

## Supporting Information

### **Relating 3D Geometry and Photoelectrochemical Activity of WO<sub>3</sub>-loaded n-Si Nanowires: Design Rules for Photoelectrodes**

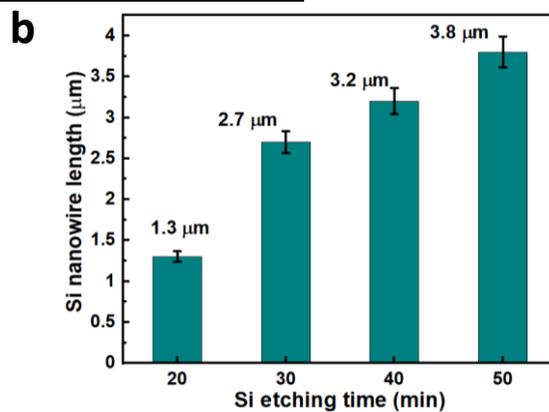
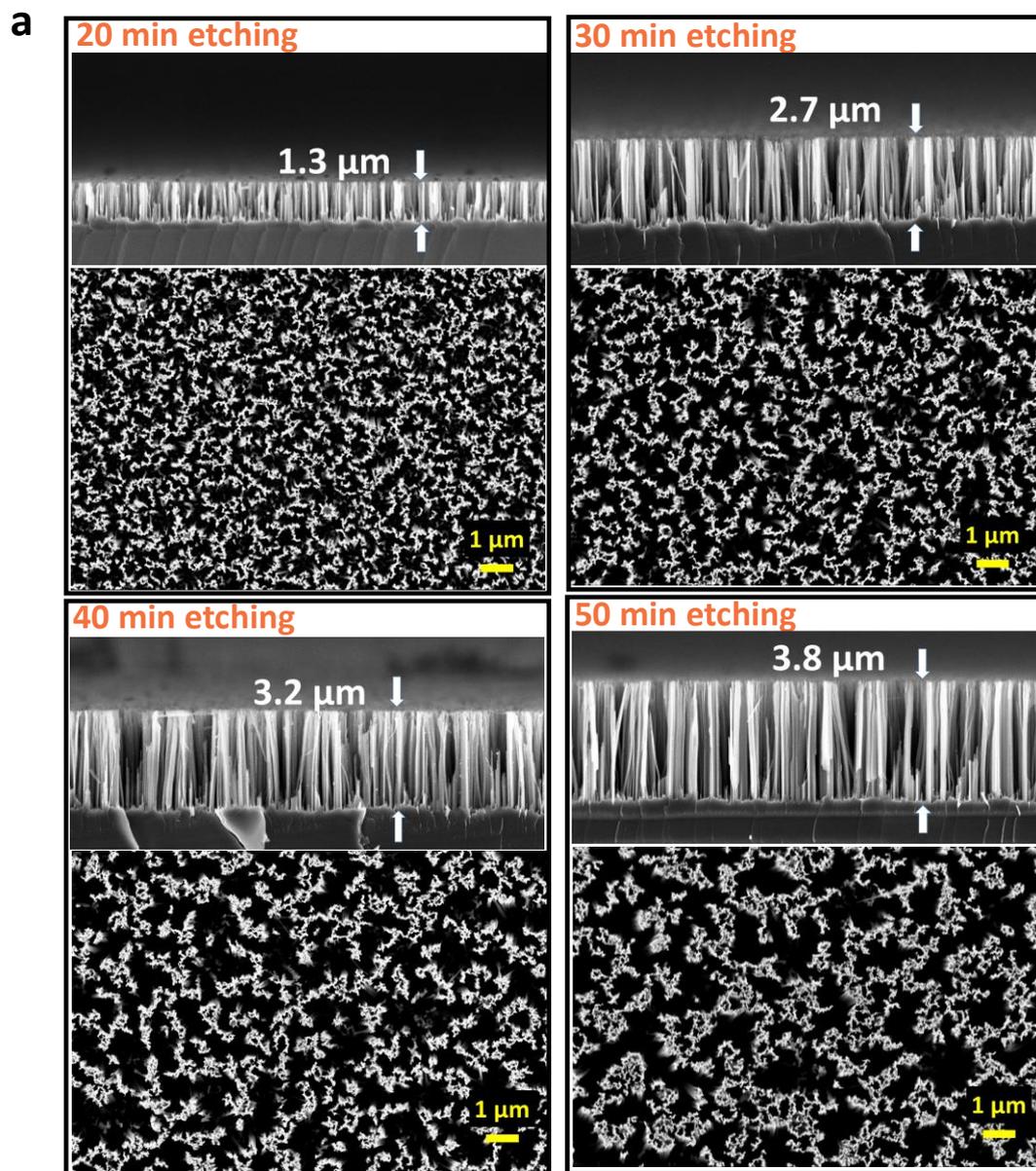
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**SEM of Si nanowire arrays with different chemical etching time and coated by ALD with  $\text{WO}_3$  with different thickness**



**Figure S1:** (a) Scanning electron microscope (SEM) images of Si nanowires fabricated with different etching time: 20 min, 30 min, 40 min and 50 min. (b) Si nanowire length as function of etching time.

