General route for RuO_2 deposition on metal oxides from RuO_4

Electronic supplementary information (ESI)

Experimental details

Synthesis

Preparation of TiO_2 Electrodes. Titanium Dioxide electrodes where prepared on Fluorine doped Tin Oxide (FTO, TEC 15, Pilkington Glass) by spin coating “Vp Disp W2730X” 30 wt% TiO_2 colloid (Ebonik Degusa GmbH) at 4000 rpm for 30 seconds. After deposition the substrates where left to dry at room temperature and calcined at 350°C, 2°C/min ramp rate for 2 hr.

Preparation of WO_3 electrodes. Tungsten trioxide electrodes were synthesized by potentionstatic electrodeposition using a Bio-Logic potentiostat (VSP) in a 3 electrode cell, where the counter electrode consisted on a platinum mesh and the reference electrode used was a SCE electrode. The electrodeposition was carried at room temperature at -0.5 V vs SCE for 20 min, after which the electrodes where copiously rinsed with Millipore DI water and dried under a stream of air. The electrodes where calcined at 450°C for 120 min. The electrodeposition solution consisted of 100mM tungsten-peroxo solution with 5 wt% SDS prepared following the method of Beack et al.[1]

Functionalization of planar substrates. Titanium dioxide and Tungsten trioxide electrodes were functionalized individually in a 25 ml scintillation vial and adding enough 20 mM Dopamine hydrochloride ($(HO)_2C_6H_3CH_2CH_2NH_2\cdot HCl$,Sigma-Aldrich) in 30 % v/v solution of methanol (99.8 % Sigma-Aldrich) in Millipore DI water to cover the substrate. The vials were placed for 30 min in an oven pre-heated to 95°C. After functionalization the electrodes were rinsed in Millipore DI water and dried under a stream of compressed air.

Functionalization of powders. One gram of titanium dioxide (P25) or tungsten trioxide powder was mixed with the 20 mM Dopamine hydrochloride solution in 30 % v/v methanol to a volume of 15 mL and was sonicated for 30 min in a centrifuge tube. After sonication the solution was centrifuged and the power was re-dispersed in DI water to remove any excess Dopamine, the washing procedure was repeated 5 times in total and the collected powder was dried in air at 95°C.

RuO_2 deposition on planar substrates. Ruthenium dioxide deposition of planar substrates was performed by attaching the substrate to a Pyrex® petri dish cap using double sided tape. A stock solution of $RuCl_3 \bullet xH_2O$ (0.25 mg/ml to 0.5 mg/ml), stirred prior to deposition was mixed with a 1 mg/ml $KMnO_4$ solution and was immediately dispensed on the petri dish and the petri-dish cap with the substrates was placed on the petri dish. Care was taken to avoid the solution in the petri dish being in contact with the substrates, similarly when the volume of the deposition solution was less than 5 ml a less concentrated solution (0.25 mg/ml) was used such that there would be an even liquid coverage all over in the petri dish. Typically the $RuCl_3$ loading consisted of 1 to 2 mg $RuCl_3/cm^2$ of functionalize metal oxide, the amount of $KMnO_4$ used was always twice the weight of the $RuCl_3$. $KMnO_4$ was used to corrode the surface of the $RuCl_3$ and produce Ru^{+8} ions[2]; however RuO_4 (0.5% stabilized aqueous solution) can also be used.

$$5KMnO_4 + 3RuCl_3 + 2H_2O \rightarrow 3RuO_4(g) + 5MnO_2 + 5KCl + 4HCl$$

The reaction was carried in the petri dish for two hours in which $RuCl_3$ would get oxidized to Ru^{8+} by the potassium permanganate, and then the Ru^{8+} would form RuO_4, which would the react and oxidize the dopamine functional group and get reduced to $RuO_2 + O_2$[3] and deposit on the metal oxide surface. The precursor mixing and reaction on the petri dish was carried under a fume hood, to prevent exposure to the RuO_4 vapors since it is highly toxic and hazardous.[4]

$$RuO_4(g) + R\text{-}COH + H_2O \rightarrow R\text{-}RuO_2 \cdot H_2O + CO_2 + O_2$$
$$RuO_2 \cdot H_2O + RuO_4(g) + H_2O \rightarrow 2RuO_2 \cdot H_2O$$

