Energy Technology

Supporting Information

An Efficient Photoelectrochemical Hydrogen Evolution System using Silicon Nanomaterials with Ultra-High Aspect Ratios

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Ultra-High Aspect ratio Silicon Nanomaterials for Efficient Photoeletrochemical Hydrogen Evolution System

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SUPPORTING FIGURES

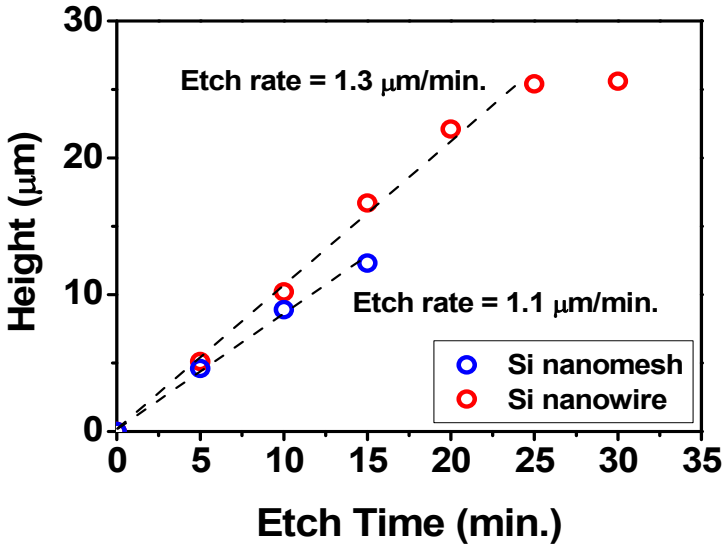

Figure S1. Nanopore depth of Si nanomesh (blue) and length of Si nanowire array (red) as a function of etching time. The height of Si nanomesh linearly increased with etch time up to 15 min., and the etch rate was 1.1 μm/min. The height of Si nanowire array linearly increased with etch time up to 25 min., and the etch rate was 1.3 μm/min.

