Au Single Atoms Anchored WO_3/TiO_2 Nanotubes for Photocatalytic Degradation of Volatile Organic Compounds

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TiO_2 nanotubes preparation and WO_3 loading

The self-organized TiO_2 nanotubes (TNTs) were first prepared through our previously developed electrochemical anodization. Briefly, A two electrode electrochemical system was used for the anodization process employing a pieces of 1 cm×3 cm of Ti foil and platinum mesh electrodes as anode and cathode respectively at a constant potential of 60 V for a period of 8 h with the 100 ml electrolyte containing 0.25 wt% NH_4F, 13.7 vol% water and 86.3 vol% Ethylene glycol after a chemical polishing treatment with a solution containing HF, HNO_3 and H_2O. Then, the resulting Ti foil was annealed in air at 450 ℃ for 2 h to obtain anatase TNTs. The loading of WO_3 on TNTs was accomplished by electrochemical deposition. In a three-electrode system, the above TNTs used as working electrode was immersed in a 100 ml mixed solution containing Na_2WO_4, CH_3COONH_4 and EDTA at a concentration of 0.1M with the immersion area of 1 cm×2 cm, then, was deposited electrochemically with WO_3 precursor under a constant current conditions of -4 mA (-2 mA/cm^2) for a period of 10 min. The platinum electrode and the saturated calomel electrode (SCE) were counter electrode and reference electrode, respectively. After the electrochemical deposition, the as-prepared samples was cleaned with deionized water, dried at 60 ℃ and annealed in ambient atmosphere at 450 ℃ for 2 h with a heating rate of 5 ℃/min. The distance between the electrodes was fixed at 3 cm in all the experiments.

Photocatalyst Characterization.

The properties of samples were analyzed by following spectroscopic analysis: field emission scanning electron microscope (FE-SEM, NANOSEM 450, FEI) and a field emission transmission electron microscope (TEM, Tecnai G2 F30, FEI) operating at an accelerating voltage of 30 kV, the elemental distribution was visualized by energy dispersive spectroscopy (EDS) of Oxford Instruments, X-ray diffraction (XRD, Rigaku Corporation, Japan) equipped with Cu-K radiation (40 kV, =1.5406 A),

diffuse reflectance UV−visible absorption spectroscopy (DRS, UV-2550, Japan). X-ray photoelectron spectroscopy with an Axis Ultra instrument (XPS, Kratos Analytical), photoluminescence emission spectroscopy (PL, FP-6500, Jasco), in situ FTIR spectrometer equipped with photocatalytic reaction cell (Vertex 70v, Bruker), electron paramagnetic resonance spectroscopy (EPR, EMXnano, Bruker), the solid powder applied to OVs was scraped from the flaky sample with a cleaning knife.

Hard XAFS measurement was recorded at the XAS station (BL11) of the Saga Synchrotron Light Research Center, Japan. The hard X-ray was monochromatized with Si (111) double-crystals. W L_3-edge and Ti K-edge XANES was recorded in a transmission mode.

IPCE

The irradiation intensity was measured by using a spectroradiometer (PL-MW2000, China). The average irradiation intensity of a 365 nm LED. The incident photon to current conversion efficiency (IPCE) and the apparent quantum yield (AQY) was calculated by using the following equation:[21]

$$\text{IPCE}\ (\%) = 1240\frac{I_P(\lambda)}{P_{inc}(\lambda)\ \lambda} \times 100 \quad (1)$$

where I_p (λ) is the photocurrent density (A m^{-2}) at 1.0 V bias and P_{inc} (λ) is the incident power density of light (W m^{-2}) at average wavelength λ (nm).

