Supporting Information

Highly Efficient Photoelectrochemical Hydrogen Generation Reaction Using Tungsten Phosphosulfide Nanosheets

Vediyappan Veeramani,[†,⊥] *Hsin-Chin Yu,* [‡,⊥] *Shu-Fen Hu,** [‡] *and Ru-Shi Liu**[†,§]

[†] Department of Chemistry, National Taiwan University, Taipei, 106 (Taiwan)

[‡] Department of Physics, National Taiwan Normal University, Taipei 116 (Taiwan)

[§] Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan

Corresponding Authors

*Shu-Fen Hu, Email:sfhu.hu@gmail.com

*Ru-Shi Liu, Email: rsliu@ntu.edu.tw

EXPERIMENTAL SECTION

Photoelectrochemical measurements

Photoelectrochemical measurement was performed using a typical three electrochemical cell setup (760D, CH Instruments). The prepared $WS_{2-x}P_x$@Si MPs were used as working photocathode electrode, connected with copper wire through silver paste, and dried at 60 °C for 2 h. Epoxy paste was applied on the silver paste to prevent further PEC reaction. Linear sweep voltammetry (LSV) profiles were determined at a scan rate of 20 mV/s by using 0.5 M H_2SO_4 (pH=0.3) supporting electrolyte solution to evaluate the solar-driven PEC hydrogen evolution reaction. Silver chloride (Ag/AgCl; sat. KCl) and platinum (Pt) wire were used as reference and counter electrodes, respectively. Xenon lamp (500 W; LSH-X500) was used as light source and equipped with AM 1.5 filter (110 $mWcm^{-2}$) for PEC measurement. The system was enclosed within the water circulation system to control the temperature of the cell at 25 °C. Chronoamperometry techniques were used to perform the stability test of the photocathode at 0 V vs. RHE.

Material characterization

Scanning electron microscopy (SEM; JSM-6700F-JEOL) analysis was conducted to investigate the morphology of the $WS_{2-x}P_x$@Si MPs and WS_2@Si MPs nanomaterials. Energy-dispersive X-ray spectroscopy (EDX) mapping studies were also performed through SEM (JSM-6700F-JEOL). The crystallinity of the samples was investigated by X-ray diffraction analysis using a Bruker D2 PHASER XRD analyzer (Cu Kα). Raman measurement was carried out using a Thermo DXR microscope (532 nm laser light) for $WS_{2-x}P_x$@Si MPs and WS_2@Si MPs nanomaterials. X-ray absorption near the edge structure (XANES) measurement was carried out in 01C1 and 17C1 beamlines of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu City, Taiwan.