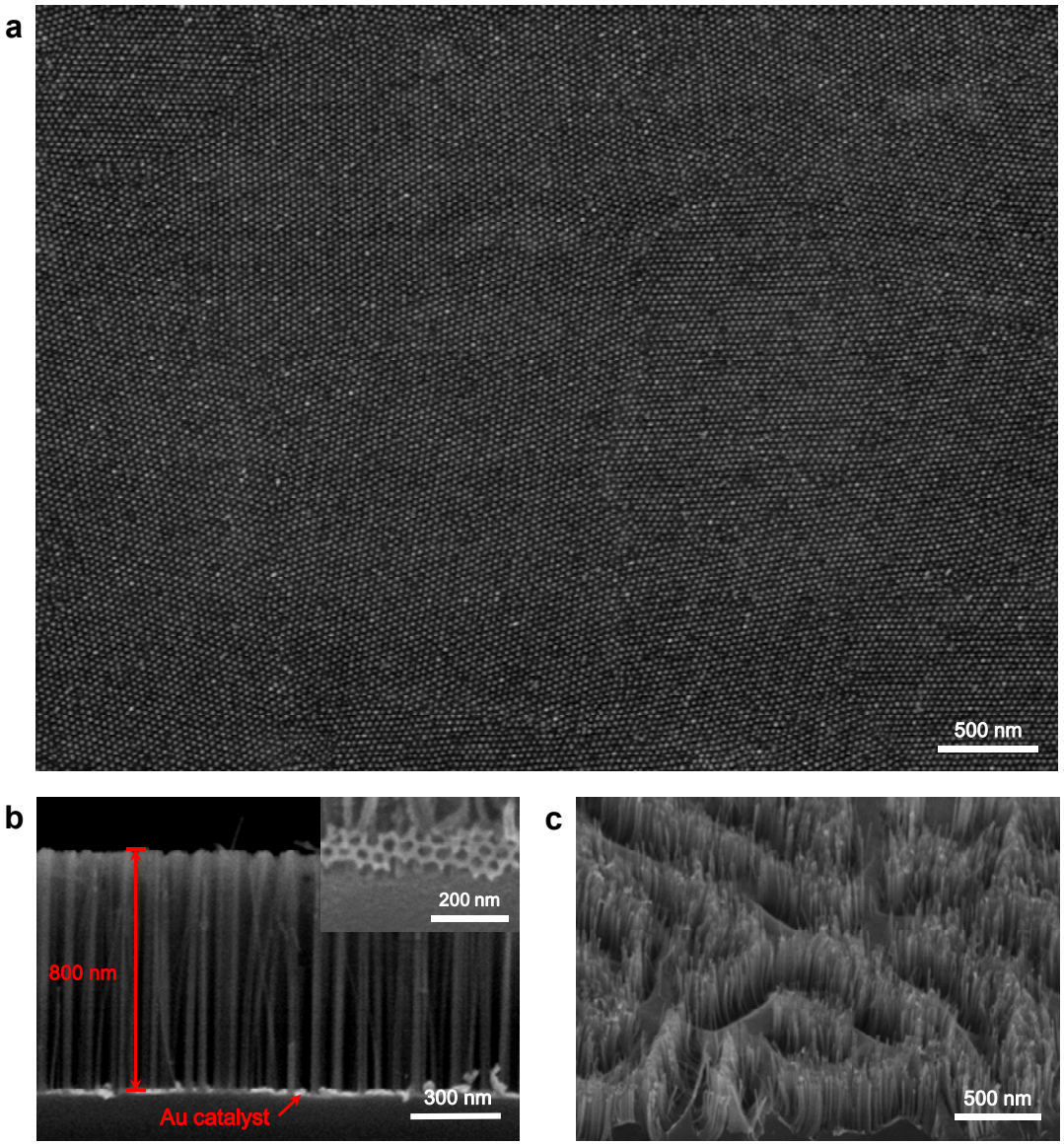

Figure S2. (a) Low magnification SEM image showing high areal density of Cr nanoparticles after lift off process. This image shows the hexagonally packed Cr nanoparticles, and such densely packed nanoparticles were obtained all over the 4-inch Si wafer. (b) Cross sectional SEM image of the Si nanowire array obtained by 40 sec. of Au assisted etching. The Si nanowires remain vertically aligned and separated after critical drying. The inset image shows

the honeycomb structure of Au catalytic film. (c) Tilted SEM image of the Si nanowire array obtained by 40 sec. of metal assisted etching with low density Cr particles. As the density of Cr particles decreased, metal assisted etching of Si substrate becomes non-uniform, and the vertical alignment of Si nanowires cannot be supported, which leads to collapsing of Si nanowires after longer than 1 min. of etching.

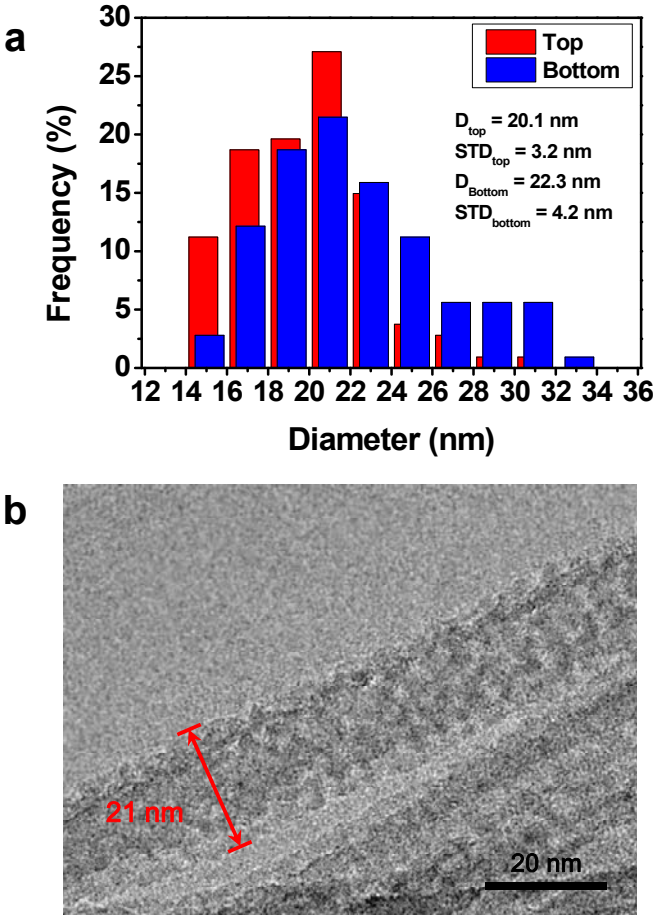

Figure S3. (a) The statistical analysis of diameters of 25 μm long Si nanowires. The data was collected over 100 nanowires. Mean diameter of top of Si nanowires was 20 nm and mean diameter of bottom was 22 nm, which indicates that the diameter is very uniform along the length (25 μm) of Si nanowire. (b) Bright-field TEM image of a segment of Si nanowires. The diameter of Si nanowire was 21 nm. The surfaces of Si nanowires were very rough, which may be attributed to the randomness of the lateral oxidation and etching in the etching solution

