

Sub-nano CoO_x attached on WO₃ for efficient photocatalytic and photoelectrochemical water oxidation

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Experimental Section

Catalyst preparation

Preparation of WO₃-CoE-2: 6 mg Ethylenediamine-N,N,N',N'-tetraacetic acid cobalt(II) disodium salt tetrahydrate (Co-EDTA) (> 98%, TCI Chemical) was mixed with 300 mg WO₃ (99.8%, Alfa Aesar) in a ratio of 2 wt% in 10 mL anhydrous methanol solution (99.9%, Innochem) by stirring at 60 °C for solvent evaporation. The resulted mixture was calcinated at 350 °C under flowing argon (99.999%) for 1 hour followed by the second calcination at 500 °C under flowing air for 1 hour.

Preparation of WO₃-CoE-1 and WO₃-CoCl₂: For comparison, two other Co-modified WO₃ materials, i.e., WO₃-CoCl₂, WO₃-CoE-1, were prepared by mixing 6 mg Co-EDTA (> 98%, TCI Chemical) or 1.6 mg CoCl₂ (99.9%, Alfa Aesar) with 300 mg WO₃ in 10 mL anhydrous methanol solution (99.9%, Innochem) under stirring at 60 °C for solvent evaporation followed by calcination at 500 °C under flowing air for 1 hour. The resulted samples were denoted as WO₃-CoE-1 and WO₃-CoCl₂, respectively.

Characterization

Powder XRD was conducted on a M21X X-ray Diffractometer with Cu K α irradiation ($\lambda = 1.541 \text{ \AA}$) with a Cu K α source. Scanning electron microscope (SEM) images of samples were obtained with a ZEISS SUPRA55 instrument operated at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) images, combined with energy dispersive X-ray spectroscopy (EDS) mapping were recorded with a field emission transmission electron microscope (JEM2100F, JEOL Co., Japan) operating at 200 kV. XPS measurements were carried out on an ESCA Lab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation and for peak calibration adventitious C 1s was set at 284.9 eV. FT-IR spectra were recorded by Nicolet 4700 spectrometer with reflection mode. The UV-Vis absorption was measured with a UV-visible spectrophotometer (Shimadzu, UV-2600) using BaSO₄ (99+%, ACROS Organics) as the reflectance standard reference. Photoluminescence (PL) spectra were recorded by a JASCO FP-6500 spectrofluorometer. The fluorescence decay curve was measured using a compact fluorescence lifetime spectrometer (QuantaTaurus-Tau, C11367) with a nano-LED lamp, excited at 340 nm. Electron spin resonance (ESR) measurements were carried out at room temperature on a JEOL JES-FA-200.

Photocatalytic tests and analysis

The photocatalytic O₂ evolution was conducted in 0.1 M AgNO₃ (99.995%, Alfa Aesar) aqueous solution with 100 mg catalyst under irradiation of 300 Xe Lamp with L42 cut-off ($\lambda \geq 420$ nm). The photoelectrochemical measurement was carried out by a CHI 760D electrochemical station (CH Instruments Co.) with a three-electrode system under simulated solar light irradiation AM 1.5 G irradiation with light intensity of 100 mW·cm⁻²).

For preparation of the electrodes, the as-prepared samples were suspended in ethanol solution with 0.3 g/L of ethyl cellulose (CP, Alddin Chemical Co., Ltd.), which were then scratch coated onto ITO glass. An aliquot of each sample suspension containing 1.6 g/L WO₃ was deposited on the same electrode area (0.9 cm*0.4 cm) by the drop-casting method. The resulting sample was dried and annealed in a furnace under air at 350 °C for 1 h to obtain the corresponding electrode. The prepared electrodes, a platinum foil, and an Ag/AgCl electrode were as working, counter and reference electrodes, respectively. 0.5 M Na₂SO₄ (99.99%, Alfa Aesar) was used as an electrolyte after saturation with Ar gas for 30 min. Incident photon to current conversion efficiency (IPCE) was carried out by measuring the photocurrent produced with chopped monochromatic light irradiation at 1.0 V vs Ag/AgCl. IPCE can be expressed by the equation: $IPCE = (1240 \times I) / (\lambda \times J_{\text{light}})$, where I (mA/cm²) is the measured photocurrent density at a specific wavelength, λ (nm) is the wavelength of incident light, and J_{light} (mW/cm²) is the measured irradiance at a specific wavelength.