RuO_2 deposition on powders. Typically 0.5 g to 1 g of powder (depending on the density) is packed on a glass tube and mounted on a 3 neck flask, in which the solid $RuCl_3$ and $KMnO_4$ is added to 10-30 ml of Millipore water. The 3 neck flask is sealed and put on a stir plate. On a separate port of the 3 neck flash a gas diffuser is inserted such that the solution that is being stirred is purged with nitrogen. The nitrogen gas will carry the RuO_4 vapors through the packed catalyst column where they will react with the metal oxide, which can be gently mixed by the reaction gas. To increase homogeneity of the powder, the packed tube is rotated once every hour during a 4 hr period that the reaction takes place. The loading of RuO_2 can be controlled by the amount of $RuO_4(g)$ that is generated in-situ by controlling the amount of $RuCl_3$ and $KMnO_4$ used or by repeating the deposition process several times. The repetition of the deposition process is a preferred route to control the loading of RuO_2, since this will guarantee a better degree of homogeneity of the coating; in the case of powders the support is removed from the reaction chamber and mixed after which it is inserted on the reaction chamber.

Calcination of samples. Thin film and powders where calcined in a box furnace (Carbolite) under air atmosphere at different temperatures for 120 minutes with a ramp rate of 2ºC/min and cooled under natural convection.

Sample Characterization

XPS. X-ray photoelectron spectroscopy spectra was performed (Sigma Probe, Thermo Scientific) using a monochromated Al Kα source for incident radiation and a six-channel detector for measurement of photoelectrons. Charge compensation was utilized during measurement, and base pressure was maintained at $< 5.0\times10^{-9}$ torr. Spectra were calibrated to the O1s at 530.0 eV and not to the C 1s spectra since these signal has contributions to advantageous carbon, dopamine and in some cases Ru 3d signals which are all in the C1s region. Multiple oxidation states of the dopamine as well as that of Ru in the C1s-Ru3d region makes the spectra difficult to interpret. XPS interpretation was based on literature values.[3, 5]

XPS spectra (S4f-R2) of the deposited samples shows the disappearance of the N 1s peak at 402 eV after the RuO_2 deposition, however the O 1s and Ti 2p regions remain unchanged. In the C 1s - Ru 3d XPS region (Figure S4d), the TiO_2 powder (R0) shows advantageous carbon peak at 285 eV and peaks at 286.5 eV and 289 eV, which could be related to organic traces[6] of the TiO_2 precursor. Upon deposition of the RuO_4(g) (Figure S4d,e R2) two new peaks at 281.2 and 282.5 eV in the Ru 3d5/2 region and the corresponding peaks in the Ru 3d3/2 at 285.7, and 287 eV appear corresponding to Ru^{3+} or hydrated RuO_2,[7] and Ru^{6+} respectively,[5a, 6] C 1s is at 284.9 eV and the second carbon peak at 288.8 eV.[6] Upon calcination at 250°C (Figure S4d, f R3) the XPS spectra peaks at 280.2 and 281.3 eV for the Ru 3d5/2 and 284.7 and 285.9 eV for Ru 3d3/2 corresponding to Ru^{4+} and Ru^{3+} or hydrated RuO_2[7] respectively and C 1s peak at 285.3 eV while the second carbon related peak is still present at 288.7 eV.

SEM. Scanning electron microscopy (SEM) was performed the thin films and powder samples substrate samples with an acceleration voltage of 5-10 keV and a working distance of ~5 mm from the tip to the sample plane (FEI Co. FEGSEM 200F).

TEM. The microscope used is a FEI Titan 80-300ST TEM microscope with a monochromator and a CEOS CESCOR probe spherical aberration corrector. It is equipped with scanning coils for STEM operation and a detector for High Angle Annular Dark Field (HAADF). The microscope was operated in STEM mode at 300 kV accelerating voltage with 70.8 mrad inner detector angle. The powdered samples were dispersed on TEM copper grids with lacey carbon film. EDX elemental mapping and line scans were performed using a dwell time of 2 seconds per point using a slightly focused monochromator to maximize signal. The sample suffered from beam damage under these conditions, so the scans had to be performed after imaging.

