Supporting Information

From Geometry to Activity: A Quantitative Analysis of WO_3/Si Micropillar Arrays for Photoelectrochemical Water Splitting

*Yihui Zhao, Pieter Westerik, Rudi Santbergen, Erwin Zoethout, Han Gardeniers, Anja Bieberle-Hütter**

Cystaline Structure of WO_3

The crystalline phase of the WO_3 film was characterized by a Bruker D8 Eco X-ray diffractometer (XRD) with a Cu Kα (λ = 1.5406 Å) source and a Lynx-eye detector in a grazing incidence configuration at an incident angle of 3° and in the 2θ range from 20° to 60°. Figure S1 shows the GIXRD spectra of the WO_3/Si micropillar arrays elcectrode before (red) and after (black) annealing in Ar at 450℃ for 1 h. The diffraction peaks of the pattern after annealing agree well with monoclinic WO_3 corresponding to JCPDS No. 83-0950 indicating that monoclinic WO_3 was obtained after annealing.

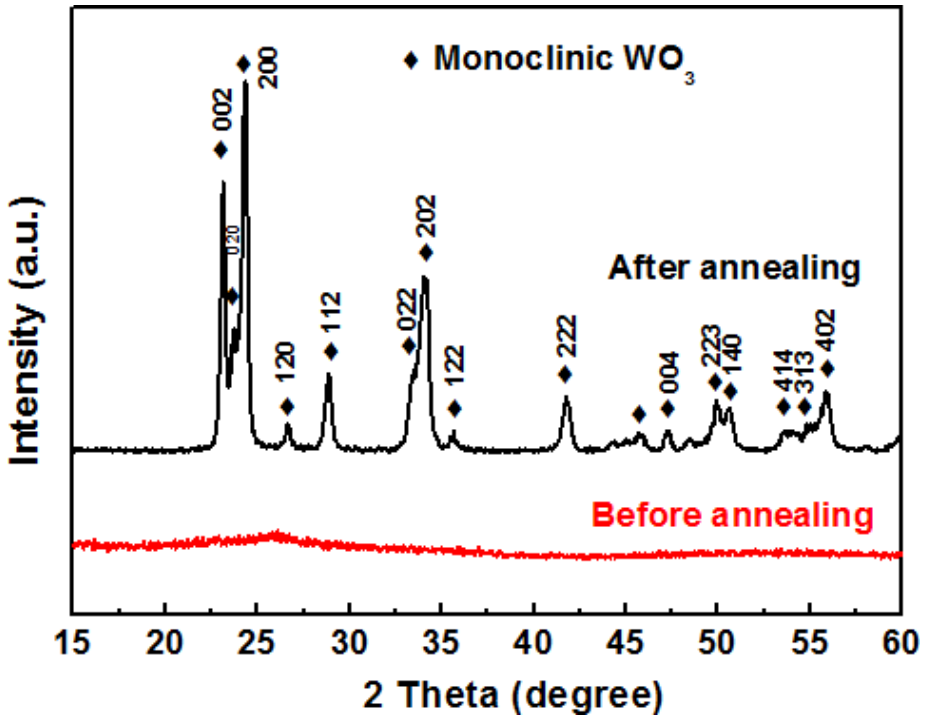

Figure S1: *GIXRD spectra of Si micropilar arrays coated WO_3 after annealing in Ar.*

Light Reflectance

The light reflectance of WO_3/Si micropillar array electrodes was investigated using a Perkin Elmer 1050 UV/Vis/NIR spectrophotometer along with 150 mm integrating sphere in the wavelength range of 300 nm to 850 nm with a step size of 5 nm. Figure S2 shows the reflectance spectra of the WO_3/Si micropillar arrays with different height and pitch of the pillars. All reflectance curves show a meandering shape as a function of wavelength, which is related to the interference of the light reflected from the WO_3 surface and the WO_3/Si interface. As shown in Figure S2a, the micropillar array structures have lower light reflectance than the planar electrode. As the pillars become longer, the light reflectance decreases. In the wavelength range below 400 nm (inset in Figure S2a), in which the light is absorbed by the WO_3, the reflectance of micropillar array electrodes, with 10 μm height and 40 μm height, decreased around 10% and 15%, respectively, compared with the planar electrode. For 40 μm long pillars, the light reflectance slightly decrease with reduced pillars pitch (Figure S2b).

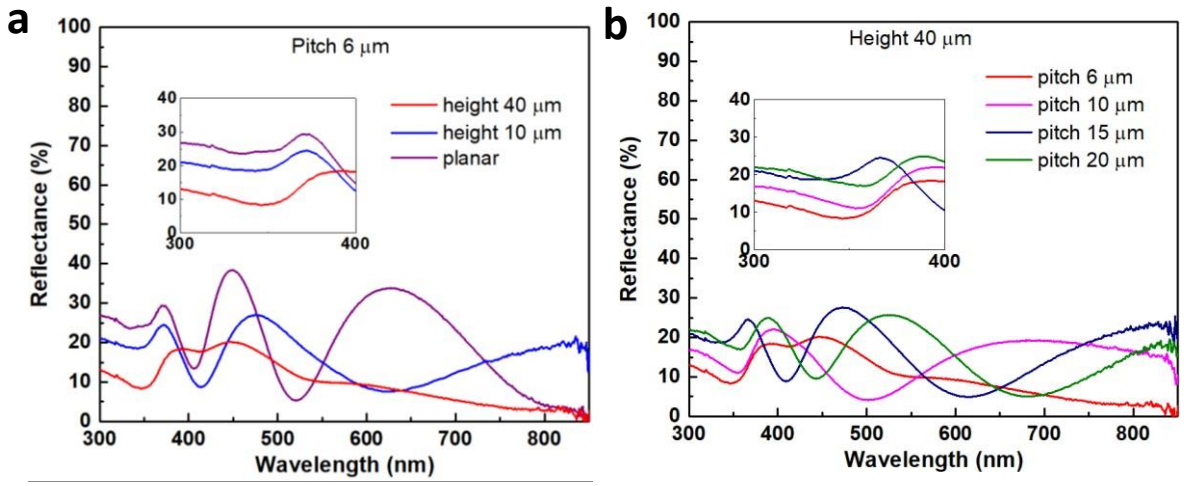

Figure S2: *Reflectance spectra of WO_3/Si micropillar arrays with (a) different pillars height, and (b) different pillars pitch.*