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Electronic supplementary information (ESI)

Electrochemical synthesis of nanoporous tungsten carbide and its application as electrocatalysts for photoelectrochemical cells

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Table S1. *J-V* characteristics of DSCs employing tungsten carbide as counter electrode material reported in previous publications.

Counter Electrodes	V_{oc} **/ V**	J_{sc} **/ mA cm^{-2}**	***FF* / %**	***Efficiency* / %**	***References***
WC	0.763	14.17	65	7.01	(i)
WC	0.65	14.01	56	5.10	(ii)
WC/OMC	0.65	14.45	57	5.34	
WC/OMC	0.804	14.59	70	8.18	(iii)
W/W_2C	0.785	12.43	56	5.47	(iv)
W_2C	0.807	12.72	65	6.68	
WC/W_2C	0.799	12.92	60	6.23	
WC/C	0.76	15.35	67	7.77	(v)
WC	0.53	2.71	28	0.41	(vi)
WC/W_2C	0.37	5.44	29	0.59	(vii)
$WC/W_2C\text{-}ZrO_2$	0.69	9.51	35	2.29	
WC	0.839	13.16	65.1	7.19	(viii)
WC/C	0.842	15.52	72.1	9.42	

(i) *Chem. Commun.*, 2010, **46**, 8600-8602

(ii) *Appl. Phys. Lett.*, 2011, **98**, 221102

(iii) *Angew. Chem. Int. Ed.*, 2011, **50**, 3520-3524

(iv) *J. Mater. Chem. A*, 2013, **1**, 7519-7524.

(v) *Nano Energy*, 2014, **9**, 392-400

(vi) *J. Mater. Sci.: Mater. Electron.*, 2015, **26**, 7977-7986

(vii) *Electrochim. Acta*, 2016, **211**, 375-384

(viii) *J. Power Sources*, 2016, **33**, 399-405

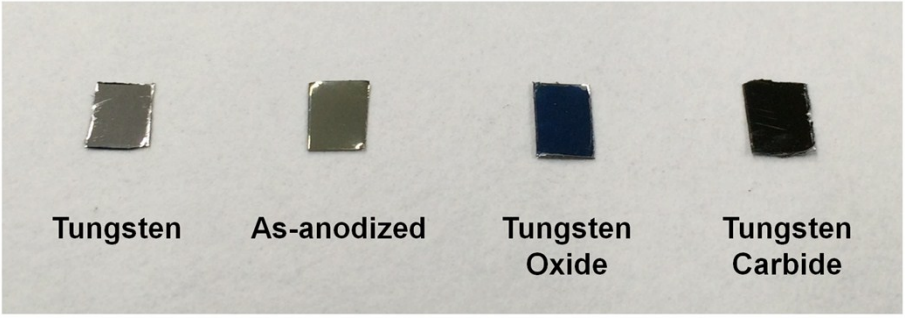

Fig. S1. Digital photograph images of tungsten, as-anodized tungsten, np-WO_3, and np-WC.