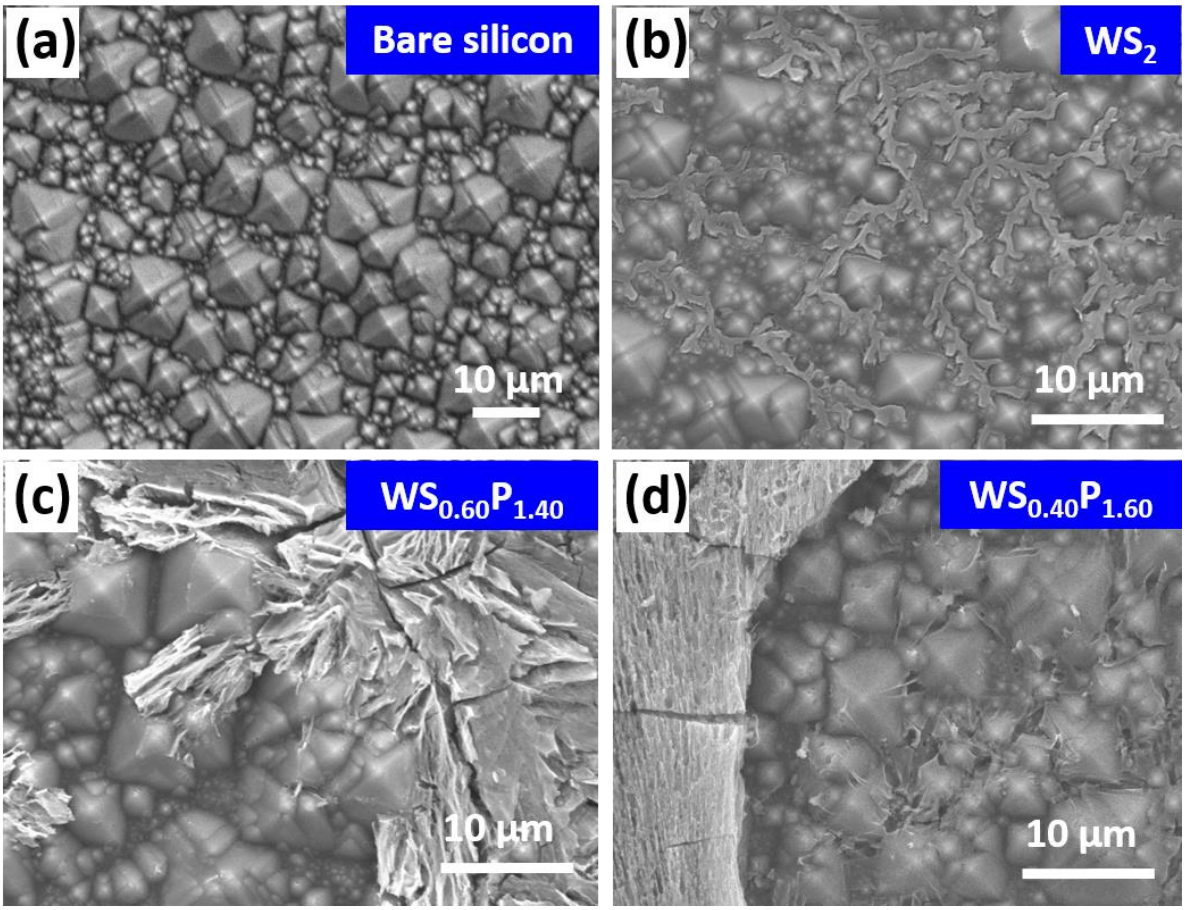

Figure S1. Top-view SEM images of the (a) bare Si MPs, (b) WS_2@Si MPs, (c) $WS_{0.60}P_{1.40}$@Si MPs, and (d) $WS_{0.40}P_{1.60}$@Si MPs photoelectrodes.

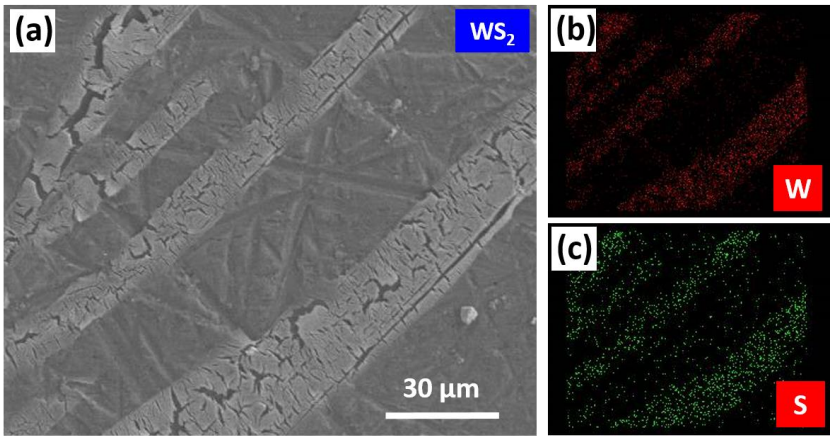

Figure S2. (a) SEM image and elemental mapping images of (b) W and (c) S of the WS_2 sample.

