Supporting Information

Pseudocubic Phase Tungsten Oxide as a Photocatalyst for Hydrogen Evolution Reaction

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Keywords: tungsten oxide; phase transition; oxygen vacancy; photocatalytic hydrogen evolution; band structure engineering

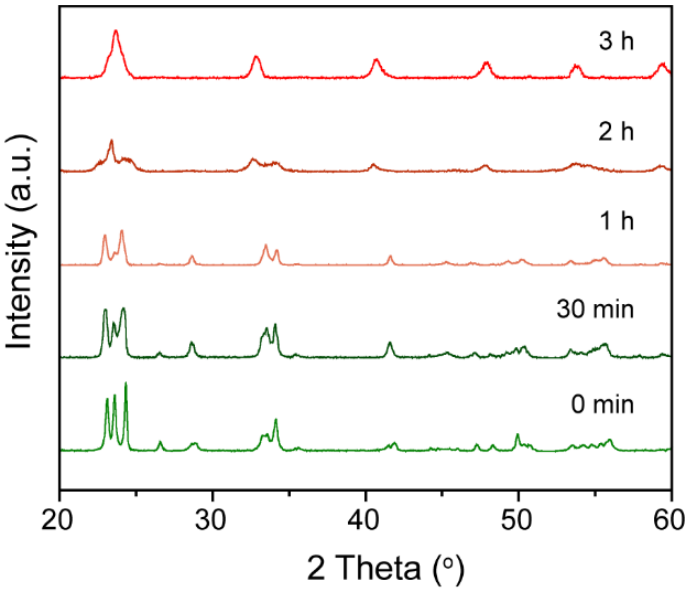

Figure S1. Time-resolved XRD patterns obtained from the WO_3 treated with a 1:1 mixture of TOP and TOPO (W-11).

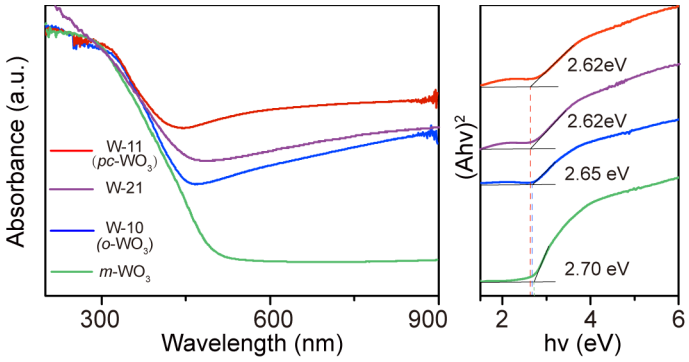

Figure S2. UV-Vis diffusive reflectance spectra (UV-Vis DRS) and the corresponding Tauc-plot of *m*-WO_3, W-10 (*o*-WO_{3-x}), W-21, and W-11 (*pc*-WO_{3-x}).

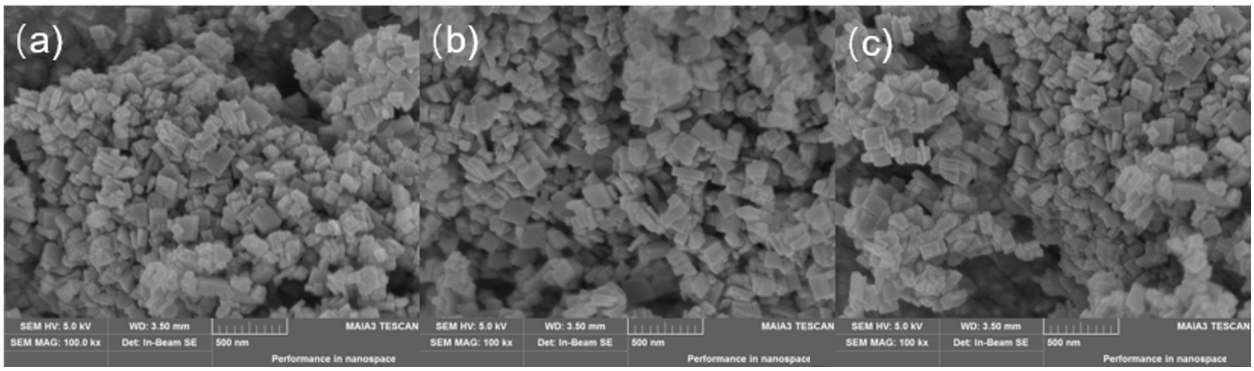

Figure S3. SEM images of (a) *m*-WO_3, (b) *o*-WO_{3-x}, and (c) *pc*-WO_{3-x}.