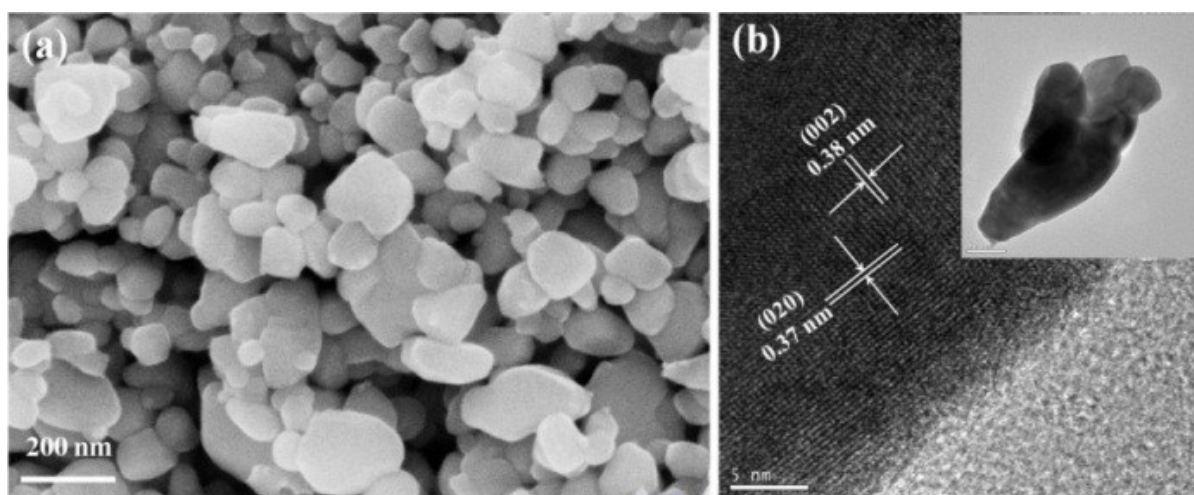


Figure S1 SEM (a) and HRTEM (b) images of $\text{WO}_3\text{-CoE-2}$. Inset of (b) is the low-magnification TEM image.