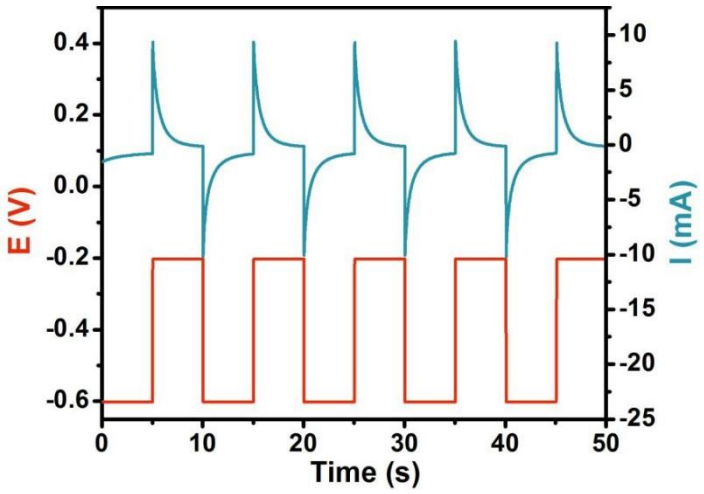


Fig. S1 *I-V* curves of square wave pulse method for anchoring Au atoms on OVs-WO_3/TNTs

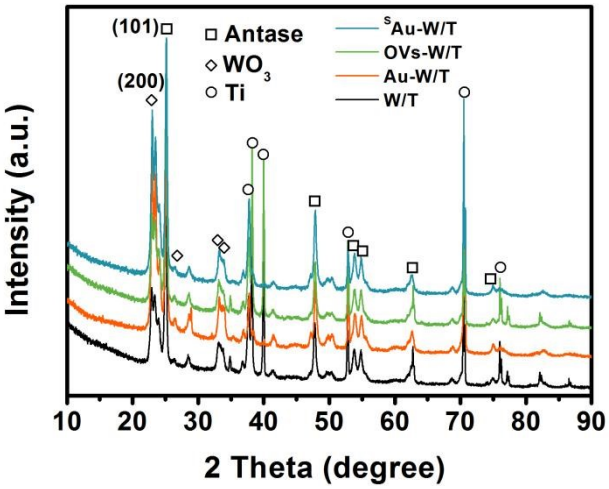
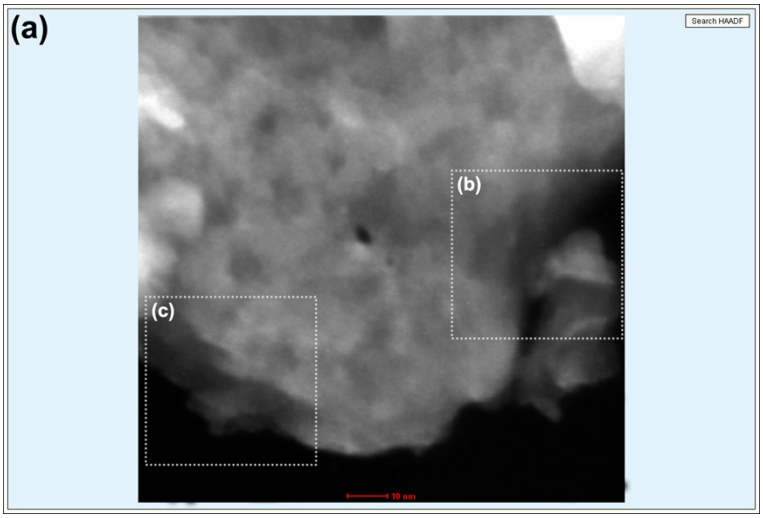
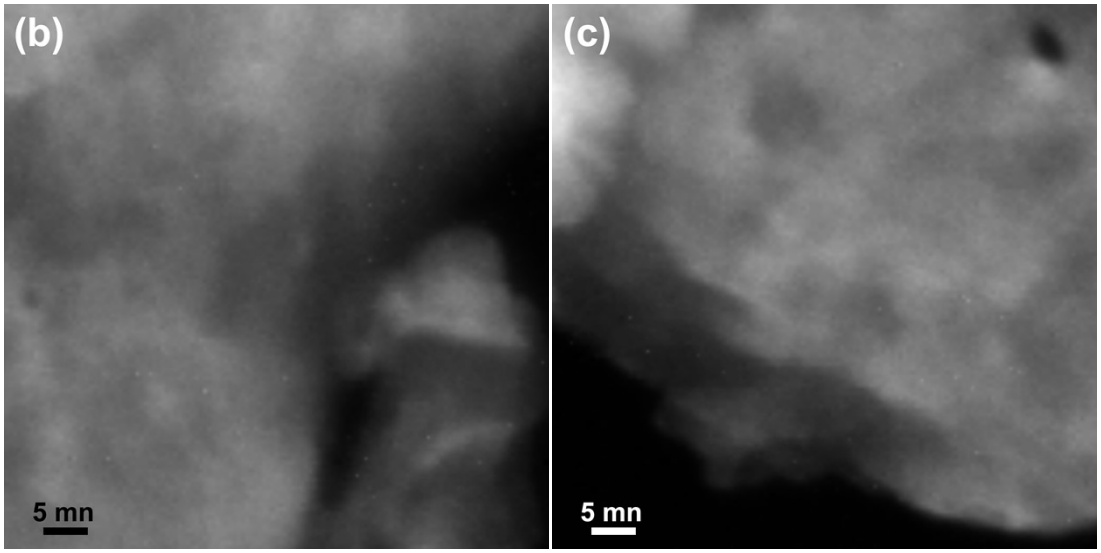