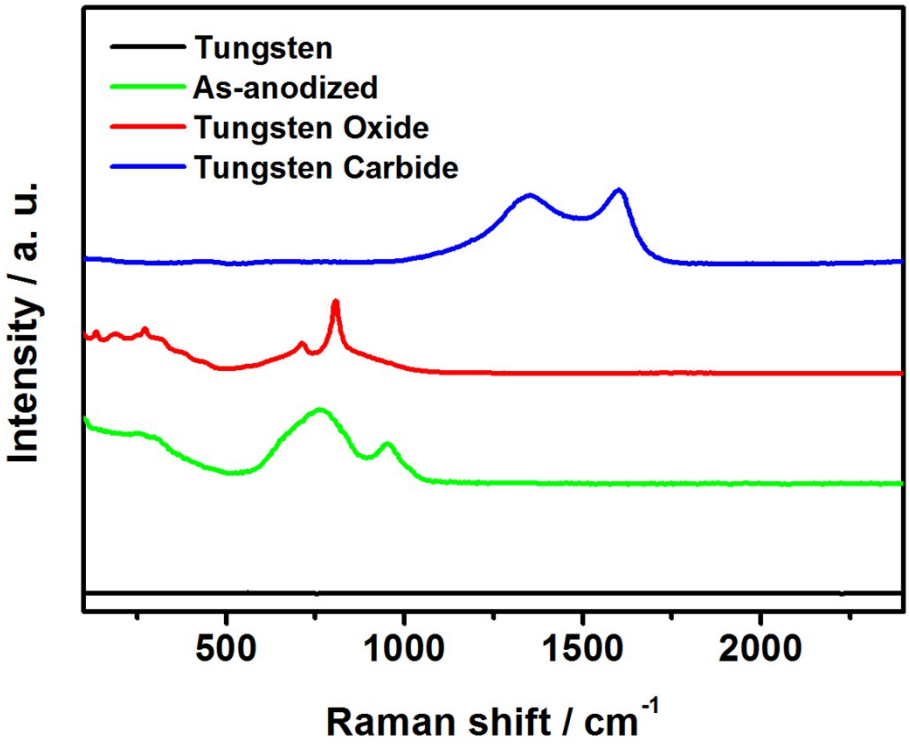

Fig. S2. Raman spectra of tungsten foil and anodized tungsten before and after heat treatments in air or CO atmosphere. D and G signals located at 1350 cm^{-1} and 1580 cm^{-1}, respectively, verify the presence of carbon shells in tungsten carbide.