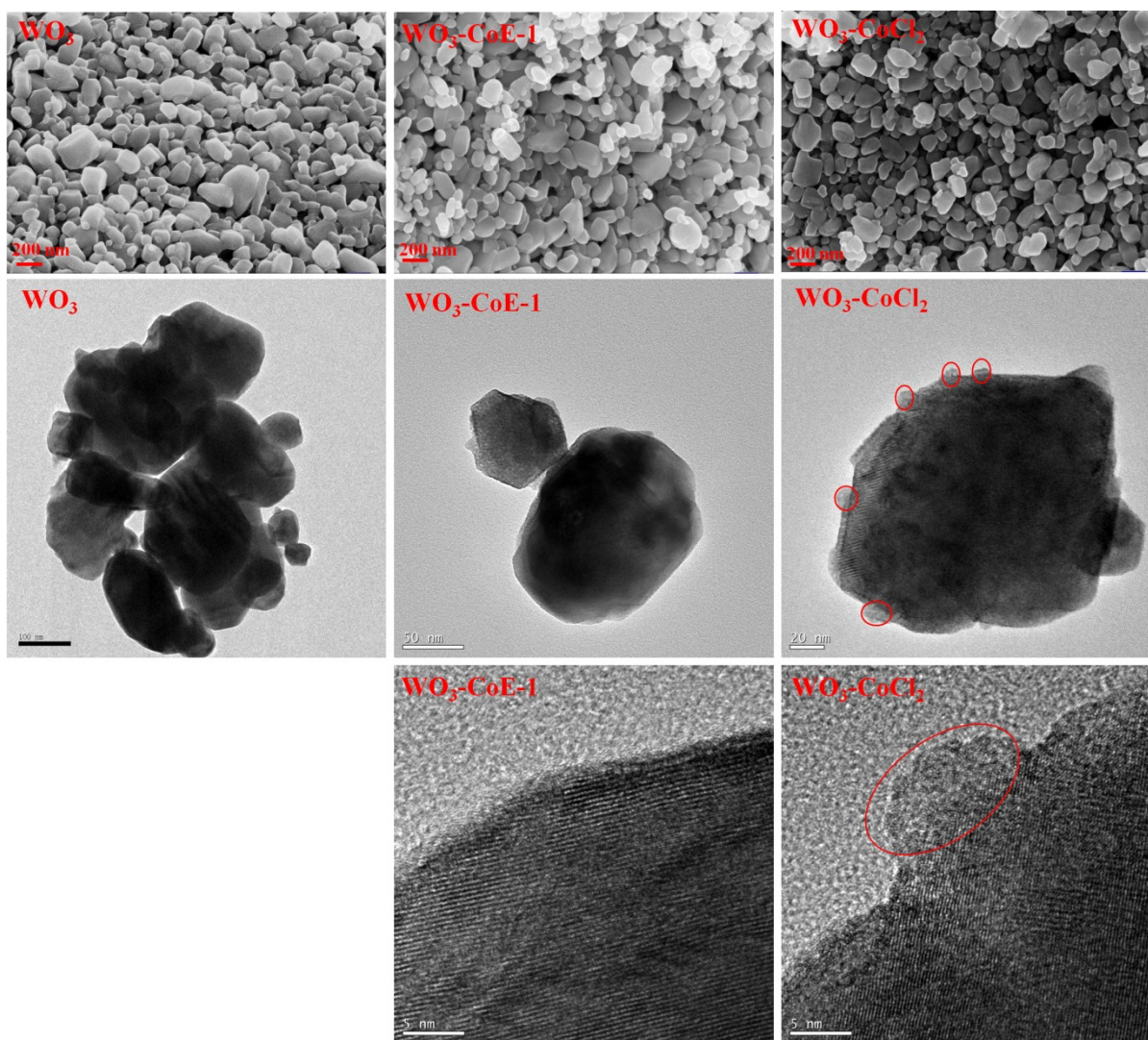


Figure S2 SEM and TEM images of WO_3 and CoO_x loaded WO_3 samples.

