Electronic Supplementary Information (ESI) for

Impact of a Conductive Oxide Core in Tungsten Sulfide-Based Nanostructures on the Hydrogen Evolution Reaction

*Bora Seo,[a] Hu Young Jeong,[b] Sung You Hong,[c] Alla Zak,[d] and Sang Hoon Joo[a,c]**

[a]Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea.

[b]UNIST Central Research Facilities (UCRF), Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea.

[c]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea.

[d]Department of Sciences, Holon Institute of Technology (HIT), 52 Golomb St., Holon 5810201, Israel.

*E-mail: shjoo@unist.ac.kr (S.H.J.)

1. Experimental Details

1.1. Synthesis of tungsten sulfide nanotubes (WS_2 NTs) and tungsten oxide/tungsten sulfide core-shell nanorods ($W_{18}O_{49}$@WS_2 NRs)

Inorganic nanotubes of tungsten disulfides were synthesized *via* the combined reduction-sulfidization process[S1] from tungsten oxide (WO_x) by the solid-gas reaction with hydrogen (H_2) and hydrogen sulfide (H_2S) at elevated temperatures of 840 °C over 6 h. The quartz reactor used in this synthesis was designed specifically for this process. The detailed growth mechanism of the nanotubes in this reaction has been recently elucidated.[S2] The reaction mechanisms consists of two steps, namely growth of the oxide whiskers, and subsequent sulfidization, under the flow of H_2S/H_2. In the first step of the mechanism, the spherical nanoparticle (NP) precursors of tungsten oxide (WO_x) grow into oxide whiskers of approximately 5-50 μm length and 20-120 nm diameter (Figure S1). The whiskers subsequently undergo sulfidization in the second step, resulting in formation of WS_2 nanotubes. These oxide whiskers grow as a result of partial reduction of the oxide precursor NPs and formation of a volatile suboxide phase, which serves as a building material for one-dimensional crystal synthesis. The growth of the whiskers results in the formation of a stable $W_{18}O_{49}$ ($WO_{2.72}$) phase, and followed by sulfidization. A fast reaction of H_2S with the oxide nanowhiskers leads to the quick formation of a number of cylindrical closed WS_2 layers encapsulating the oxide core. A slow diffusion-controlled reaction then leads to full replacement of the oxygen atoms with sulfur atoms, and subsequently to the synthesis of the hollow WS_2-NTs. In this study, partially and fully sulfidized WS_2 nanotubes were prepared. In order to obtain the partially sulfidized nanotubes (actually, nanorods with few sulfide layers and an oxide core, denoted as $W_{18}O_{49}$@WS_2 NRs), the reaction was stopped in the early stages.

1.2. Characterization Methods

Scanning electron microscopy (SEM) analysis was conducted on a field emission scanning electron microscope (Nanonova 230, FEI). High-resolution transmission electron microscopy (TEM) images were taken using a low-voltage spherical aberration (Cs)-corrected TEM (FEI Titan^3 G2 60-300) with an acceleration voltage of 80 kV. Energy dispersive spectroscopy (EDS) elemental mapping analyses were performed using a JEOL JEM 2100F with a probe-

side Cs corrector. X-ray powder diffraction (XRD) patterns were obtained with a high power X-ray diffractometer (Rigaku) equipped with Cu K_α radiation, operated at 40 kV and 200 mA. XRD patterns were measured in a 2θ range from 10° to 90° with a scan rate of 4° min^{-1}. The chemical states of the samples were analyzed using an X-ray photoelectron spectrometer (XPS, K-alpha, ThermoScientific) equipped with a monochromatic Al K_α X-ray source (1486.6 eV). The oxidation state of the samples was investigated using X-ray absorption near edge spectroscopy (XANES) analysis, performed on a Beamline 10C from the Pohang Accelerator Laboratory (PAL) in South Korea, with beam energy of 3 GeV and current of 280 mA. X-ray photon energy was monochromatized by a Si(1 1 1) double-crystal monochromator, which was detuned by approximately 30% to remove high-order harmonics. Data for W L_1- and W L_3-edge XANES spectra were taken at room temperature (RT) using a fluorescence detector.