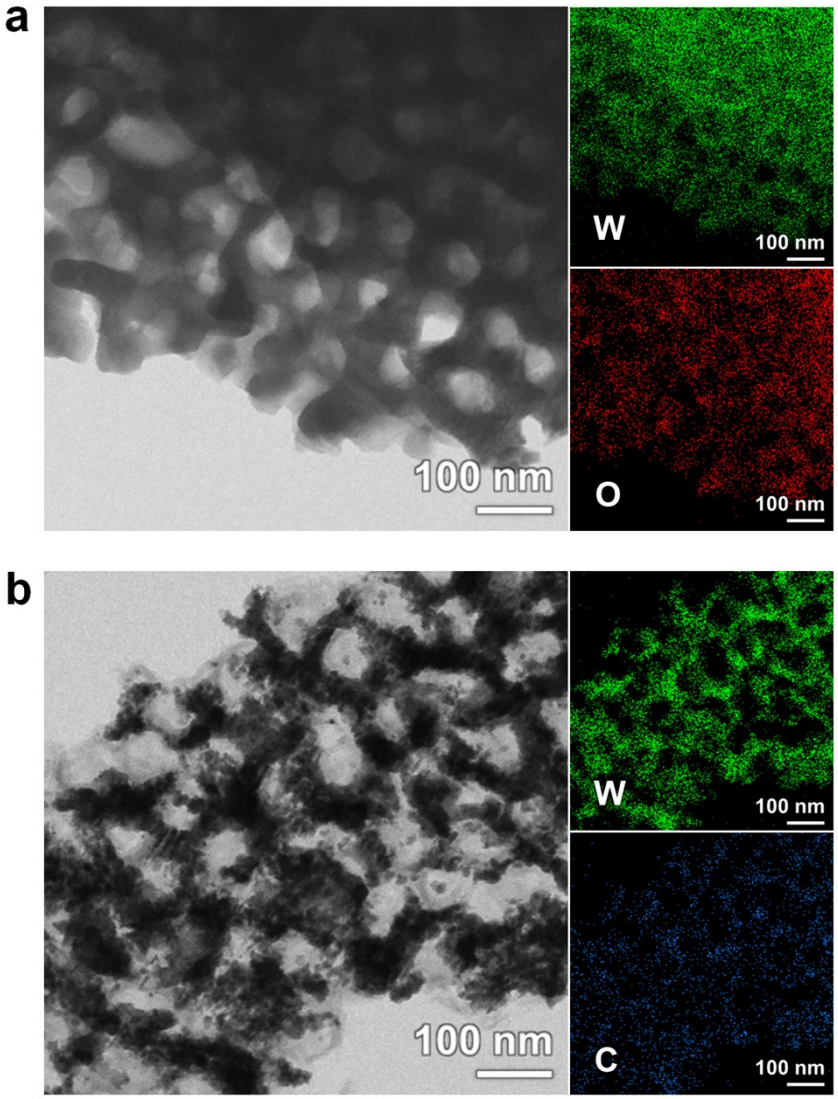

Fig. S3. STEM images and corresponding elemental EDS maps of (a) tungsten oxide and (b) tungsten carbide.