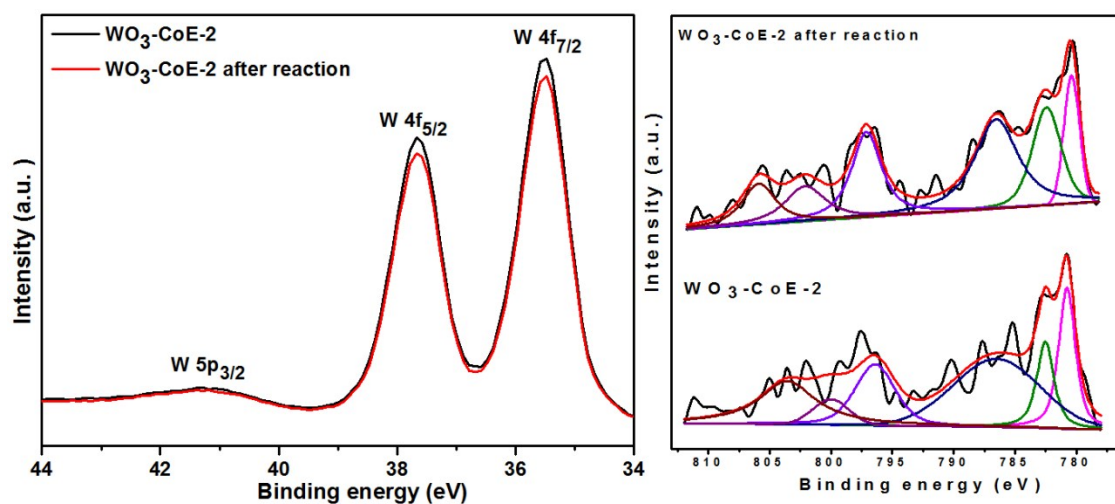


Figure S3. XPS spectra of fresh $\text{WO}_3\text{-CoE-2}$ and recovered $\text{WO}_3\text{-CoE-2}$ samples.

