Supporting Information for:

Photocatalytic Hydrogen Evolution from Sub-Stoichiometric Colloidal WO_{3-x} Nanowires

Taejong Paik[1,5‡], Matteo Cargnello[1,6‡], Thomas R. Gordon[1], Sen Zhang[1], Hongseok Yun[1], Jennifer D. Lee[1], Ho Young Woo,[5] Soong Ju Oh,[2,7] Cherie R. Kagan[1,2,3], Paolo Fornasiero[4], and Christopher B. Murray[1,2,]*

[1]Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States

[2]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

[3]Department of Electrical and System Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

[4]Department of Chemical and Pharmaceutical Sciences, ICCOM-CNR, INSTM, University of Trieste, Trieste, Italy

[5]School of Integrative Engineering, Chung-Ang University, Seoul, South Korea

[6]Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University, Stanford, CA, United States

[7]Department of Materials Science and Engineering, Korea University, Seoul, South Korea

[‡]*These authors have equally contributed to this work*

[*]Address correspondence to cbmurray@sas.upenn.edu

EXPERIMENTAL SECTION

Chemicals. Tungsten hexachloride (WCl_6, 99.995%) is purchased from Acros Organic chemicals. 1-octadecanol (97%) is purchased from Alfa Aesar. Oleylamine, trioctylamine, nitrosonium tetrafluoroborate($NOBF_4$), triethyloxonium tetrafluoroborate, platinum(IV) chloride (99.9%) are purchased from Sigma Aldrich. All chemicals are used as received without further purification.

Synthesis of WO_x NWs. Colloidal WO_x NWs are synthesized high temperature non-hydrolytic (solvothermal) reaction. Briefly, 2 mmol of tungsten hexachloride (WCl_6) are added into 12.93g of 1-octadecenol and 30ml of oleylamine mixture in a 125 mL three-neck flask. The reaction mixture is degassed at 125°C for 2 h and then the solution is heated to 320°C under N_2 environment at a rate of 15°C/min. When temperature reaches to 300°C, reaction solution turns from greenish blue to dark navy in color. The reaction temperature is maintained at 320°C for an hour. Next, anhydrous toluene is added into the reaction mixture while cooling down the reaction mixture to room temperature. The reaction solution is purified by precipitating NCs in excess methanol and centrifugation at 6000 RPM for 2 min. Purification process is conducted 3 times using anhydrous toluene and methanol. After purification, hexane is added dissolve NCs.

Ligand exchange of WO_x NWs. BF_4-modified WO_x NWs are prepared using a method reported in the literatures.[1,2]

Characterization. TEM images and electron diffraction patterns are collected using a JEM-1400 microscope operating at 120 kV. HRTEM images are collected using JEM2100 microscope. HAADF-STEM images are collected using Cs-corrected JEOL JEM-ARM300F microscope. Scanning electron microscopy (SEM) analysis is conducted using a JEOL 7500F HRSEM. Powder X-ray diffraction patterns are measured using a Rigaku Smartlab high-resolution

diffractometer. To collect powder X-ray diffraction patterns of randomly oriented anisotropic NCs, X-ray diffraction measurements are performed using concentrated NC solutions filled in a glass capillary. UV-Vis-NIR spectra are collected on a Varian Cary 5000 spectrometer. UPS spectra were obtained by AXIS Ultra DLD (Kratos. Inc) equipped with He I source (hv=21.2 eV) at Korea Basic Science Institute (KBSI). Diffuse reflectance spectra is collected using Harrick praying Mantis accessory. Samples are prepared as 5wt in KBr grinded and blended with potassium bromide (KBr).

Photocatalytic activity test. The photocatalytic H_2 evolution reaction from WO_x NWs is conducted using alcohols as the model sacrificial reagent. Commercial samples that were used for comparison are WO_3 yellow powder (Sigma-Aldrich) and $WO_{2.9}$ blue powder (both from Sigma-Aldrich and from Alfa Aesar, this latter having catalog number 89949). Approximately 27 mg of the WO_x NCs (bare or ligand exchanged) or the commercial powders are dispersed in 80 mL of H_2O/alcohol solution mixture (50/50 vol. %) and $PtCl_4$ is added for the formation of Pt NCs as 1 wt. % of a final loading. The temperature of reaction solution is regulated by external recirculation bath to keep the temperature constant at 20 °C. For the photocatalytic reaction, the NC suspension is irradiated using a white light 150 W Hg-Xe arc lamp or Solar Simulator (LOTOriel) equipped with a 150 W Xe lamp filtered with an atmospheric filter. Gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) is used to analyze gaseous products and to quantify H_2 and CO_2 under He flow as the carrier.