XRD. X-ray diffraction (XRD) was conducted on samples deposited on FTO and powder samples on the using a powder diffractometer (Phillips PANalytical X'PERT) using Cu K radiation with a CNRS position sensitive detector.

References of Supporting Information:

(1) Baeck, S. H.; Choi, K. S.; Jaramillo, T. F.; Stucky, G. D.; McFarland, E. W., *Adv. Mater.* **2003,** *15* (15), 1269-1273.

(2) Swider-Lyons, K. E.; Love, C. T.; Rolison, D. R., *J. Electrochem. Soc.* **2005,** *152* (3), C158-C162.

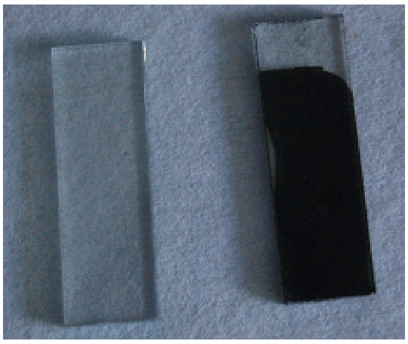
(3) Yuan, Z.; Puddephatt, R. J.; Sayer, M., *Chem. Mat.* **1993,** *5* (7), 908-910.

(4) Care should be taken to minimize exposure of the RuO4 to organic chemicals, since it can react violently as well as keep it at temperatures lower than 100 C

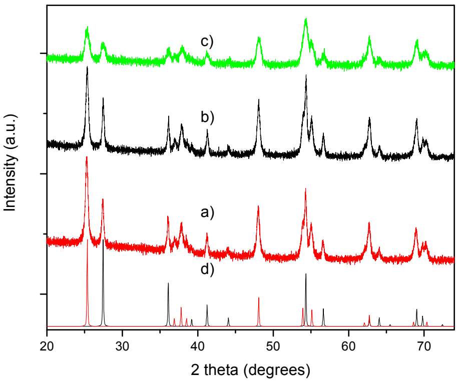
(5) (a) Bhaskar, S.; Dobal, P. S.; Majumder, S. B.; Katiyar, R. S., *J. Appl. Phys.* **2001,** *89* (5), 2987-2992; (b) Sakurai, T.; Hinatsu, Y.; Takahashi, A.; Fujisawa, G., *J. Phys. Chem.* **1985,** *89* (10), 1892-1896.

(6) Holm, J.; Glanneskog, H.; Ekberg, C., *J. Nucl. Mater.* **2009,** *392* (1), 55-62.

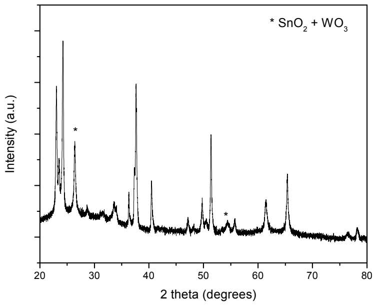
(7) Kim, K. S.; Winograd, N., *J. Catal.* **1974,** *35* (1), 66-72.