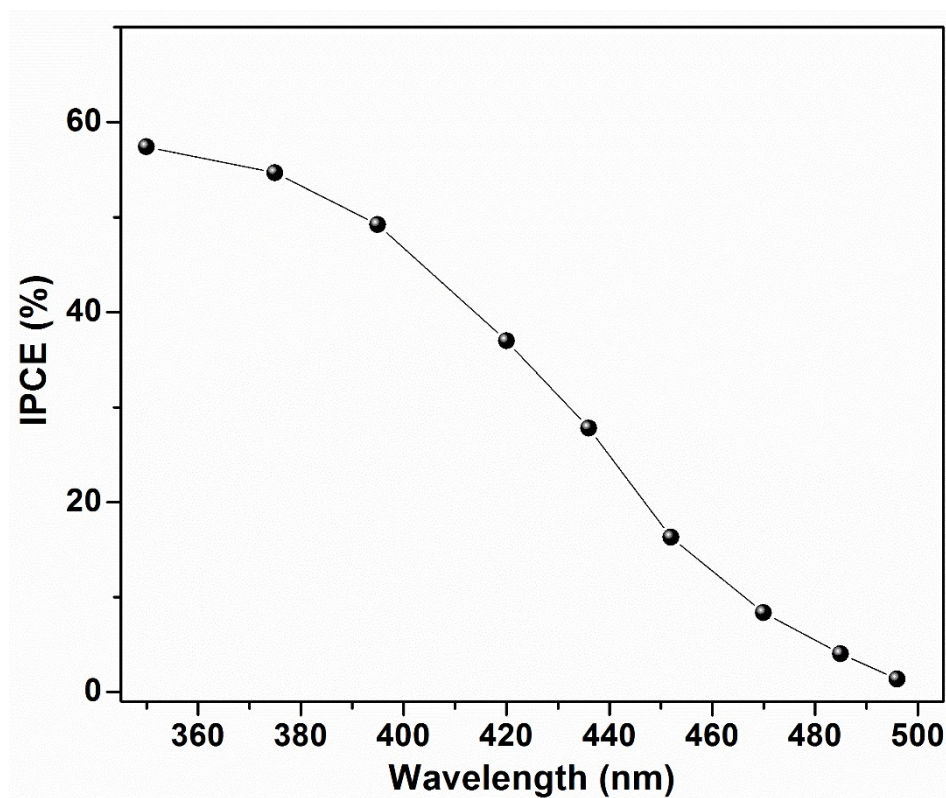


Figure S4. IPCE plot of $\text{WO}_3\text{-CoE-2}$ measured at 0.62 V vs Ag/AgCl

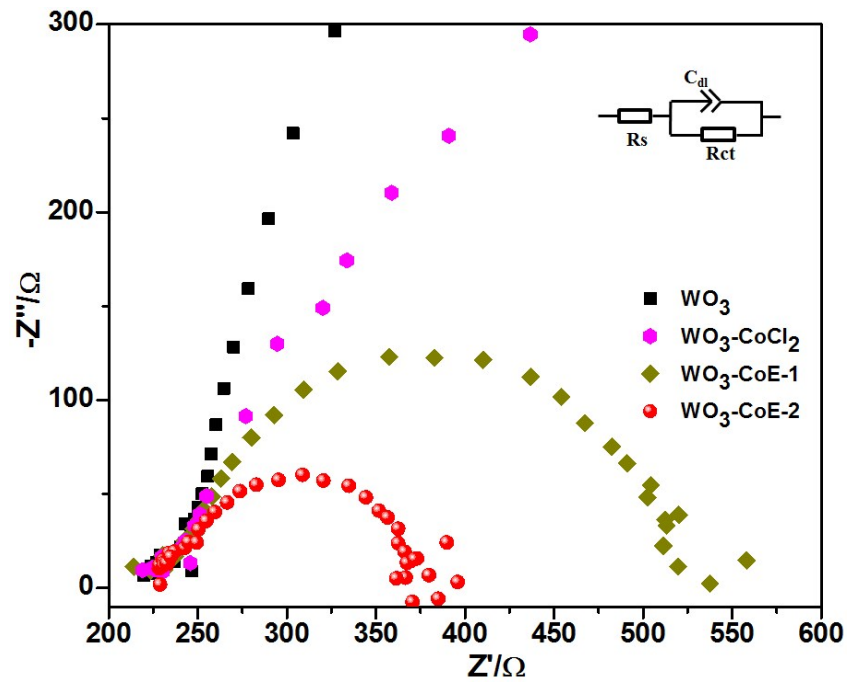


Figure S5. Enlarged EIS Nyquist plots of WO_3 and CoO_x loaded WO_3 in 0.5 M Na_2SO_4 electrolyte at 0.62 V vs Ag/AgCl. Light source: AM 1.5 G with light intensity of 100 mW cm^{-2} .

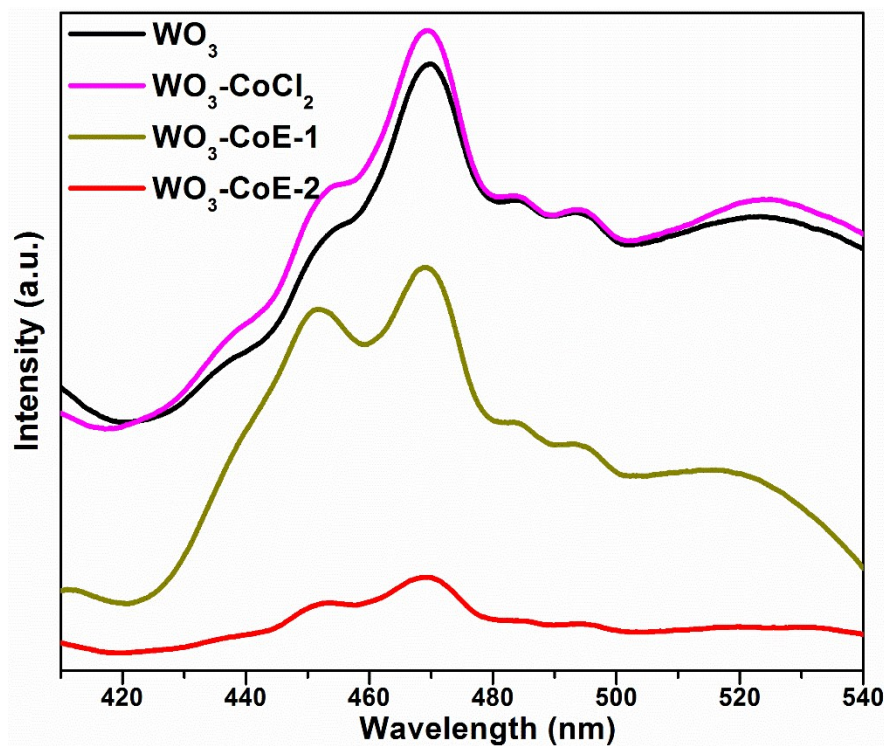


Figure S6. Photoluminescence spectra of samples by exciting at 390 nm.

