Coordination polymer-based supercapacitor with matched energy levels: enhanced capacity under visible light illumination in the presence of methanol

Hong an Tang, [a] Miao Miao Zhang, [a] Yun Gong [*a] and Jian Hua Lin[*a,b]

[a]*College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, P. R. China Tel: +86-023-65678932 E-mail: gongyun7211@cqu.edu.cn*

[b]*State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China Tel: +86-010-62753541 E-mail: jhlin@pku.edu.cn*

Table S1 Selected bond lengths (Å) and angles (º) for CPs **1** and **2**

	CP 1		
Cu(1)-O(1)#1	1.962(4)	Cu(1)-N(5)#1	1.990(5)
Mo(1)-O(1)	1.757(4)	Mo(2)-O(9)#2	2.426(4)
Mo(4)-O(12)	1.678(4)	O(1)-Cu(1)-N(5)	91.23(19)
O(1) -Cu(1)-O(1) #1	180.00(9)	N(5)#1-Cu(1)-N(5)	180.00(12)
O(1)#1-Cu(1)-N(5)	88.77(19)	O(11)-Mo(2)-O(4)	156.58(17)
O(4)-Mo(1)-O(8)	69.37(15)	Mo(3)-O(8)-Mo(1)	90.16(14)
O(10)-Mo(2)-O(9)#2	178.99(18)	Mo(4)-O(13)-Mo(3)	114.34(19)
Mo(4)#2-O(4)-Mo(1)	146.8(2)		
	CP 2		
Cu(1)-N(1)	1.978(10)	Cu(1)-N(2)	1.987(10)
Cu(1)-O(45)	1.916(8)	Cu(1)-O(57)	1.963(9)
Cu(1)-O(32)	2.701(9)	Cu(2)-O(41)	1.959(8)
Cu(2)-O(59)	1.960(8)	Cu(2)-O(58)	2.278(9)
Cu(2)-N(6)	1.997(9)	Cu(2)-N(5)	1.996(9)
Cu(3)-O(49)	1.938(8)	Cu(3)-O(51)	1.936(9)
Cu(3)-N(4)	1.974(11)	Cu(3)-N(3)	1.987(9)
Cu(4)-O(60)	1.991(9)	Cu(4)-O(61)	2.235(9)
Cu(4)-N(8)	1.974(10)	Cu(4)-N(7)	1.989(10)
O(45)-Cu(1)-O(57)	92.5(4)	O(57)-Cu(1)-O(32)	112.1(4)
N(1)-Cu(1)-N(2)	82.6(4)	O(45)-Cu(1)-N(1)	172.0(4)

N(2)-Cu(1)-O(32)	77.8(3)	O(59)-Cu(2)-O(58)	92.6(3)
O(59)-Cu(2)-N(5)	170.6(4)	O(41)-Cu(2)-N(5)	91.5(4)
N(5)-Cu(2)-N(6)	80.0(4)	O(51)-Cu(3)-O(49)	88.9(4)
O(49)-Cu(3)-N(4)	96.3(4)	N(3)-Cu(3)-O(51)	93.5(4)
O(49)-Cu(3)-N(3)	175.4(4)	N(4)-Cu(3)-N(3)	81.7(4)
O(43)-Cu(4)-O(60)	92.7(3)	N(8)-Cu(4)-N(7)	81.3(4)
O(61)-Cu(4)-N(7)	91.0(4)	O(43)-Cu(4)-N(7)	170.0(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z; #2 -x+2,-y+2,-z;