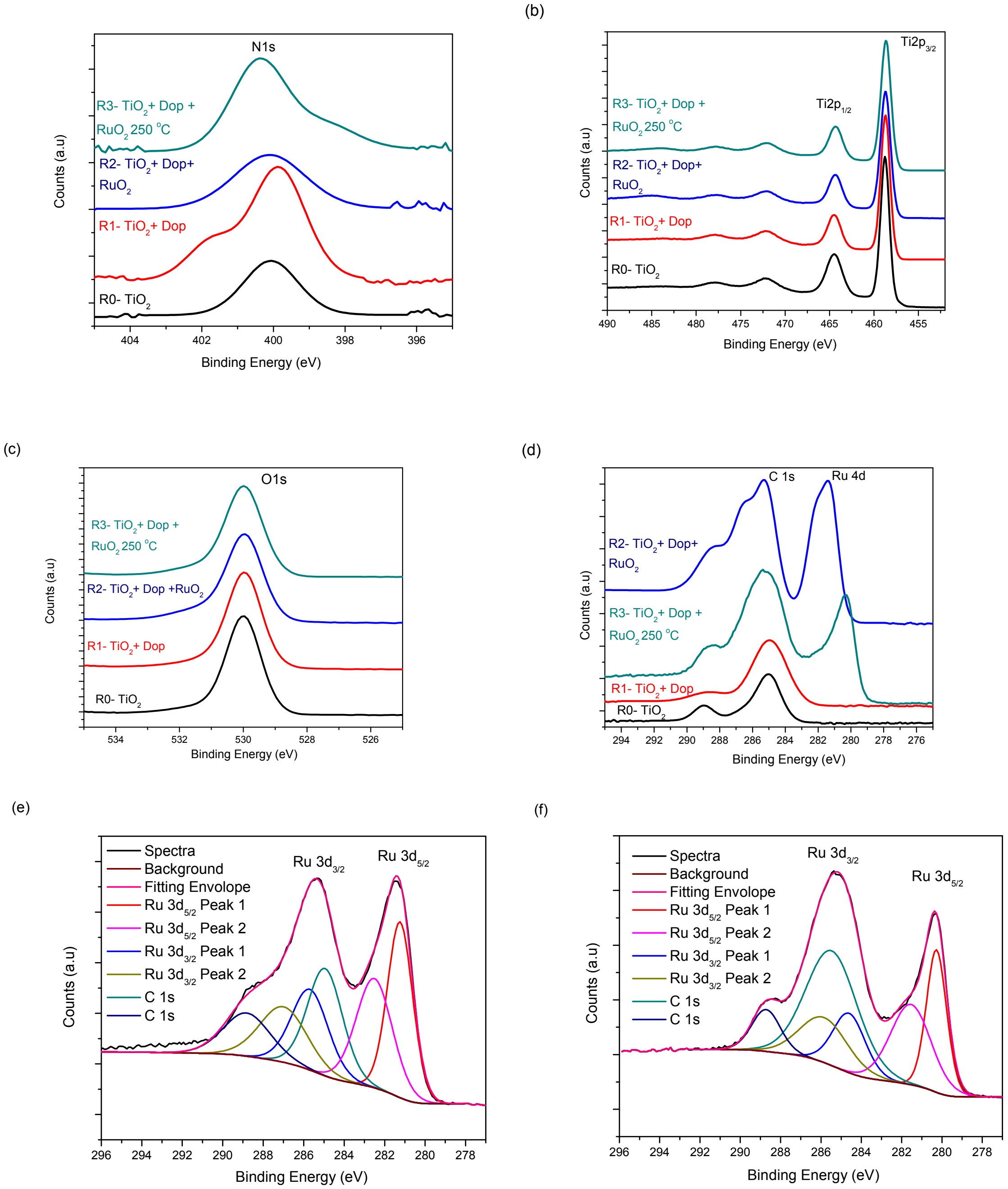
S1.(a) Picture of (i) spin-coated TiO_2 on FTO (ii) spin-coated TiO_2 on FTO after RuO_2 after 250°C heat treatment in air.



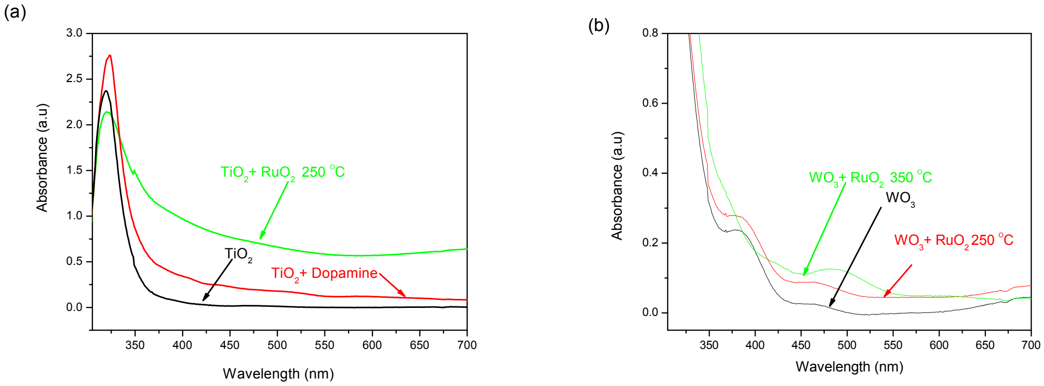
S2. X-ray diffraction pattern of (a) P25 powder (red), (b) P25 powder after RuO_2 deposition (black), (c) P25 powder after RuO_2 deposition calcined in air at 450°C (green) and (d) standard powder pattern of rutile (00-02-1276, black line) and anatase (00-004-0477 red line).