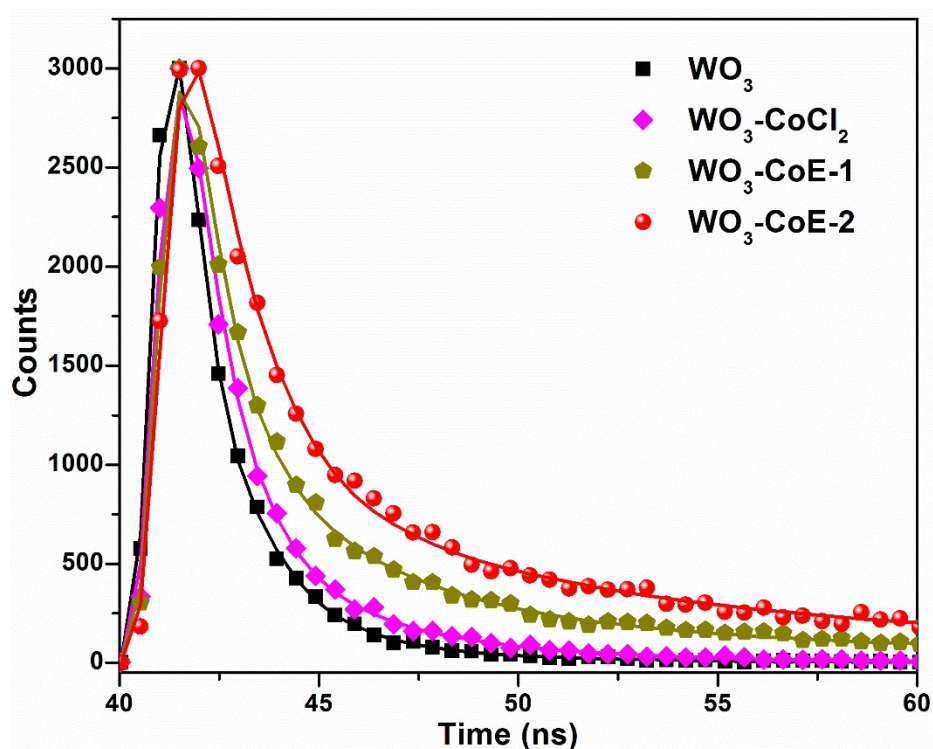


Figure S7. Time-resolved fluorescence decay spectra of samples monitored at 470 nm, respectively, by time-correlated single-photo counting. The samples were excited by the incident light of 390 nm.

Table S1. The fitting results of the fluorescence decay curves through a tri-exponential function.

	T	T1	T2	T3	A1(%)	A2(%)	A3(%)
WO ₃	1.393	0.318	1.326	3.872	73.4	23.7	2.9
WO ₃ -CoCl ₂	2.02	0.718	1.985	4.438	79.5	13.5	7.0
WO ₃ -CoE-1	9.207	0.738	3.883	23.412	78.1	19.3	2.6
WO ₃ -CoE-2	19.524	1.327	8.409	48.504	80.6	16.8	2.6