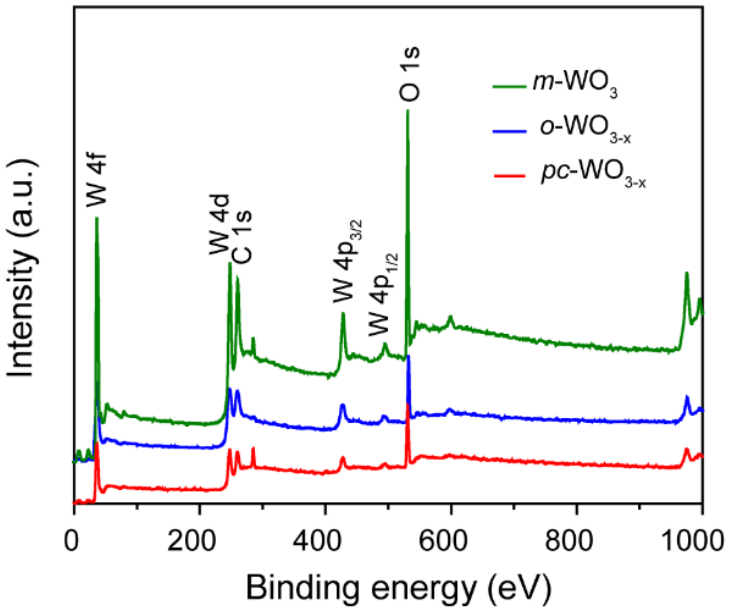

Figure S4. XPS survey spectra of *m*-WO_3, *o*-WO_{3-x}, and *pc*-WO_{3-x}.

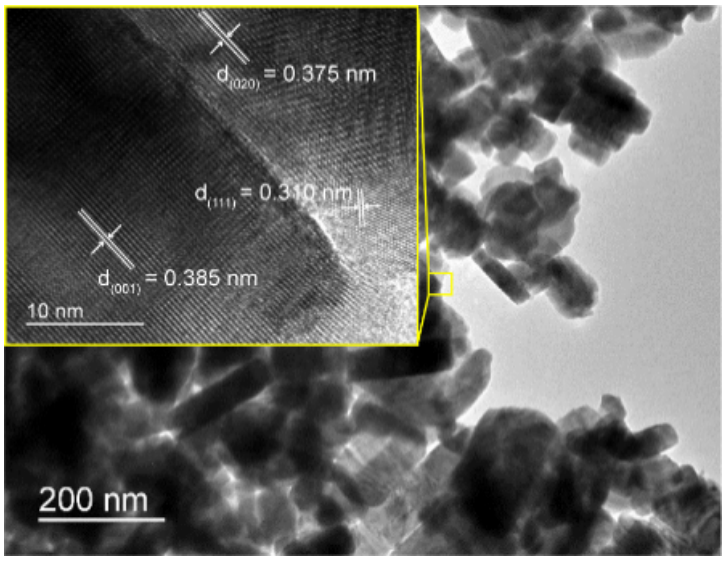

Figure S5. Low-resolution TEM image of post-*o*-WO_{3-x}. Inset is the HR-TEM image of the selected area (yellow square) of the sample.