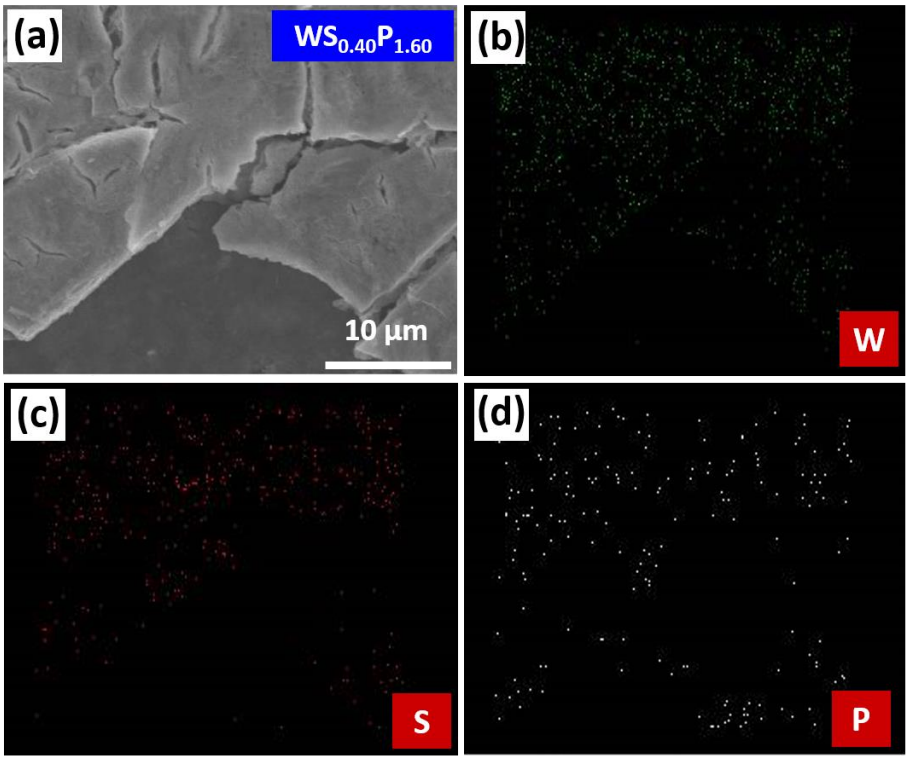

Figure S3. (a) SEM image and elemental mapping images of (b) W, (c) S, and (d) P of the $WS_{0.40}P_{1.60}$ samples.

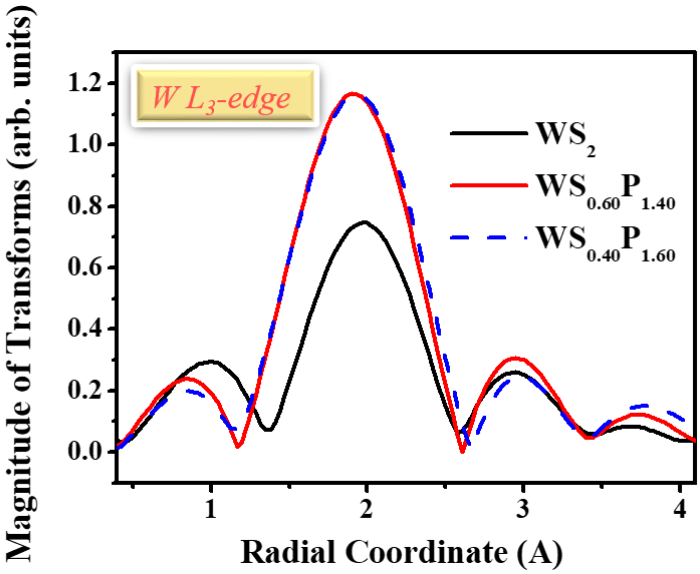

Figure S4. EXAFS (W L_3-edge) spectra of the WS_2, $WS_{0.60}P_{1.40}$, and $WS_{0.40}P_{1.60}$ samples.