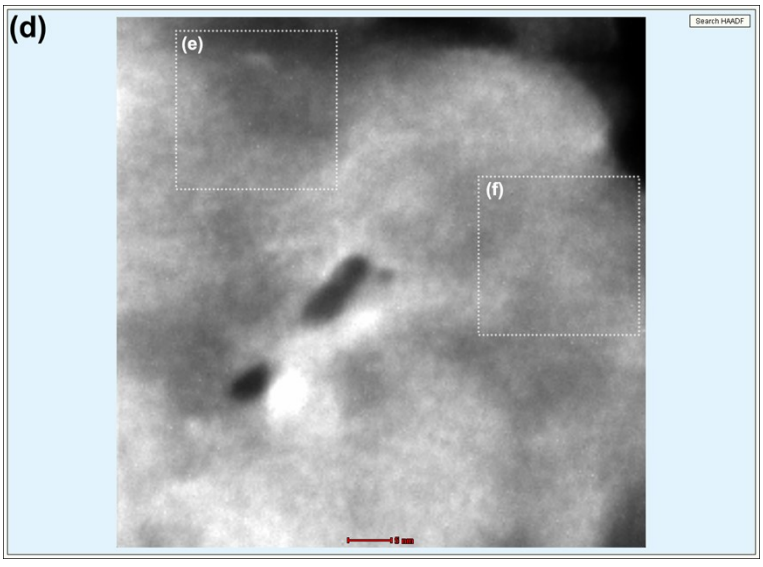
Fig. S2 XRD spectra of W/T, Au-W/T, OVs-W/T and ^{S}Au-W/T. For both W/T,^{S}Au-W/T and ^{S}Au-T/W composites, besides characteristic diffraction peaks of anatase TiO_2 (JCPDF no. 21-1272), a couple of alternative peaks observed at 24.4° and 26.6° indicated the (200) and (101) planes of monoclinic WO_3 (JCPDS no. 97-001-4332), respectively.