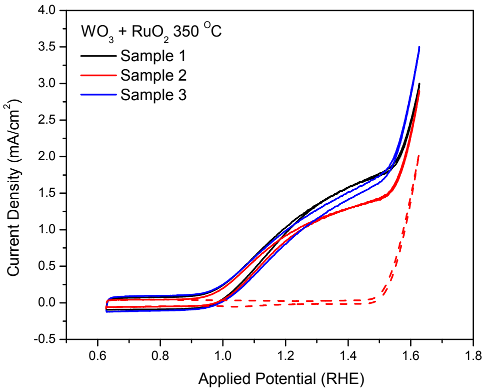
S3. X-ray diffraction pattern of WO_3 sample after calcination at 450°C. All peaks are matched to WO_3 (JCPDS 00-043-1035), FTO peaks are matched to SnO_2 (JCPDS 01-077-0450) and shown in the figure with (*) where SnO_2 +WO_3 peaks overlap; no other substrate peaks are observed.



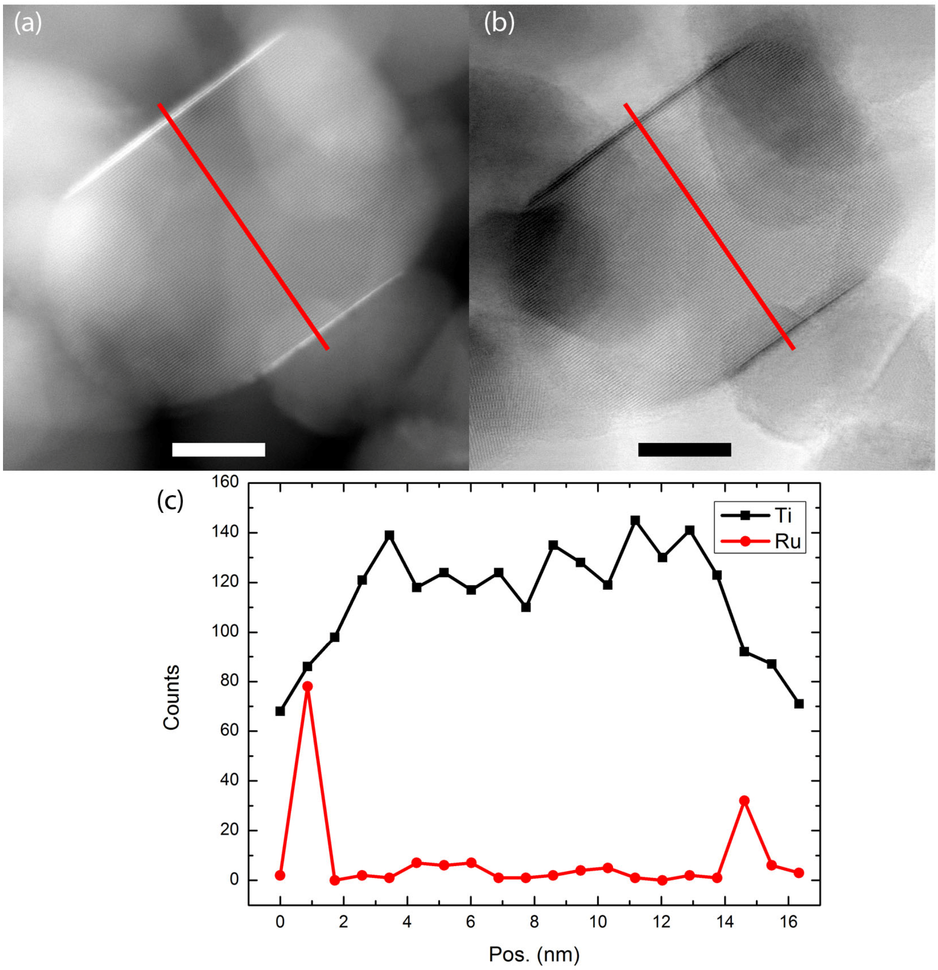
S4. XPS spectra of (a) N 1s, (b) Ti 2p, (c) O 1s, (d) C 1s and Ru 3d, (e) peak fitting of C 1s-Ru 3d for TiO_2 + dopamine + RuO_2; (f) peak fitting of C 1s and Ru 3d for TiO_2 + dopamine + RuO_2 calcined at 250°C. In the graphs dopamine has been abbreviated as "Dop".