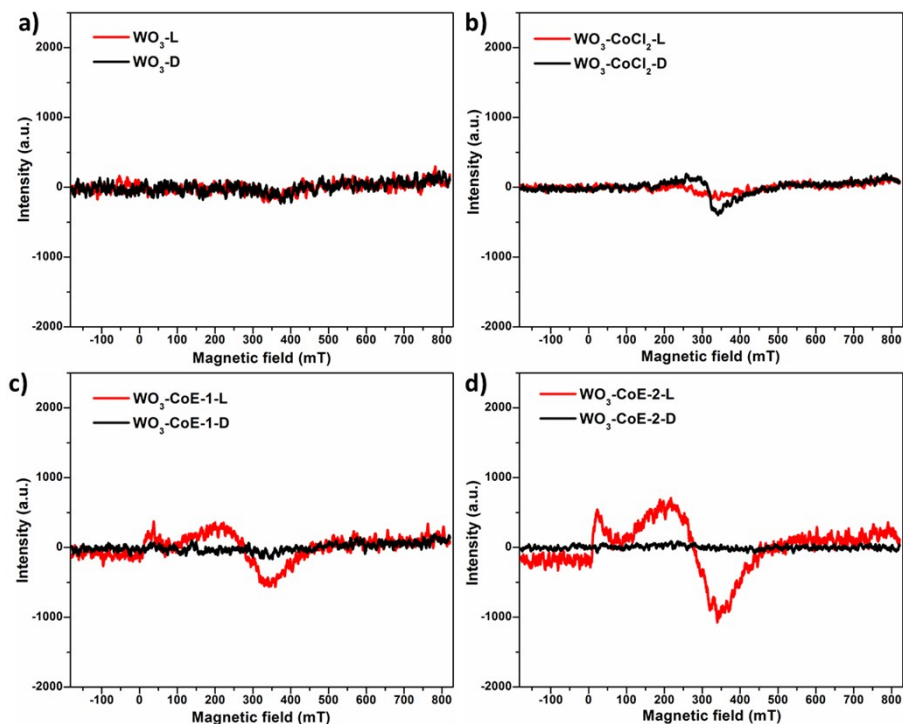


Figure S8. Semi *in-situ* ESR spectra of WO_3 and Co loaded WO_3 under dark and irradiation condition.

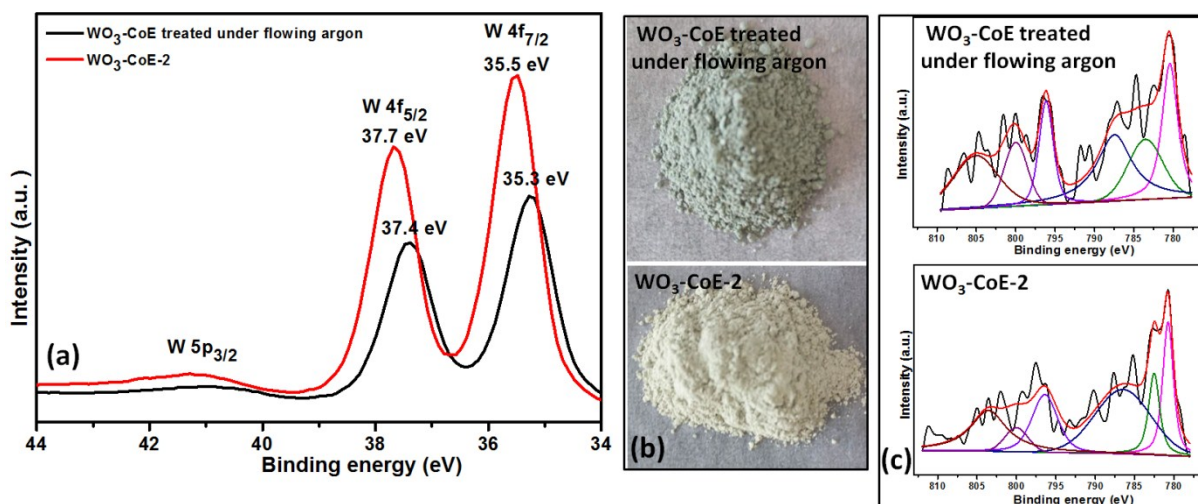


Figure S9. (a) W 4f and W 5p XPS spectra, (b) sample color, (c) Co 2p XPS spectra of WO_3 -CoE treated under flowing Ar at 350 °C for 1 h and WO_3 -CoE-2.