### Si etching time

20 min

30 min

40 min

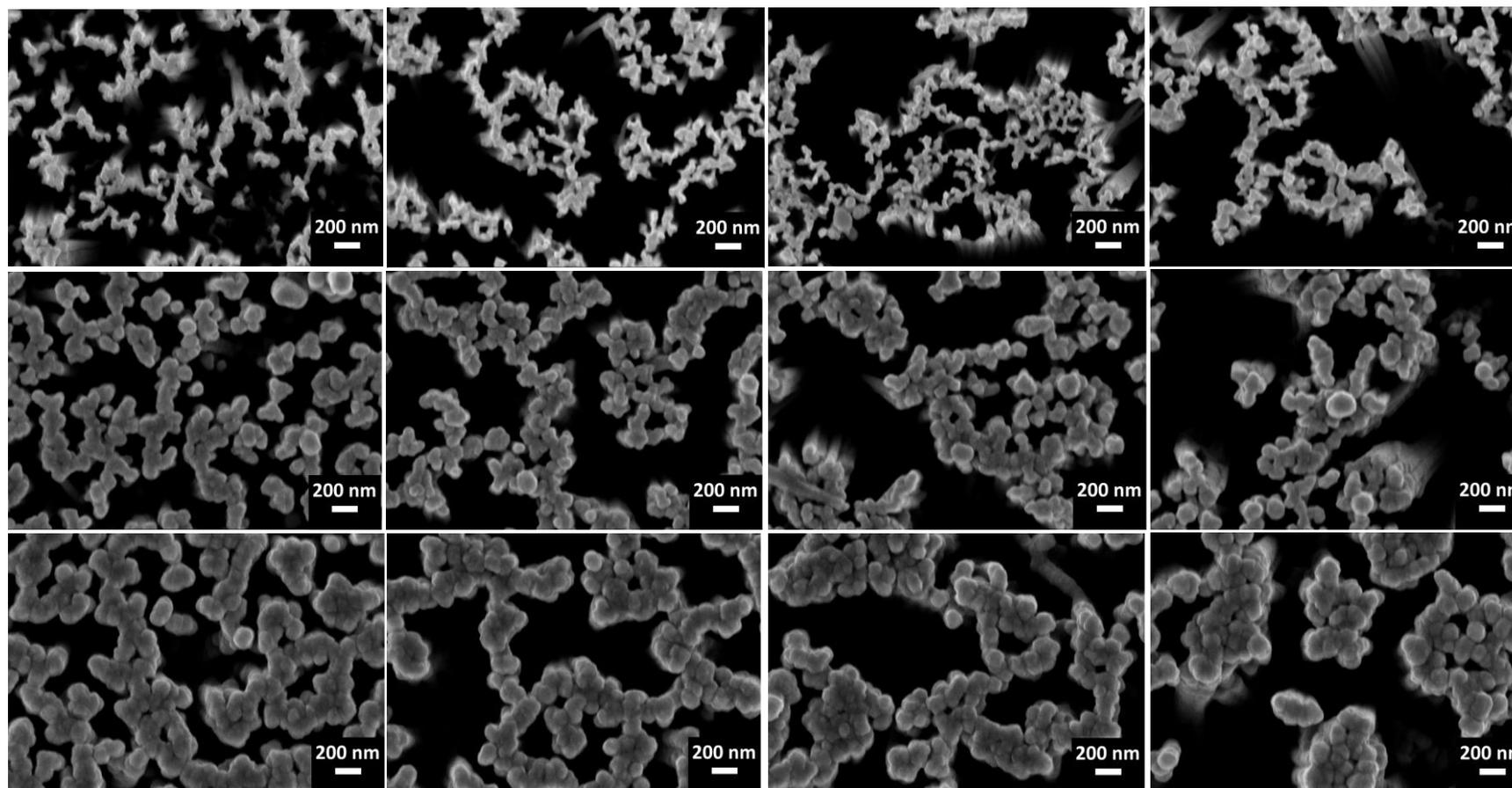
50 min

ALD  $\text{WO}_3$  thickness

10 nm

30 nm

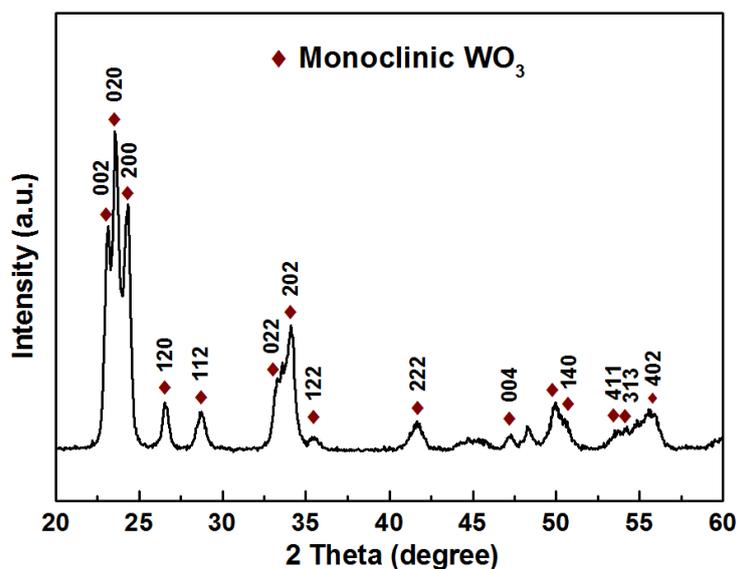
50 nm



*Figure S2: SEM images of  $\text{WO}_3/\text{Si}$  nanowires fabricated with different Si etching time: 20 min, 30 min, 40 min and 50 min, and coated  $\text{WO}_3$  films with different thickness: 10 nm, 30 nm, 50 nm.*

## GIXRD of WO<sub>3</sub>/Si Nanowires Array

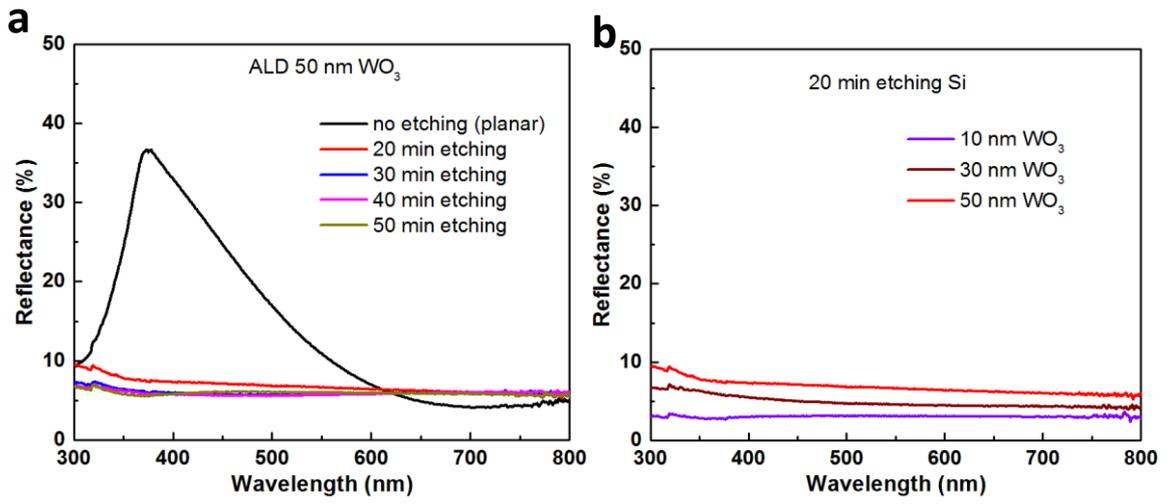
The crystalline phase of the WO<sub>3</sub> film was characterized by a Bruker D8 Eco X-ray diffractometer (XRD) with a Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) source and a Lynx-eye detector in a grazing incidence configuration at an incident angle of 3° and in the 2 $\theta$  range from 20° to 60°. Figure S3 shows the GIXRD spectra of the WO<sub>3</sub>/Si nanowires array electrode after annealing in Ar at 450°C for 1 h. The diffraction peaks agree well with monoclinic WO<sub>3</sub> corresponding to JCPDS No. 83-0950 indicating that monoclinic WO<sub>3</sub> was obtained after annealing.



**Figure S3:** GIXRD spectra of Si nanowires (50 min etching) coated WO<sub>3</sub> (50 nm) after annealing in Ar. (monoclinic WO<sub>3</sub> corresponding to JCPDS No. 83-0950)

## Light Reflectance

The light reflectance of WO<sub>3</sub>/Si nanowires arrays electrodes were investigated using a Perkin Elmer 1050 UV/Vis/NIR Spectrophotometer in the wavelength range of 300 nm to 850 nm with a step of 5 nm. Figure S4 shows the reflectance spectra of the WO<sub>3</sub>/Si nanowires arrays with different Si etching time and different WO<sub>3</sub> thickness. As shown in Figure S4a, comparing with the planar electrode, the nanowires array structures decrease light reflectance. For 20 min Si etching with different WO<sub>3</sub> thickness, the light reflectance increases with the reduced WO<sub>3</sub> film thickness (Figure S4b).



**Figure S4:** UV-Vis reflectance spectra of (a) WO<sub>3</sub>/Si nanowires with different Si etching time (a) and (b) WO<sub>3</sub>/Si nanowires with different WO<sub>3</sub> film thickness.