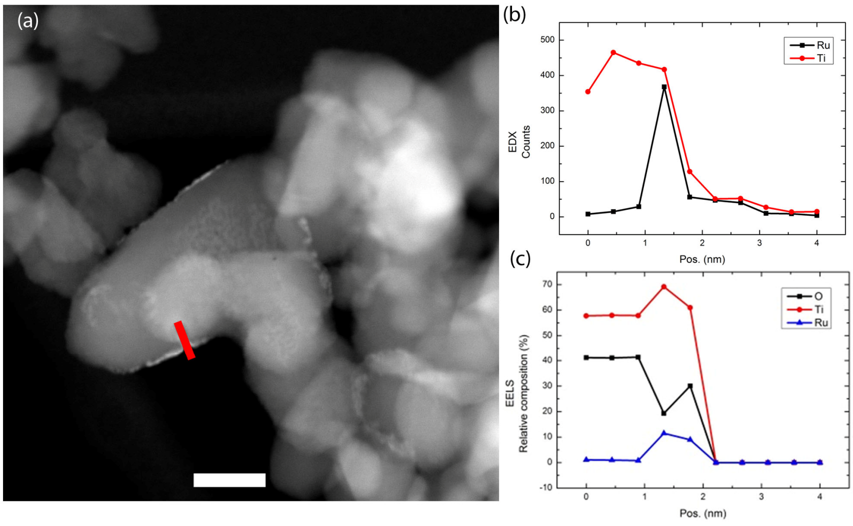
S5. UV-Vis spectra of (a) TiO_2 on FTO with and without RuO_2, (b) WO_3 on FTO with and without RuO_2. Bandgap of TiO_2 is 3.2 eV (indirect transition from the Tauc Plot, not shown), the bandgap of electrodeposited WO_3 is 2.7 eV (indirect transition as observed from the Tauc plots, not shown). W2730X Dispersion was used as the TiO_2 source (see experimental Section).