1.3. Electrochemical Measurements

All electrochemical measurements were performed on an IviumStat electrochemical analyzer at RT and atmospheric pressure, using a three-compartment electrochemical cell. A graphite rod was used as the counter electrode, with Ag/AgCl (in 3 M NaCl solution) as the reference electrode. The Ag/AgCl reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE) before every use. For the calibration, the hydrogen reference electrode (Hydroflex®, Gaskatel) and the Ag/AgCl electrode were immersed in a 0.5 M H_2SO_4 solution for 30 min. The open circuit voltage (OCV) was recorded for use in the following calculation: E(RHE) = E(Ag/AgCl) − OCV. All potentials quoted in this study are presented on the RHE scale. For electrochemical measurements, a rotating disk electrode (RDE) containing a glassy carbon (GC) central disk (4-mm diameter, 0.126-cm^2 area) was used as the working electrode. The RDE was polished with a 1.0-μm alumina suspension, followed by a 0.3-μm suspension to generate a mirror finish before use. Catalyst inks were prepared by mixing catalyst (8 mg) with Nafion (80 μL, 5 wt% in isopropanol, Sigma-Aldrich) in a solution of DI water (800 μL) and EtOH (200 μL, 99.9%), and the mixture was sonicated for 30 min to give an homogeneous slurry. A sample of the catalyst ink (5 μL) was then dropped onto the glassy carbon electrode, and dried at RT for 30 min, with a rotation speed of 700 rpm. The resulting catalyst loading on the GC disc was calculated to be 300 $μg \cdot cm^{-2}$. Before electrochemical measurements were taken, a stream of N_2 was bubbled through the 0.5 M H_2SO_4 electrolyte solution for 20 min. Cyclic voltammetry (CV) was then carried out for

electrochemical activation, which consisted of 20 repetitions in a potential range of 0.05 to 1.2 V (*vs.* RHE) at a scan rate of 100 mV s^{-1}. Linear sweep voltammetry (LSV) for the hydrogen evolution reaction (HER) was conducted from 0.1 V to −0.4 V (*vs.* RHE) at a scan rate of 2 mV s^{-1} with a rotating speed of 1500 rpm in a 0.5 M H_2SO_4 solution, continuously purged with H_2 gas. Electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical system. After electrochemical activation by CV, the Nyquist plots were observed in a frequency range of 100 kHz to 0.01 Hz at an overpotential of 100 mV.