Table S1 The specific surface area (S_{BET}) and Au content of samples. The N_2 adsorption/desorption measurements were performed on the samples with peeling off the powder from the Ti substrate. Au content was measured by ICP-AES.

samples	S_{BET} (m^2/g)	Au content (wt %)
^{S}Au-T/W	0.343	2.41
OVs-W/T	0.339	—
Au-W/T	0.327	3.28
W/T	0.327	—


(a)
Search HAADF
(b)
(c)


(b)
5 mn
(c)
5 mn


(d)
Search HAADF
(e)
(f)

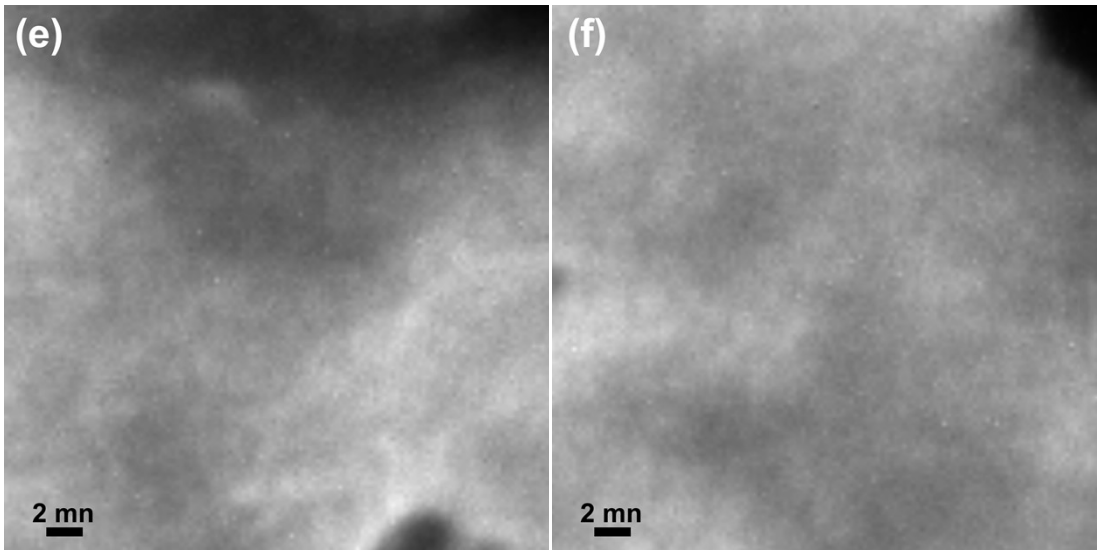


Fig. S3 (a) HAADF-STEM images of ^{S}Au-W/T. A large number of bright spots could be observed.on on the surface of the support.

