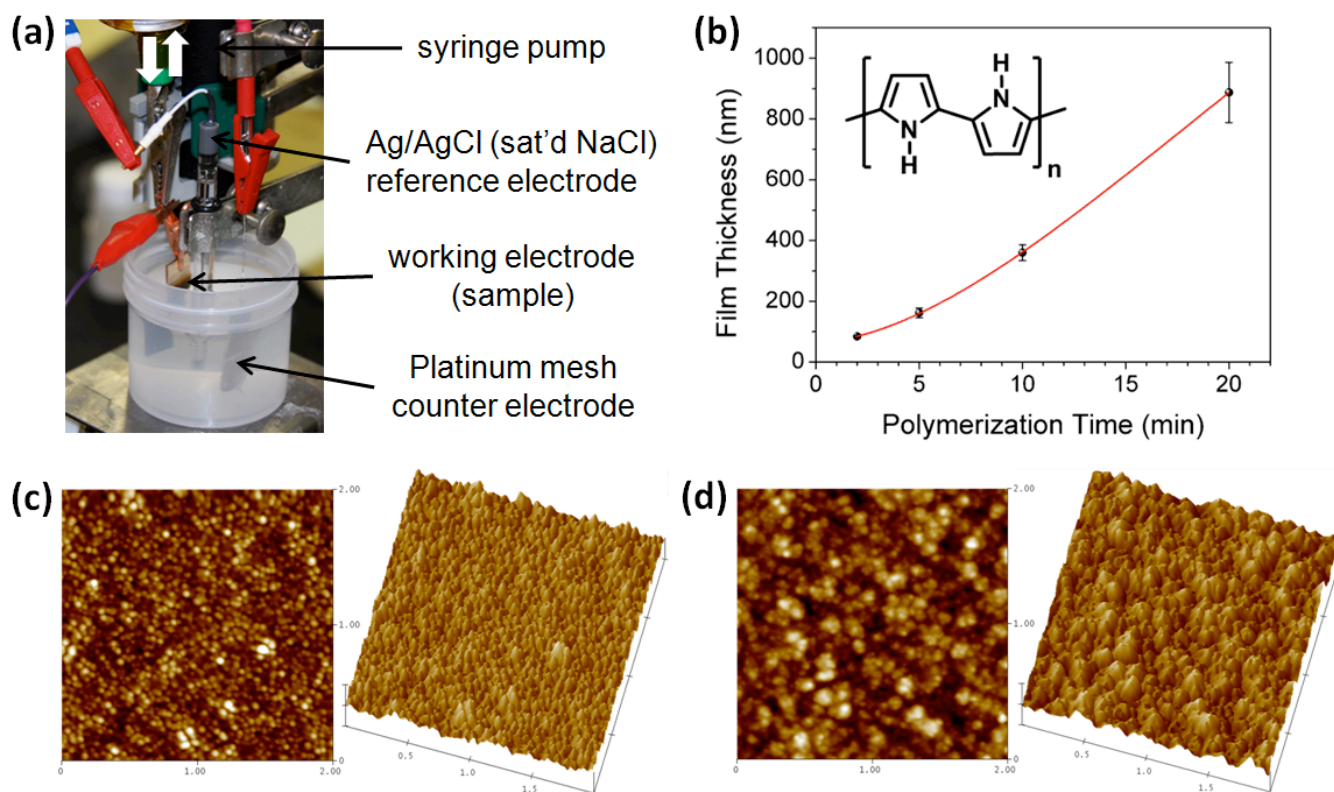


Figure S1. (a) Experimental setup for electrodeposition and gradient sample fabrication. (b) Thickness of PPy film formed on a flat substrate as a function of deposition time (0.55 V vs. Ag/AgCl, aqueous solution of 0.1 M NaDBS and 0.1 M pyrrole) showing the linearity of the polypyrrole deposition rate. (c) AFM height images (top view and tilted view) of 100 nm thick sputter coated gold on epoxy substrate. (d) AFM height images of a freshly deposited PPy(DBS) film on the gold surface shown in (c). RMS roughness = 4.00 nm and 4.70 nm, for (c) and (d), respectively. Scan area = 2 μm \times 2 μm .