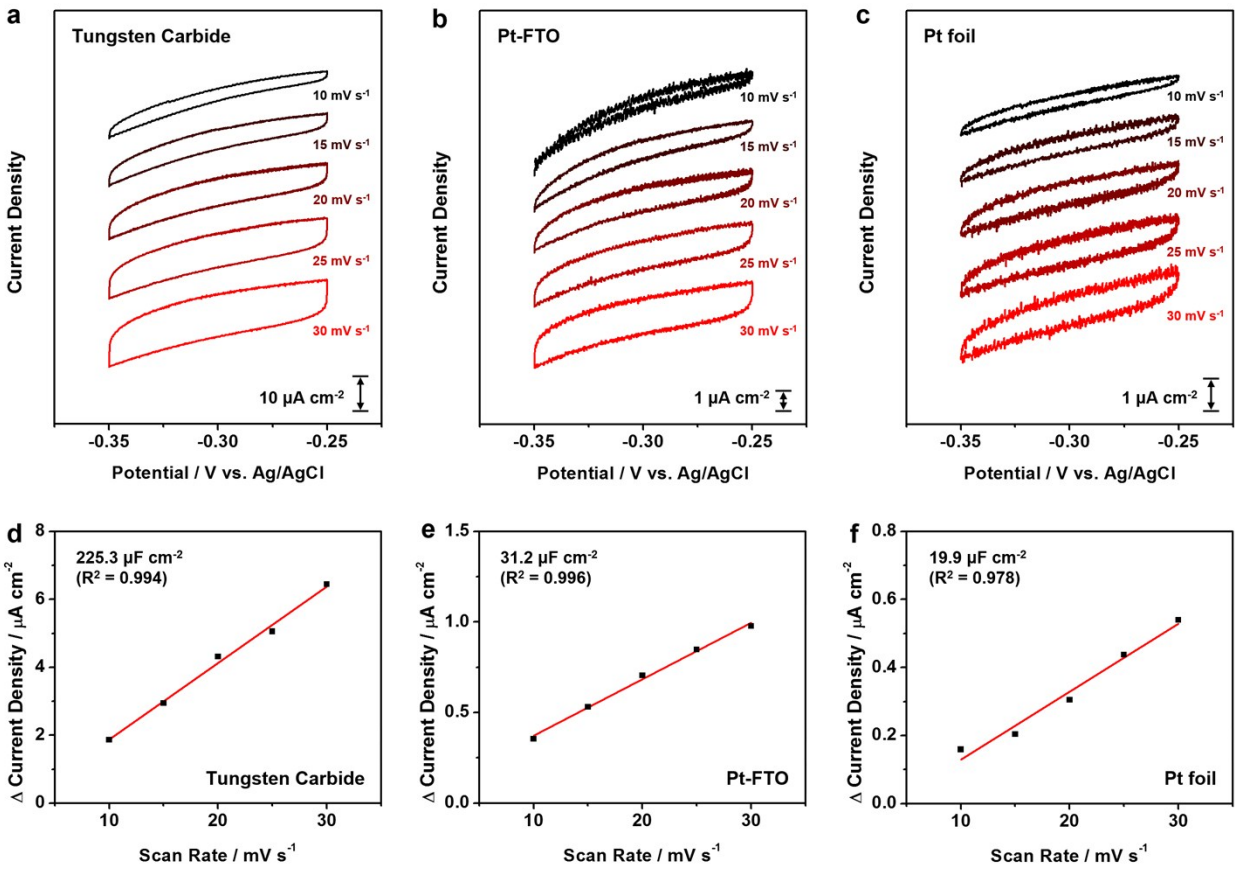

Fig. S4. (a-c) CV diagrams of (a) np-WC, (b) Pt-FTO, and (c) Pt foil measured in the cobalt redox electrolyte at various scan rates. (d-e) Capacitive current densities obtained at -0.3 V vs. Ag/AgCl with regard to the scan rates and their linear fits in the case of (d) np-WC, (e) Pt-FTO, and (f) Pt foil. Electrochemical double layer capacitances were calculated by the slopes of the linear fits.