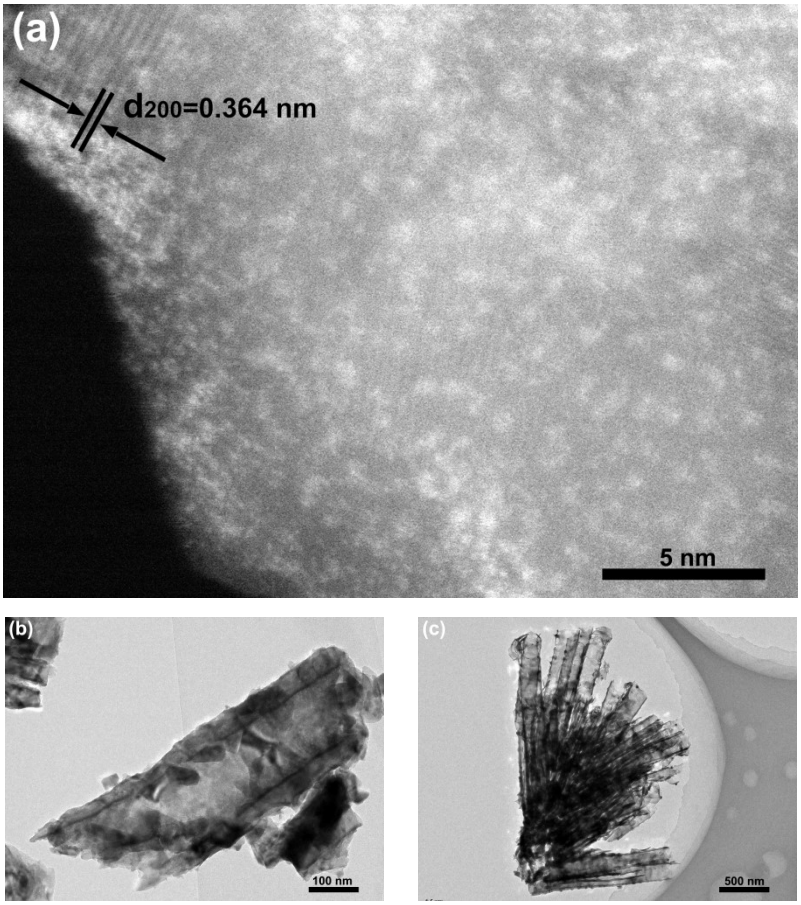
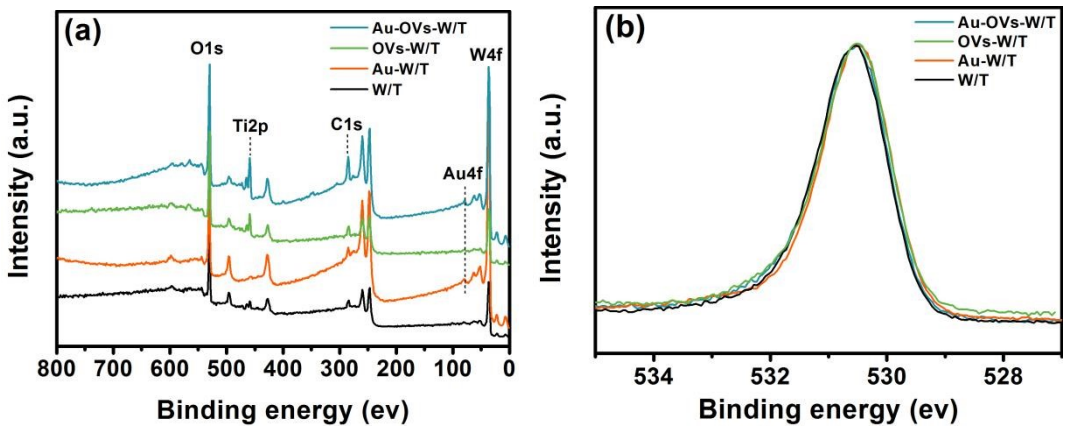


Fig. S4 (a) HAADF-STEM image and (b) (c) STEM image of Au-W/T. Au was dispersed on the surface of WO_3 as cluster consisting of several Au atoms.



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113 **Fig. S5** (a) XRD spectra and (b) O1s XPS spectra of samples.

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115 **Table S2.** BE and PA of W 4f, and MP of W^{5+} and W^{6+} species of samples

Samples	BE (eV)				PA (Counts)				MP (%)	
	W^{6+}		W^{5+}		W^{6+}		W^{5+}		W^{6+}	W^{5+}
	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$		
^{S}Au-T/W	37.59	35.52	37.02	34.98	32186.0	34285.3	6127.7	10375.1	80.1	19.9
OVs-W/T	37.59	35.51	37.04	34.98	25370.2	27782.0	11086.2	18796.5	64.0	36.0
Au-W/T	37.62	35.53	37.02	34.97	12695.6	13992.7	1063.9	2602.5	87.9	12.1
W/T	37.61	35.54	37.01	34.98	43842.1	48758.9	5009.1	7258.6	88.3	11.7

116

117 **Table S3** Binding energy (BE) and relative peak area (PA) of Ti 2p, and molar