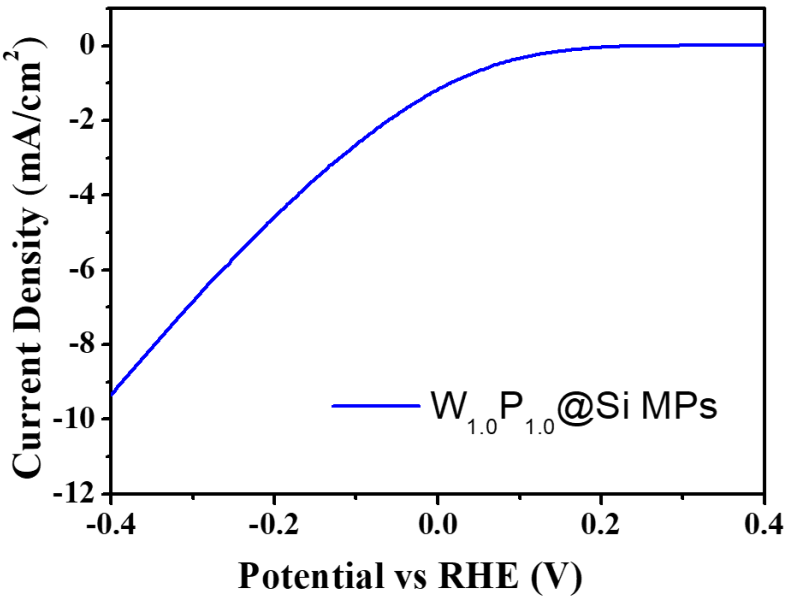

Figure S5. J–V curves of $W_{1.0}P_{1.0}$@Si MPs photocathode at current density at 0 V vs. RHE.

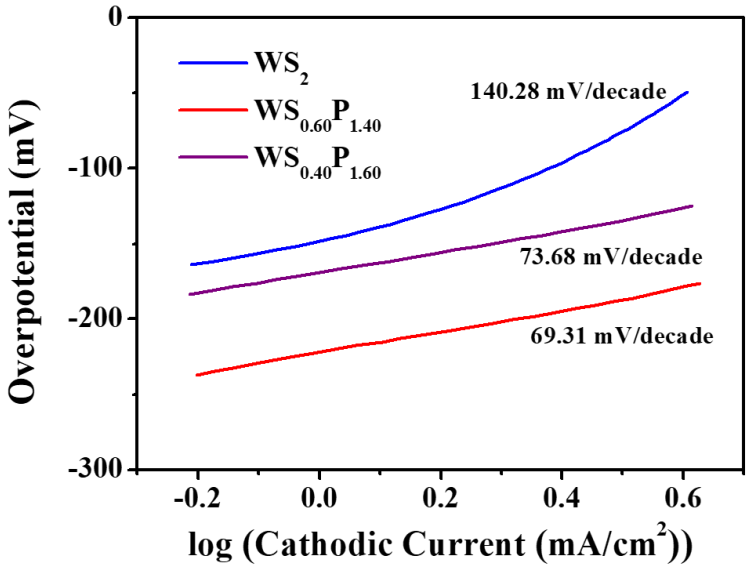

Figure S6. Tafel slopes of WS_2@Si MPs, $WS_{0.60}P_{1.40}$@Si MPs, and $WS_{0.40}P_{1.60}$@Si MPs electrodes.

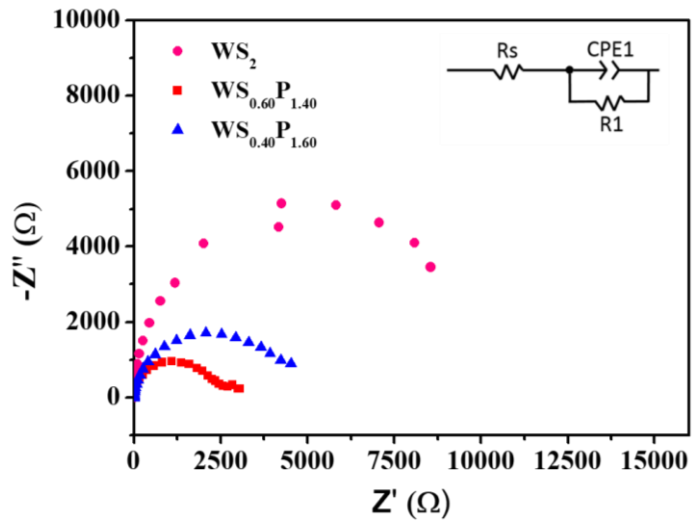

Figure S7. Nyquist plots of WS_2@Si MPs, $WS_{0.60}P_{1.40}$@Si MPs and $WS_{0.40}P_{1.60}$@Si MPs electrodes.