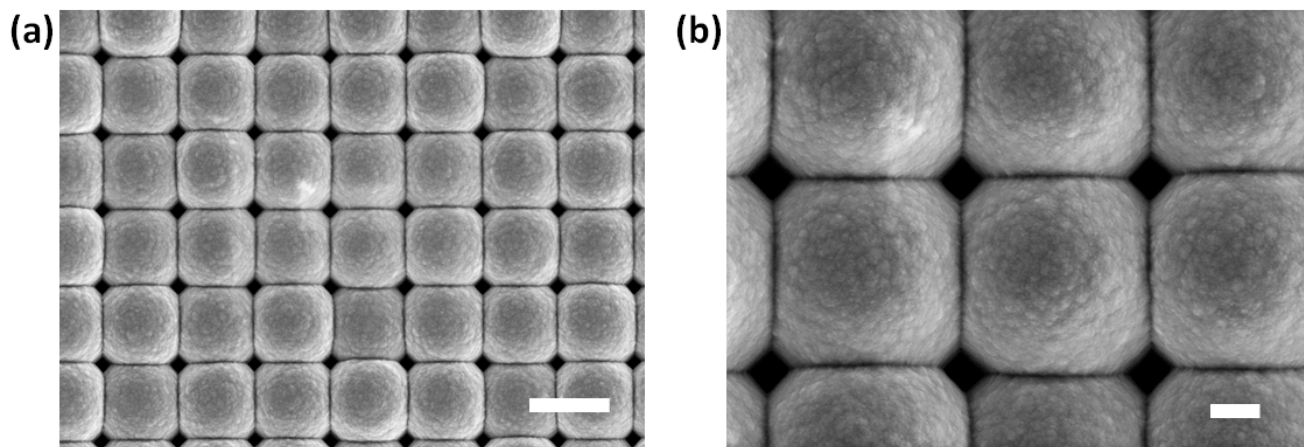


Figure S2. SEM images of a diamond shaped nanowell array. Scale bars: (a) 1 μm, (b) 0.5 μm.