118 percentages (MP) of samples

Samples	BE (eV)				PA (Counts)				MP (%)	
	Ti^{4+}		Ti^{3+}		Ti^{4+}		Ti^{3+}		Ti^{4+}	Ti^{3+}
	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$		
^{S}Au-T/W	464.99	459.17	464.09	458.73	5807.8	12983.7	1570.5	1065.6	87.7	15.3
OVs-W/T	465.00	459.18	464.11	458.72	2738.4	8126.2	1224.2	952.8	83.3	16.7
Au-W/T	465.00	459.15	464.12	458.73	2893.4	6213.7	282.2	495.7	92.1	7.9
W/T	465.00	459.18	464.10	458.75	8611.8	15126.9	689.9	1148.5	92.8	7.2

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120 **Table S4** IPCE and the AQY of R-WO_3/TNTs and WO_3/TNTs

Samples	W/T	Au-W/T	OVs-W/T	^{S}Au-W/T
Illuminant	365 nm LED			
Average wavelength (nm)	365 nm	365 nm	365 nm	365 nm
Power density (W cm^{-2})	0.132	0.132	0.132	0.132
Photocurrent (mA cm^{-2})	0.11	0.82	1.14	1.79
IPCE (%)	0.70	5.19	7.22	11.34

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122 **Table S5** IR modes assigned to various functional groups identified in the in-situ
123 FTIR photodegradation spectra of toluene.

IR modes	Functional group
1610 cm^{-1} 1500 cm^{-1} 1599 cm^{-1} 1492 cm^{-1}	skeleton stretching and bending vibrations of aromatic ring
2361 cm^{-1} 2340 cm^{-1}	C=O stretching vibrations of CO_2
1467 cm^{-1} 1462 cm^{-1}	C-O stretching vibration of benzyl alcohol
1690 cm^{-1} 1676 cm^{-1}	stretching vibration of aldehydes
1565 cm^{-1} 1548 cm^{-1} 1529 cm^{-1}	asymmetric stretching vibration of the carboxylate group COO− from benzoic acid
1581 cm^{-1} 1481 cm^{-1}	the C=C stretching vibration of benzoic acid
1658 cm^{-1}	p-benzoquinone-type species
1510 cm^{-1}	C = O stretching vibrations of maleate
1413 cm^{-1}	C = O stretching vibrations of saturated aliphatic acids (formate and acetate)
1442 cm^{-1}	COO– stretching vibration of the maleate species
1640 cm^{-1} 1630 cm^{-1}	surface water species
2884 cm^{-1} 2937 cm^{-1}	C-O stretching vibration mode of aromatic ring
3695 cm^{-1} 3682 cm^{-1}	bridged−OH acted as the adsorption sites

3662 cm^{-1} 3641 cm^{-1} 3603 cm^{-1}	
3621 cm^{-1}	O-H bending and stretching vibrations of carboxylic acids
3739 cm^{-1} 3727 cm^{-1} 3716 cm^{-1} 3704 cm^{-1}	O-H stretching vibration of the terminal hydroxyls, •OH radicals

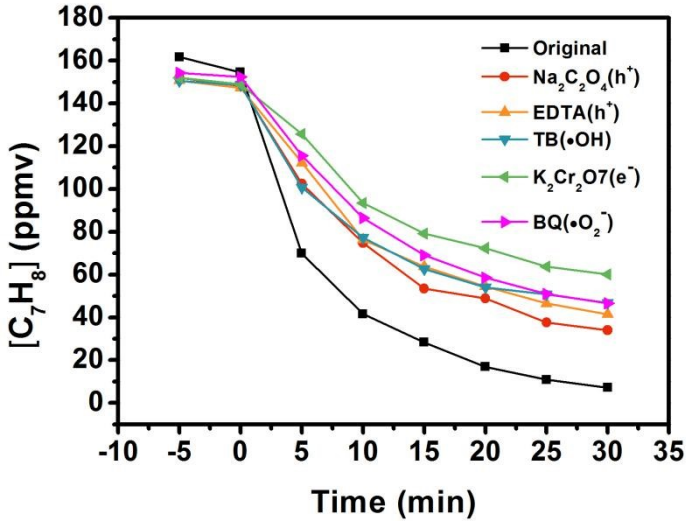

Fig. S6 Quenching experiment over ^{S}Au-W/T. the quenchers were loaded on suface of ^{S}Au-W/T film by impregnation method. In detail, the film was impregnated into a quencher solution with a 0.1 mM concentration for 30 min followed by a drying at 60 ℃, then was used for degradation of toluene.