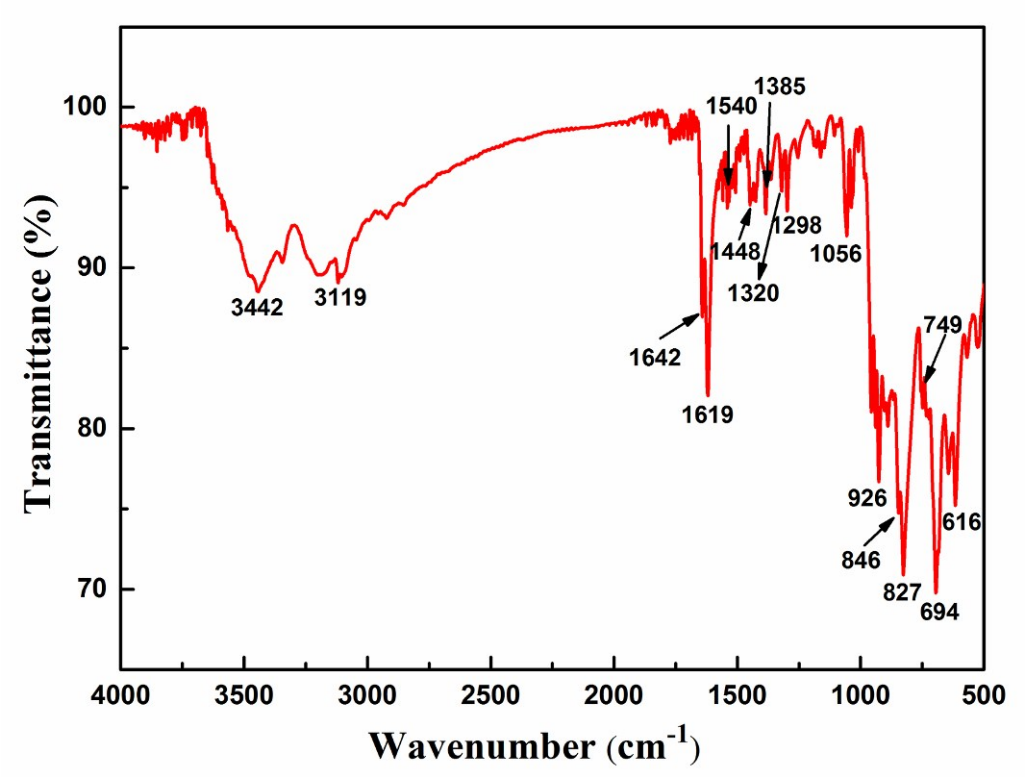
Table S2 Distances (Å) and angles (°) of the selected intermolecular H bonds in CP **2**

D	H	A	D-H	D···A distance	H···A distance	∠D–H···A
O58	H58C	O64#1	0.85	2.929(15)	2.08	172
O60	H60B	O68#2	0.85	2.810(13)	1.99	161
O61	H61C	O40#3	0.85	2.943(12)	2.12	162
O61	H61D	O61#3	0.85	3.161(15)	2.34	162
O63	H63C	O35#4	0.85	3.075(18)	2.31	150
O63	H63D	O48#5	0.85	3.137(18)	2.36	151
O64	H64C	O63	0.85	2.72(2)	1.88	168
O64	H64D	O65#5	0.85	2.881(19)	2.05	167
O66	H66E	O53#6	0.85	2.55(3)	1.74	159
O66	H66F	O55#6	0.85	2.36(2)	1.56	157
O67	H67C	O27#6	0.85	2.937(14)	2.12	160
O67	H67D	O44#7	0.85	2.998(14)	2.19	160
O68	H68C	O26#6	0.85	2.925(13)	2.09	168
O68	H68D	O67	0.85	2.782(16)	1.95	168

Symmetry transformations used to generate the equivalent atoms:

#1 –x+2, -y+1, -z+1; #2 x+1, y, z; #3 –x+2, -y+1, -z; #4 –x+1, -y, -z+1;#5 –x+1,-y+1,-z+1;#6 –x+1, -y+1, -z; #7 x-1, y, z.