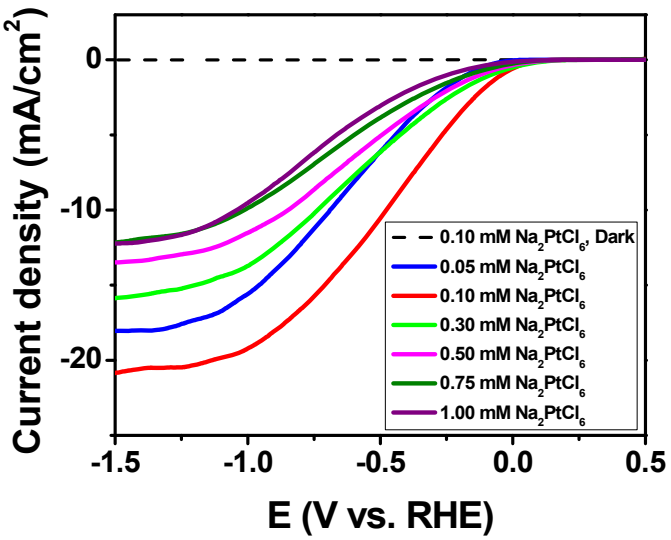

Figure S4. *J – E* curves of Pt/bare *p*-Si nanowire hydrogen evolution electrodes prepared with different $Na_2PtCl_6 \cdot 6H_2O$ concentration of 0.05 mM (blue), 0.1 mM (red), 0.3 mM (green), 0.5 mM (magenta), 0.75 mM (Olive), and 1 mM (purple). The length of Si nanowire is 1.2 μm, and the data was acquired under 70 mW/cm^2 illumination. The concentration of 0.1 mM $Na_2PtCl_6 \cdot 6H_2O$ yielded the highest hydrogen evolution efficiency.

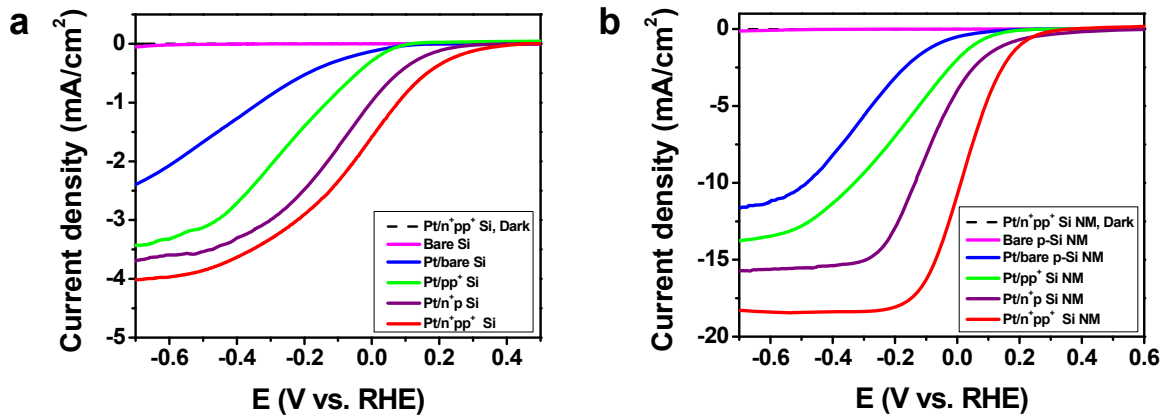

Figure S5. (a) $J - E$ curves of bare p-Si (magenta), Pt/bare p-Si (blue), Pt/pp^+ Si (green), Pt/n^+p Si (purple) and Pt/n^+pp^+ Si. (b) $J - E$ curves of bare p-Si nanomesh (magenta), Pt/bare p-Si nanomesh (blue), Pt/pp^+ Si nanomesh (green), Pt/n^+p Si nanomesh (purple) and Pt/n$^+$pp$^+$ Si nanomesh. The solution for Pt deposition contains 0.1 mM $Na_2PtCl_6{\cdot}6H_2O$ and 0.5 M HF. The depth of Si nanomesh is 1.1 μm, and all the data was acquired under 70 mW/cm^2 illumination. This data clearly shows that both of n^+ doping on the frontside and $p+$ doping on the backside efficiently separate the generated charge carriers as well as increase the onset potential of photoelectrodes.