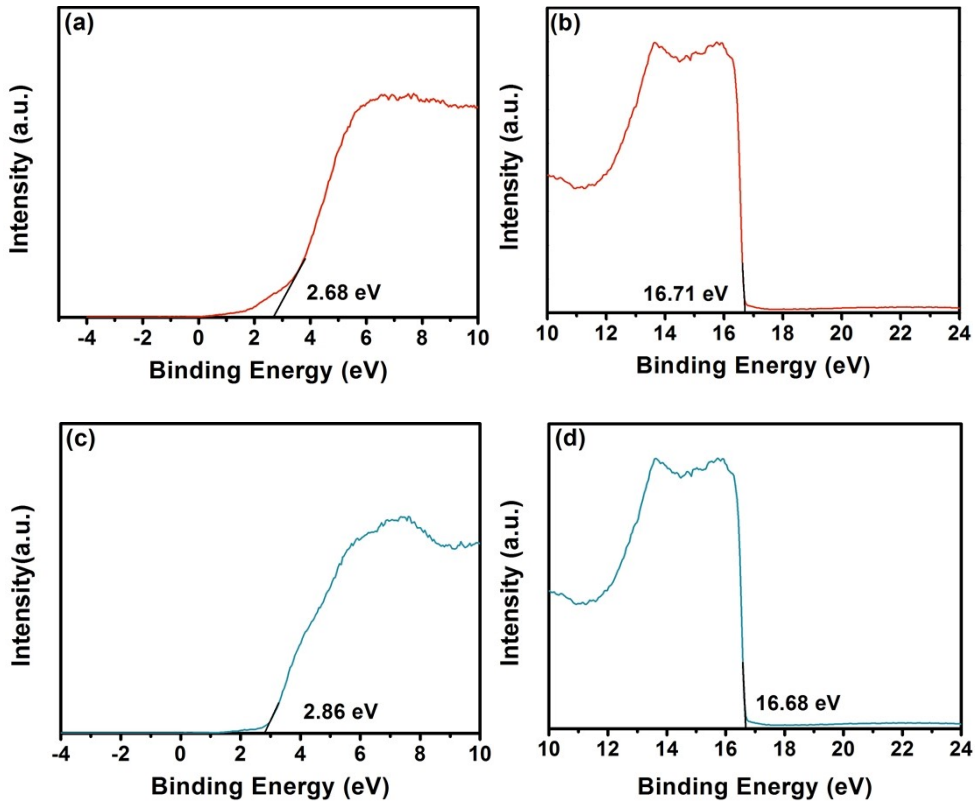

Fig. S7 UPS measurements for electrochemically reduced (a, b) TiO_2 and (c, d) WO_3.

The work function (ϕ) of TiO_2 was calculated to be 4.44 eV (hν-W=21.22 eV-16.71 eV=4.51 eV). Its band gap between Fermi level (Ef) and the VB maxima (VBM) was 2.68 eV. Therefore, TiO_2 catalyst turned out to have VBMs (E_{VBM} + E_{ϕ}-4.5 V) and CB (Eg - EVBM) at 2.61 and -0.56 V vs. NHE, respectively. Likewise, WO_3 was turned out to have VBMs and CB at 2.90 and 0.12 V vs. NHE, respectively. UPS curve of the electrochemically reduced WO_3 was obtained by measuring the WO_3 loaded on a Ti foil.