2. Supplementary Figures S1-S4

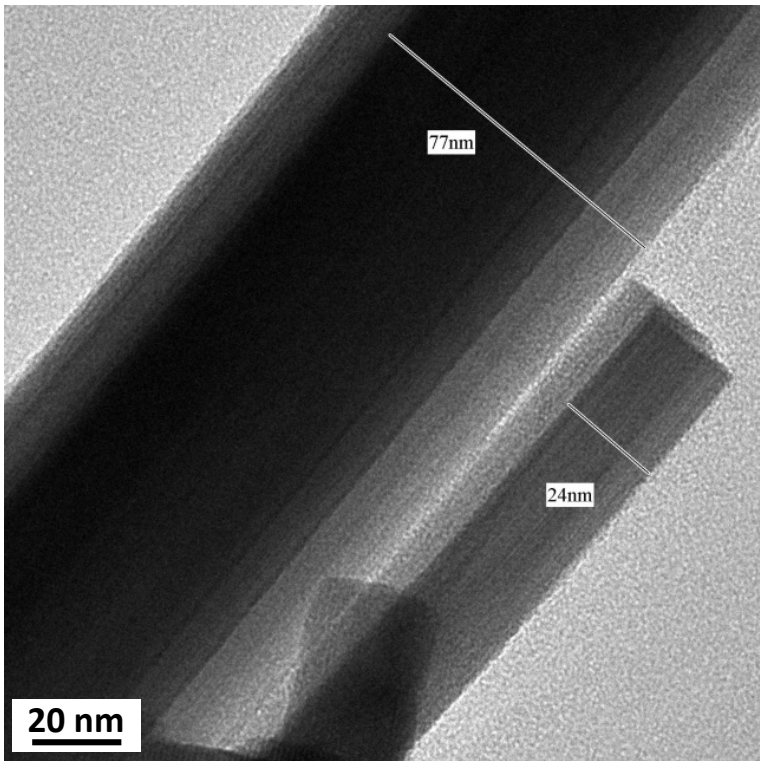

Fig. S1 Suboxide ($W_{18}O_{49}$) whiskers after reaction for a few min (no sulfide layers observed).

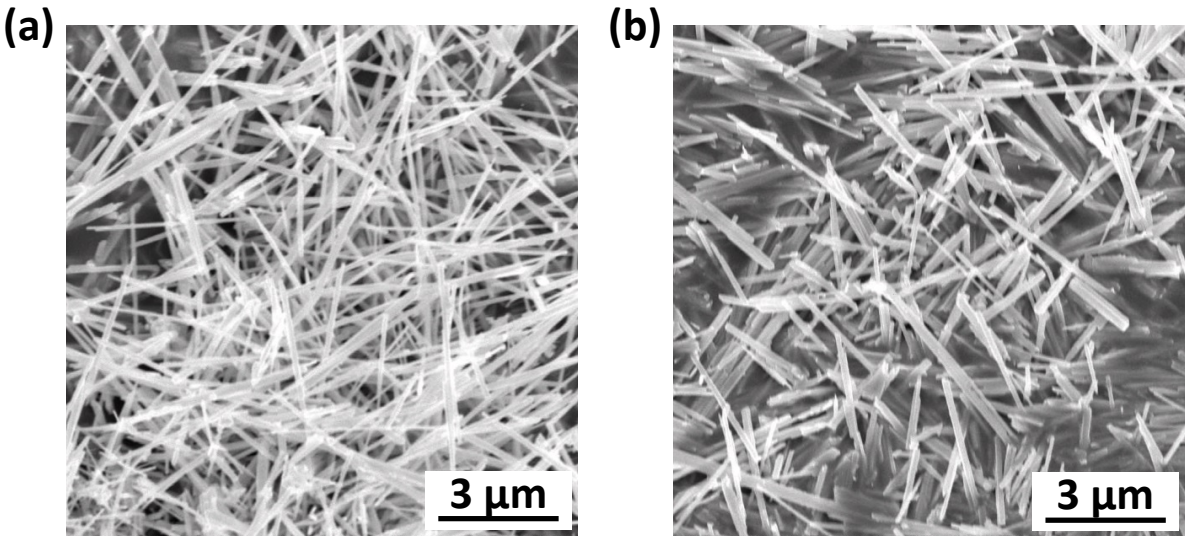

Fig. S2 SEM images of (a) WS_2 NTs and (b) $W_{18}O_{49}$@WS_2 NRs.