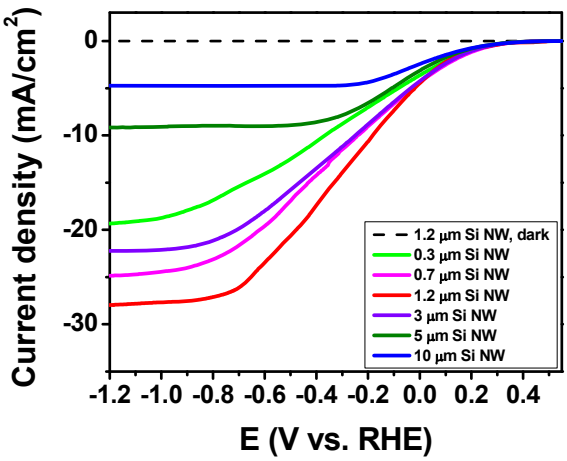

Figure S6. *J – E* curves of Pt/n^+pp^+ Si nanowire electrodes with the length of 0.3 μm (green), 0.7 μm (magenta), 1.2 μm (red), 3 μm (purple), 5 μm (Olive), and 10 μm (blue) under 70 mW/cm^2 illumination. The solution for Pt deposition contains 0.1 mM $Na_2PtCl_6 \cdot 6H_2O$ and 0.5 M HF. The data shows that the 1.2 μm long Si nanowire cell leads to the highest enhancement in current density.

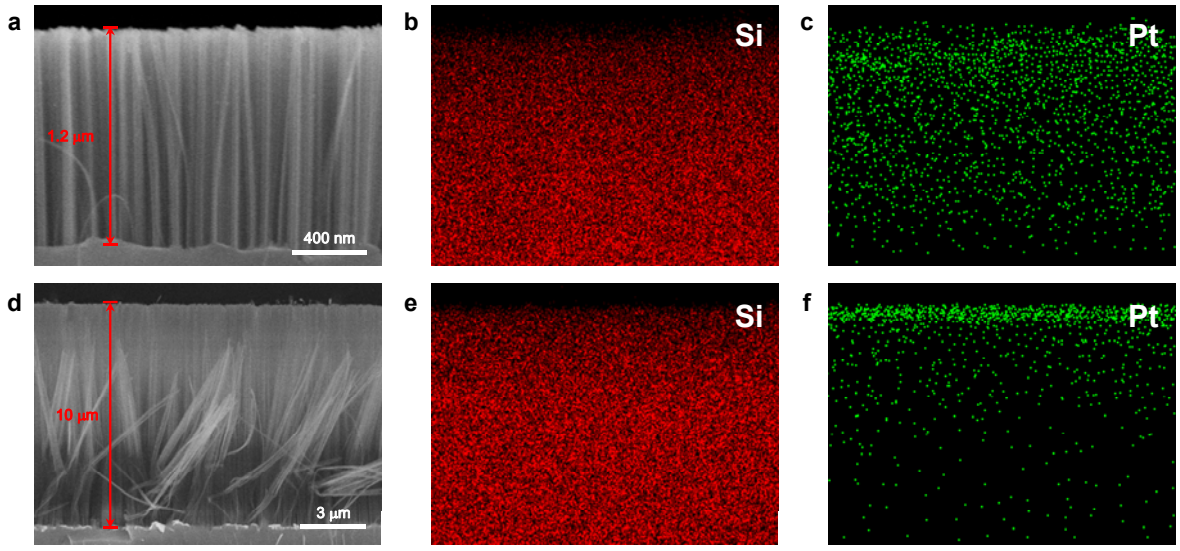

Figure S7. Cross sectional SEM images of 1.2 µm (a) and 10 µm (d) long Pt/n^+pp^+ Si nanowire array. Energy dispersive spectroscopy mapping for Si (b and e) and Pt (c and f) for 1.2 µm long Si nanowire (b and c) and 10 µm long Si nanowire (e and f). . The electroless Pt deposition method forms ~ 1µm thick high density Pt particle layer from the tip end of Si nanowires.

SUPPORTING MOVIE 1

A movie of a normal Pt/n^+pp^+ silicon nanowire array electrode evolving hydrogen at – 0.8 V vs. RHE under 70 mW/cm^2 illumination.