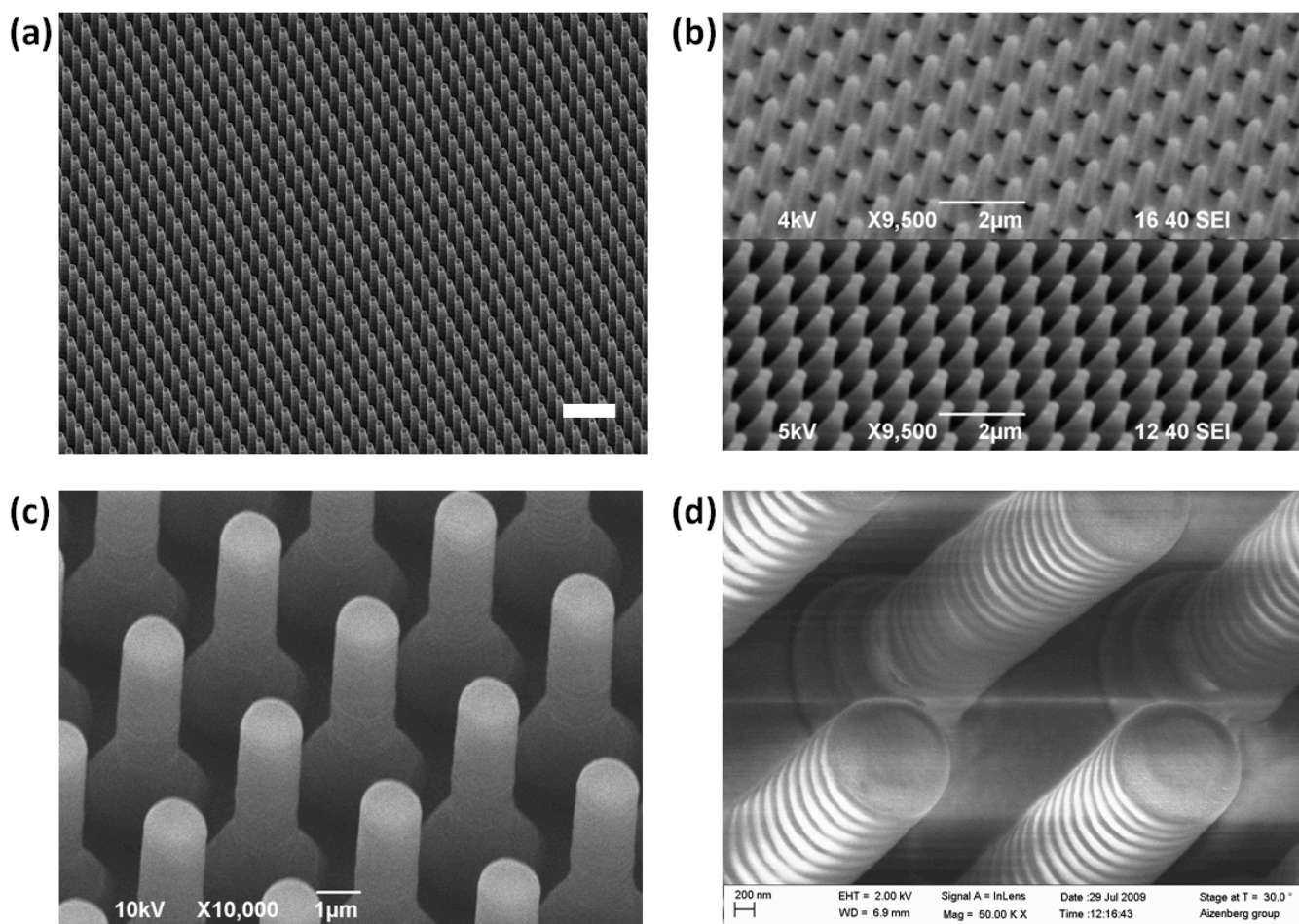


Figure S3. SEM images of microcone and nanocone arrays. (a) Nanocone array showing the uniformity of the shape over a large area. Scale bar = 5 μm. (b) Nanocone array before (top) and after (bottom)

STEPS process. (c, d) Microcone array with a short PPy deposition time yielded the deposition of PPy only around the bottom area of each micropillar, which is the evidence of the mechanism of STEPS Scheme II described in the main text.

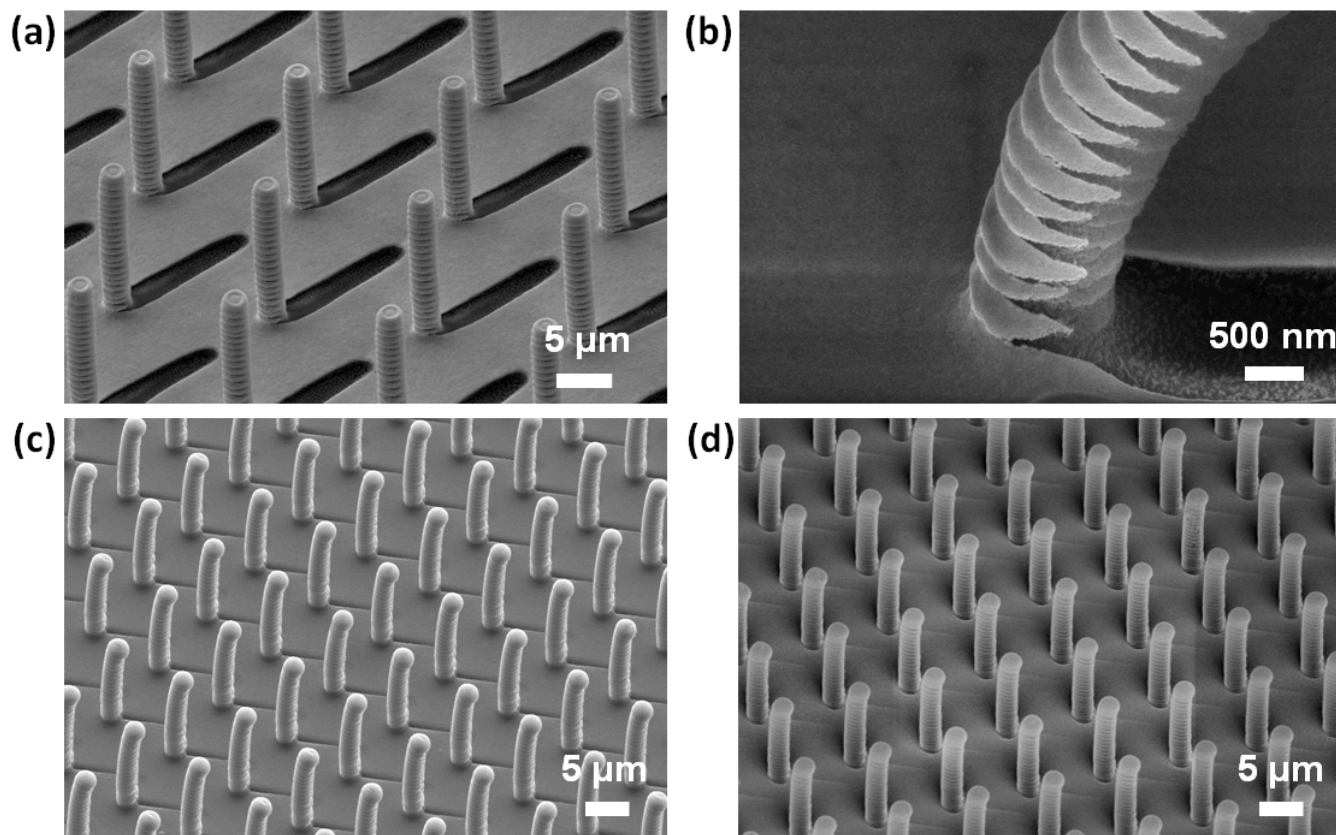


Figure S4. (a, b) SEM images of evaporated metal electrode at an angle onto an epoxy micropillar array. (c) SEM image of slightly tilted micropillar array fabricated from the parent structure shown in (a) using STEPS III process. (d) SEM image of an epoxy replica of the structure shown in (c) made using PDMS molding method. Scale bars = 5 μm.