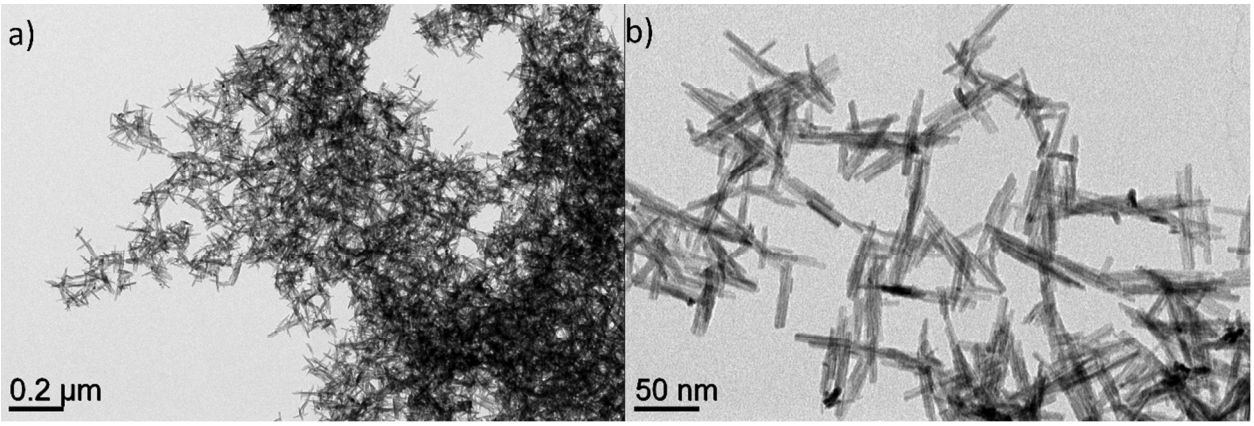

Figure S1. a) Low magnification and b) high magnification TEM images of WO_x NWs synthesized in presence of 1-octadecanol and 1-octadecene.

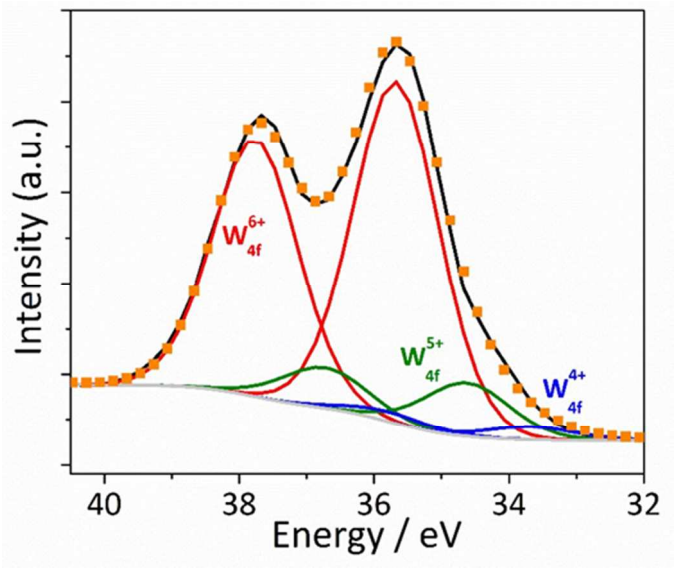

Figure S2. X-ray photoelectron spectroscopy (XPS) profiles of $NOBF_4$ treated WO_x NWs.

	W^{6+}	W^{5+}	W^{4+}
$NOBF_4$ treated WO_x NWs	83.58%	13.21%	3.21%
WO_x NWs	77.65%	17.93%	4.42%

Table S1. Relative ratio of tungsten components with different oxidation states calculated from the XPS W_{4f} spectra.

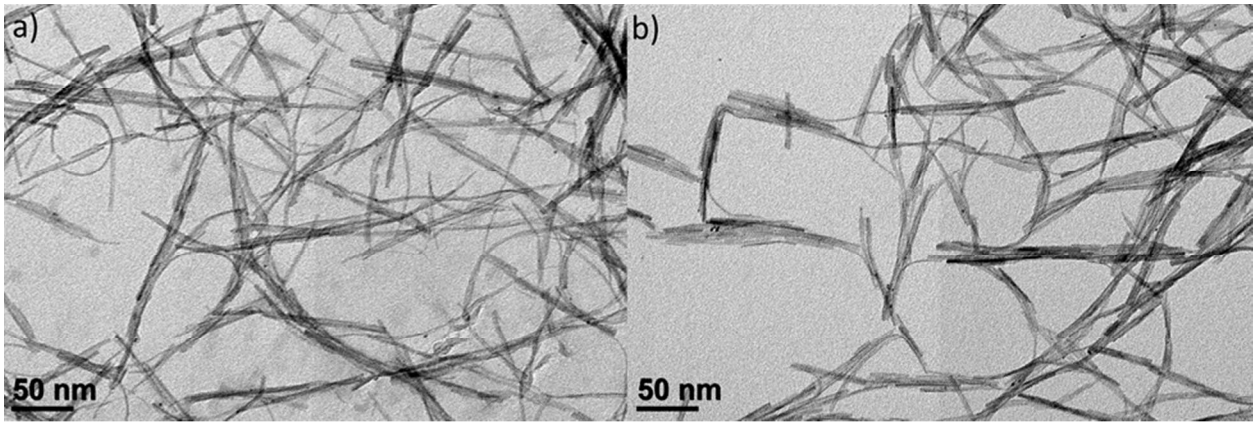

Figure S3. a) TEM image of WO_x/Pt NWs a) before and b) after photocatalytic reaction in H_2O/MeOH 50wt% solution.

(1) Dong, A.; Ye, X.; Chen, J.; Kang, Y.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. A Generalized Ligand-Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals. *J. Am. Chem. Soc.* **2011,** *133*, 998-1006.

(2) Rosen, E. L.; Buonsanti, R.; Llordes, A.; Sawvel, A. M.; Milliron, D. J.; Helms, B. A. Exceptionally Mild Reactive Stripping of Native Ligands from Nanocrystal Surfaces by Using Meerwein's Salt. *Angew. Chem. Int. Ed.* **2011,** *51*, 684-689.