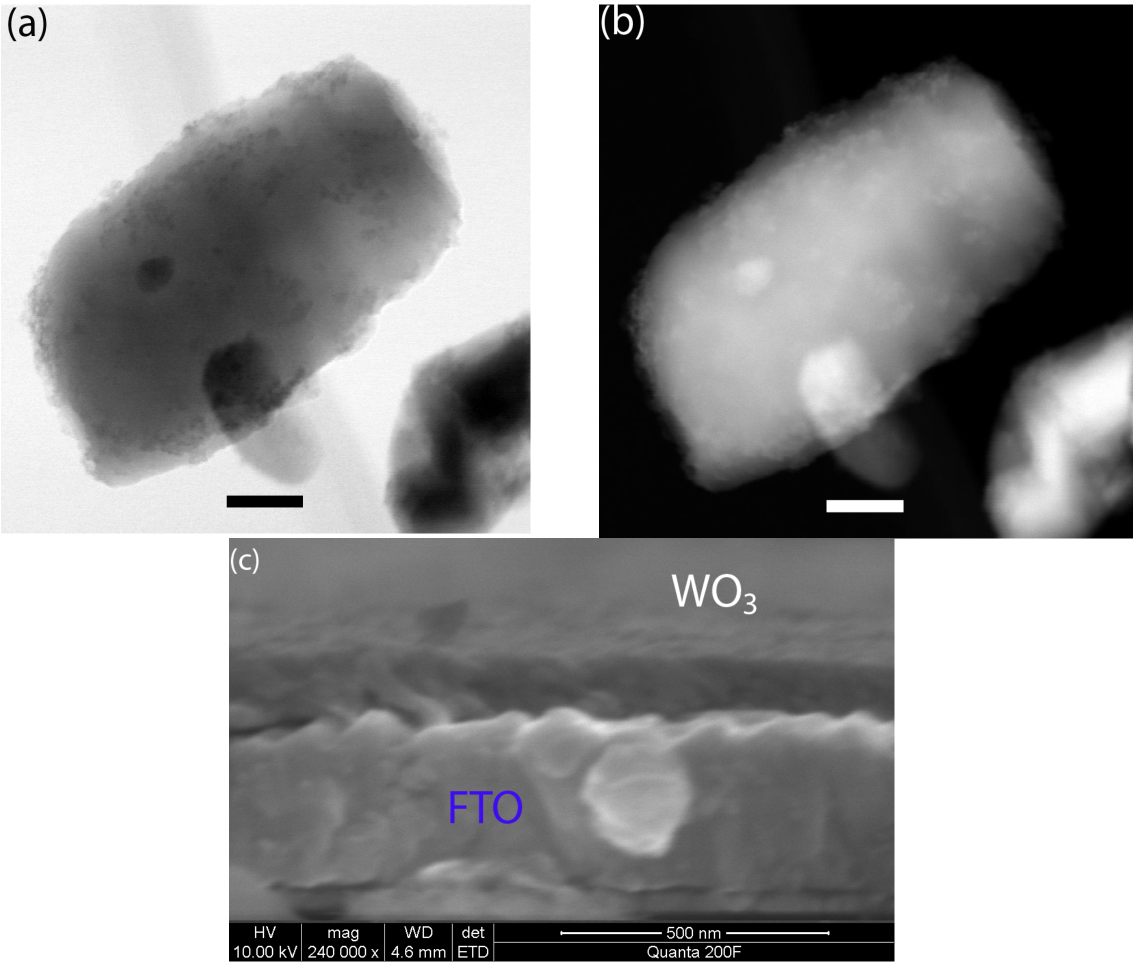
S6. Cyclic Voltamograms of electrodeposited WO_3 on FTO with RuO_2 calcined at 350°C in the dark and under illumination. Three samples prepared in the same manner are tested for their photoelectrochemical performance and show that the deposition method shown excellent photocurrent reproducibility.



S7. (a-b) STEM HAADF and BF images of a RuO_2 layer on a (113) rutile P25 TiO_2 surface after 450°C calcination and (c) Ruthenium and titanium compositional profiles, from EDX spectra acquired along the red line in (a-b). Scale bars 5 nm.



S8. Combined HAADF, EDX and EELS study of a single deposit of RuO_2 on TiO_2, showing surface layers. The agreement between EDX and EELS proves that RuO_2 forms compact thin layers on the TiO_2 surface. (a) STEM HAADF image of a P25 TiO_2 particle coated with RuO_2 prior to calcination, scale bar 10 nm; (b-c) Spatially-resolved chemical profiles of elements of interest calculated from EDX and EELS data acquired simultaneously along the red line in (a). (b) Ruthenium and titanium compositional profiles, from EDX spectra; (c) Ruthenium, titanium, and oxygen compositional profiles, from EELS core-loss spectra, quantification in at.%.



S9. (a-b) STEM HAADF and BF images of a RuO_2 on WO_3 powder as made. The WO_3 powder used was not from the tested photoelectrodes. Scale bars 10 nm. RuO_2 loading was 1.3 % as determined by XRF (c) Cross section SEM of WO_3 electrodeposited photoelectrode with RuO_2.

Table 1: Binding energy for Ru, C and N from XPS data.

	Ru 3d 5/2	C 1s	Ru 3d 3/2	N 1s	Ru Species
R0		285.0, 286.5, 289.0		400.1	
R1		284.9, 288.6		399.8, 401.7	
R2	281.2, 282.5	284.9, 288.8	285.7, 287	400.1	$Ru^{3+,}$ Ru^{6+}
R3	280.2, 281.3	285.3, 288.7	284.7, 285.9	398.6, 400.5	Ru^{3+}, Ru^{4+}