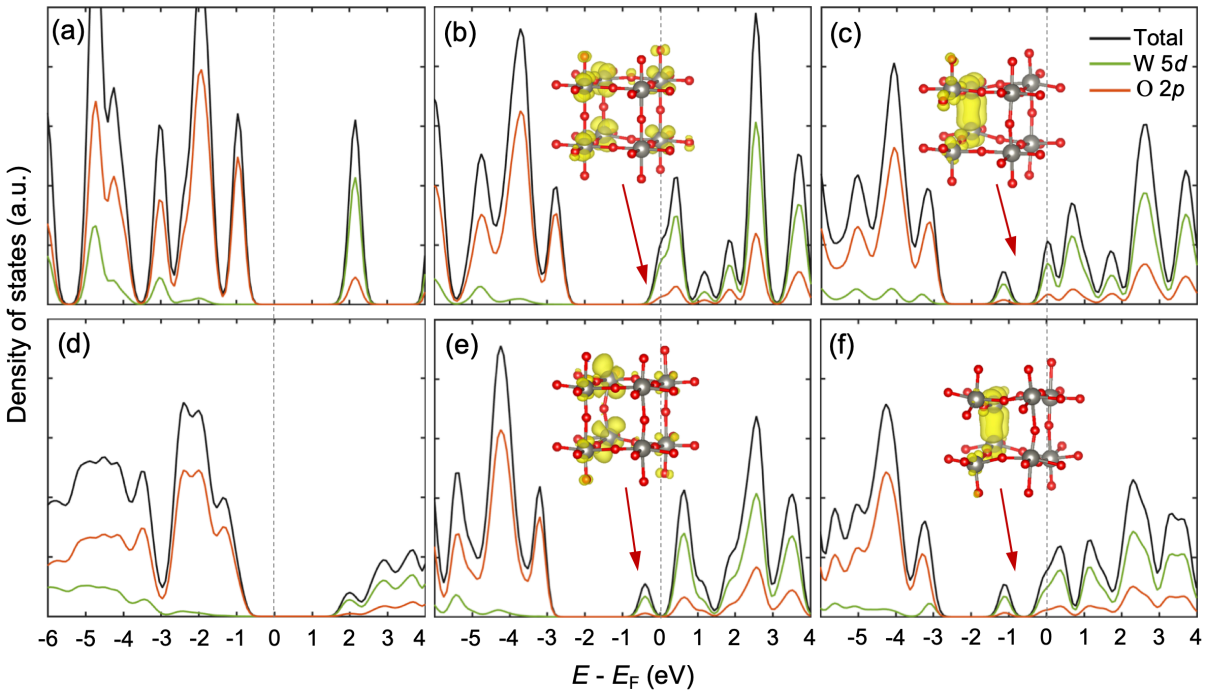

Figure S6. Electron density of states (DOS) of *pc*-WO_{3-x} (upper panels) and *o*-WO_{3-x} (lower panels) with different concentrations of oxygen vacancies in a 32-atom supercell; (a) and (d) x = 0, (b) and (e) x = 0.125, and (c) and (f) x = 0.375, from hybrid DFT calculations with E_{cut} = 600 eV and Γ-centered (4×4×4) Monkhorst-Pack k-point mesh. The energy zero is set at the Fermi level (E_F) which is indicated by the vertical dashed line. The insertions show band-decomposed charge density of the partially filled W 5*d*-O 2*p* hybridized states (with an isosurface value of 0.005 e $Å^{-1}$); grey and red balls represent W and O atoms, respectively.

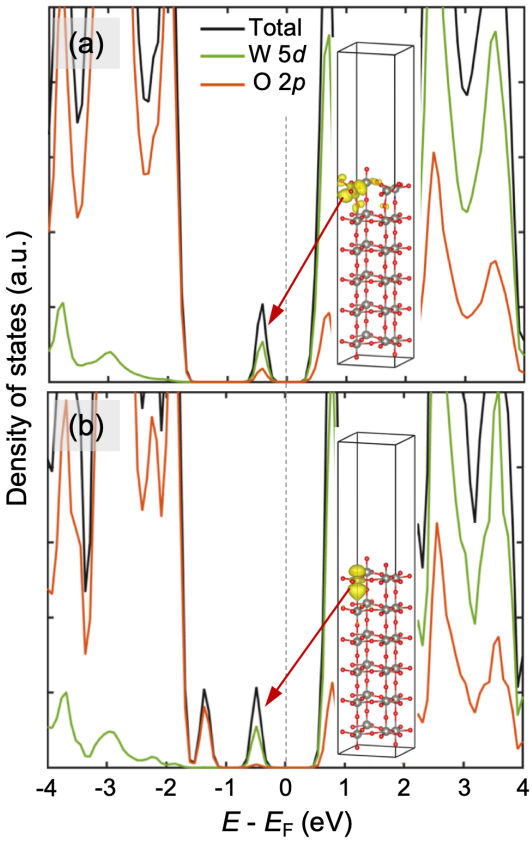

Figure S7. Local density of states (DOS) near the surface of WO_3 with an oxygen vacancy at two different positions from DFT+ U calculations with U_W = 6eV and U_O = 9 eV, and the energy zero is set at the Fermi level (E_F) which is indicated by the vertical dashed line. The surface was modeled using the 2×2×6 slab, with a vacuum space of 15 Å, where all atoms were fully relaxed until the residual forces were less than 0.02 eV $Å^{-1}$. E_{cut} of 450 eV and a Γ-centered (2×2×1) k-point mesh were employed. The insertions show band-decomposed charge density of the localized excess electron states around the oxygen vacancy (with an isosurface value of 0.004 e $Å^{-1}$); gray and red balls represent W and O atoms, respectively.

Table S1. Calculated O/W surface composition of samples by XPS analysis.

Samples	O/W*	Area of W	Area of lattice oxygen
m-WO_3	3	255,423	85,141
o-WO_{3-x}	2.76	248,652	90,026
pc-WO_{3-x}	2.69	241,659	89,702

* surface composition (O/W) = peak area of lattice oxygen / peak area of tungsten.

The surface O/W ratio was calculated according to the surface concentration of W and O detected by Casa-XPS. The original O 1*s* spectra was fitted to peak of lattice oxygen and peak of absorbed oxygen (Figure S4). Only the lattice oxygen was used to calculate the O/W ratio.

Table S2. Predicted total energy differences (in eV) per formula unit between the cubic/orthorhombic and monoclinic phases of WO_{3-x} by hybrid (standard) DFT calculations.

Samples	x = 0	x = 0.125	x = 0.25	x = 0.375
pc-WO_{3-x}	0.14 (0.09)	0.13 (0.08)	0.10 (0.06)	0.06 (0.04)
o-WO_{3-x}	0.004 (0)	0.001 (0)	0 (0)	0 (0)