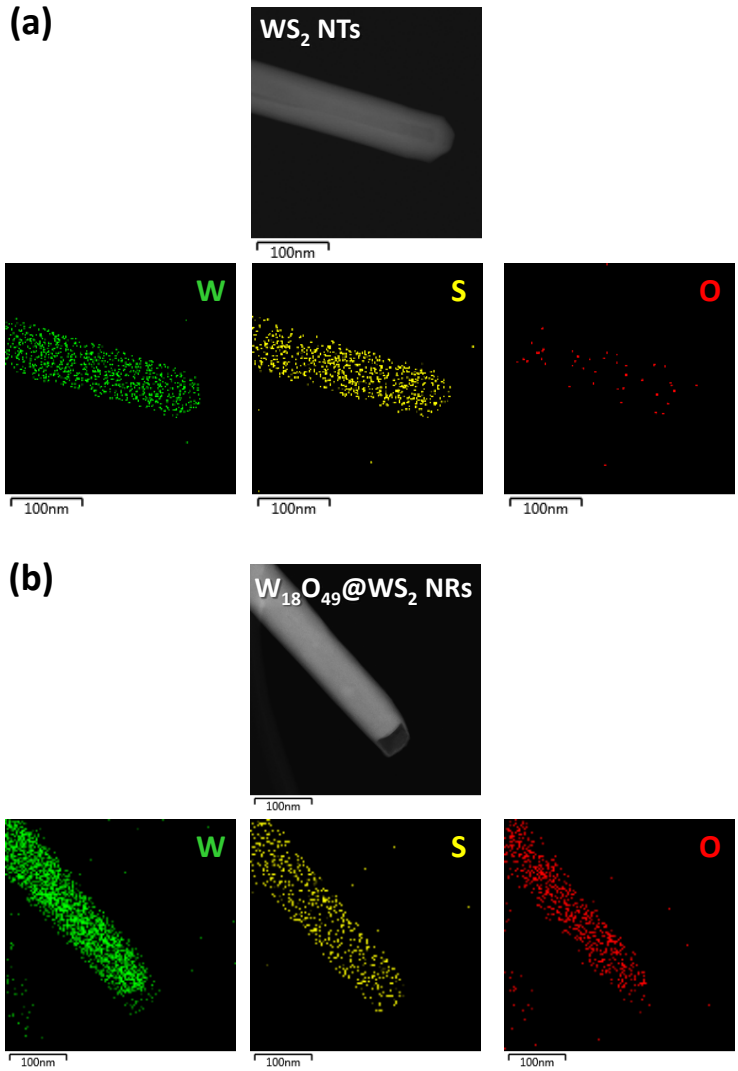

Fig. S3 EDX elemental mapping images of (a) WS_2 NTs and (b) $W_{18}O_{49}$@WS_2 NRs.

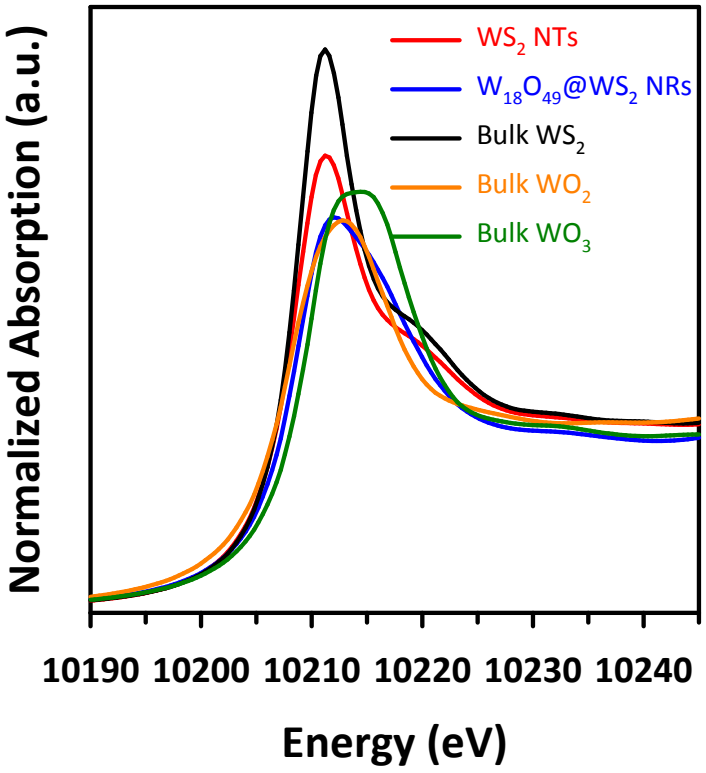

Fig. S4 W L_3-edge XANES spectra

3. References for Electronic Supplementary Information

S1. A. Rothschild, J. Sloan, and R. Tenne, *J. Am. Chem. Soc*. 2000, **122**, 5169-5179.

S2. A. Zak, L. Sallacan-Ecker, A. Margolin, Y. Feldman, R. Popovitz-Biro, A. Albu-Yaron, M. Genut, and R. Tenne, *Fullerene, Nanotubes, Carbon Nanostruct.* 2011, **19**, 18-26.