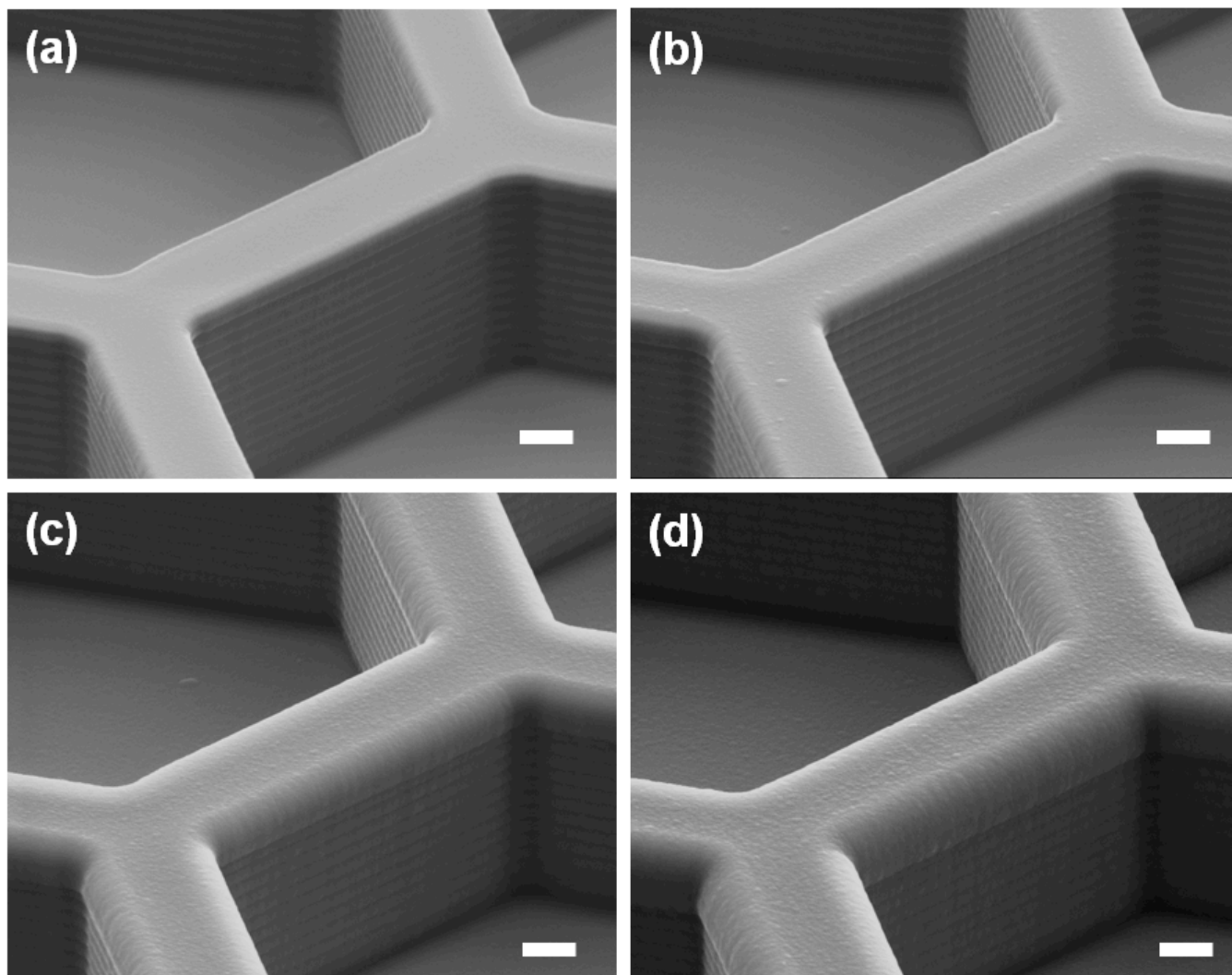


Figure S5. SEM images of STEPS II-modified closed cell microstructure showing gradually increasing height due to vertical growth of PPy, followed by the development of overhanging structure due to lateral growth of PPy, then finally downward growth of PPy with increasing processing time from (a) to (d). The number of scallops was initially 12 in (a) which was decreased to 11 in (d). Scale bars = 2 μm .