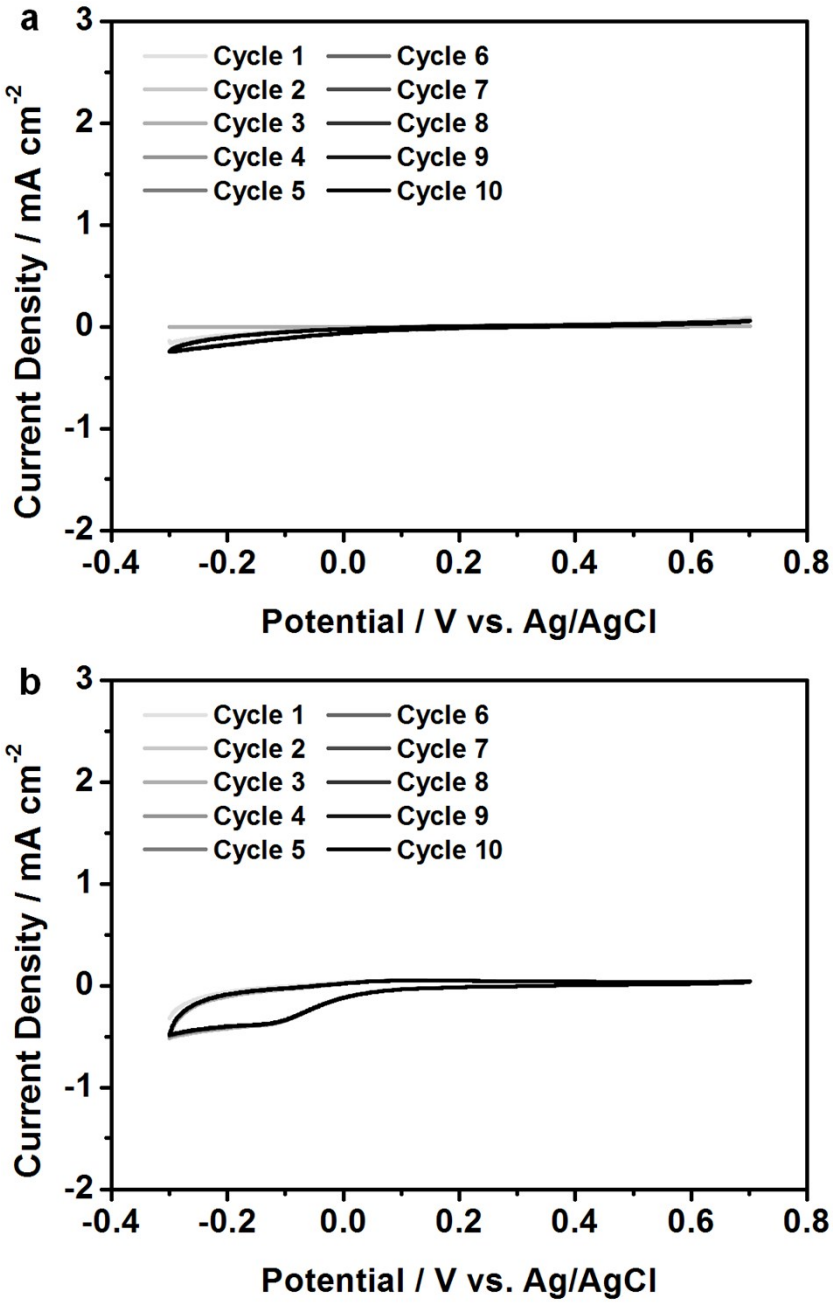

Fig. S5. CV diagrams of tungsten foil and as-anodized tungsten in $[Co(bpy)_3]^{3+/2+}$ redox electrolyte.

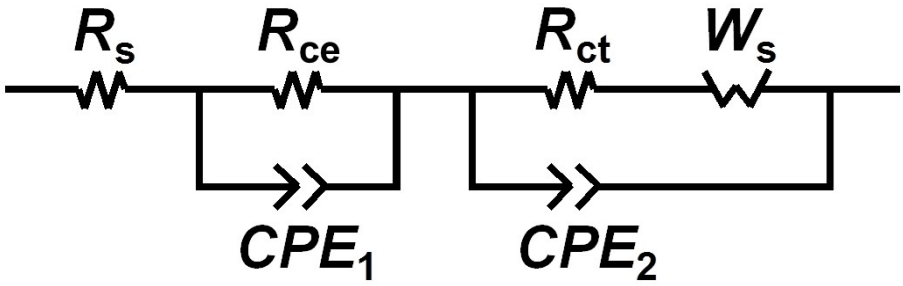

Fig. S6. Equivalent circuit for EIS analysis of DSCs.

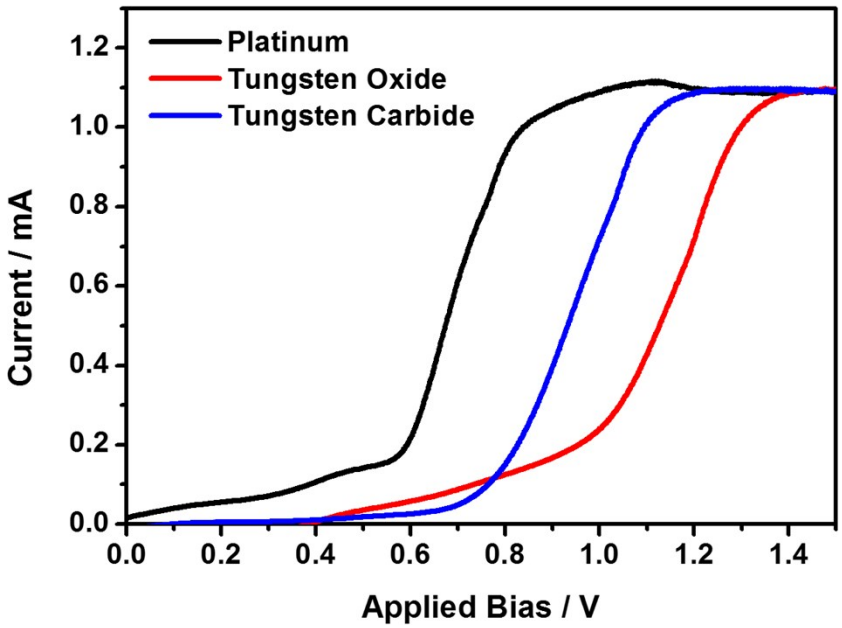

Fig. S7. *I-V* characteristics of two-electrode photoelectrochemical water splitting cell employing Pt, np-WO_3, or np-WC as counter electrode and mesoporous WO_3 as photoanode. The active areas of the counter electrodes and the photoanode were 1.0 cm^2 and 2.0 cm^2, respectively.