(a)



(b)

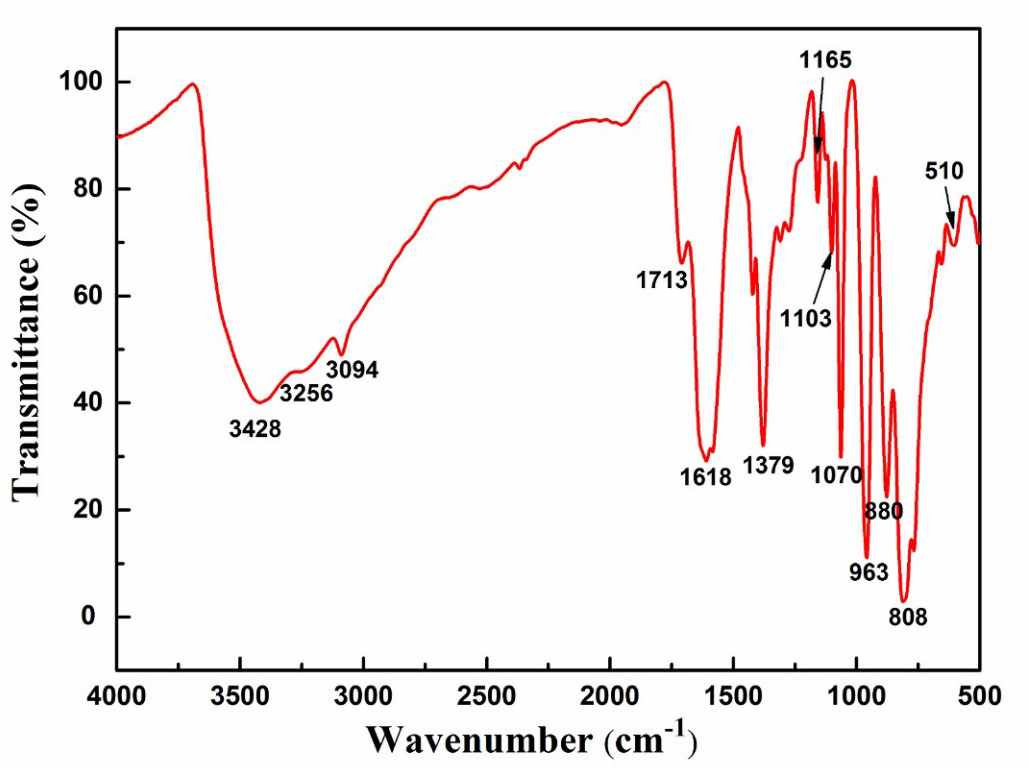
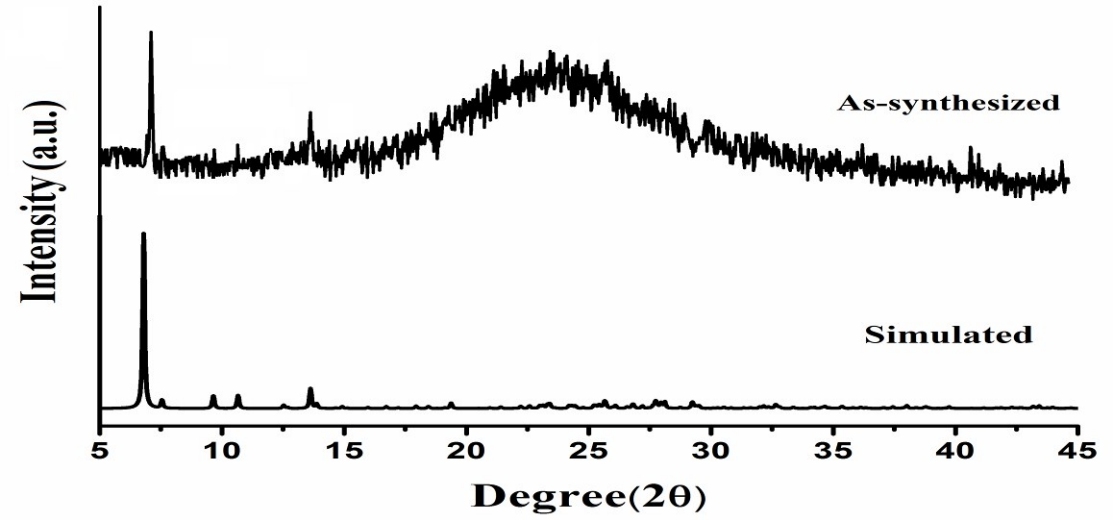


Fig. S1 IR spectra of CPs **1** (a) and **2** (b).

(a)



(b)

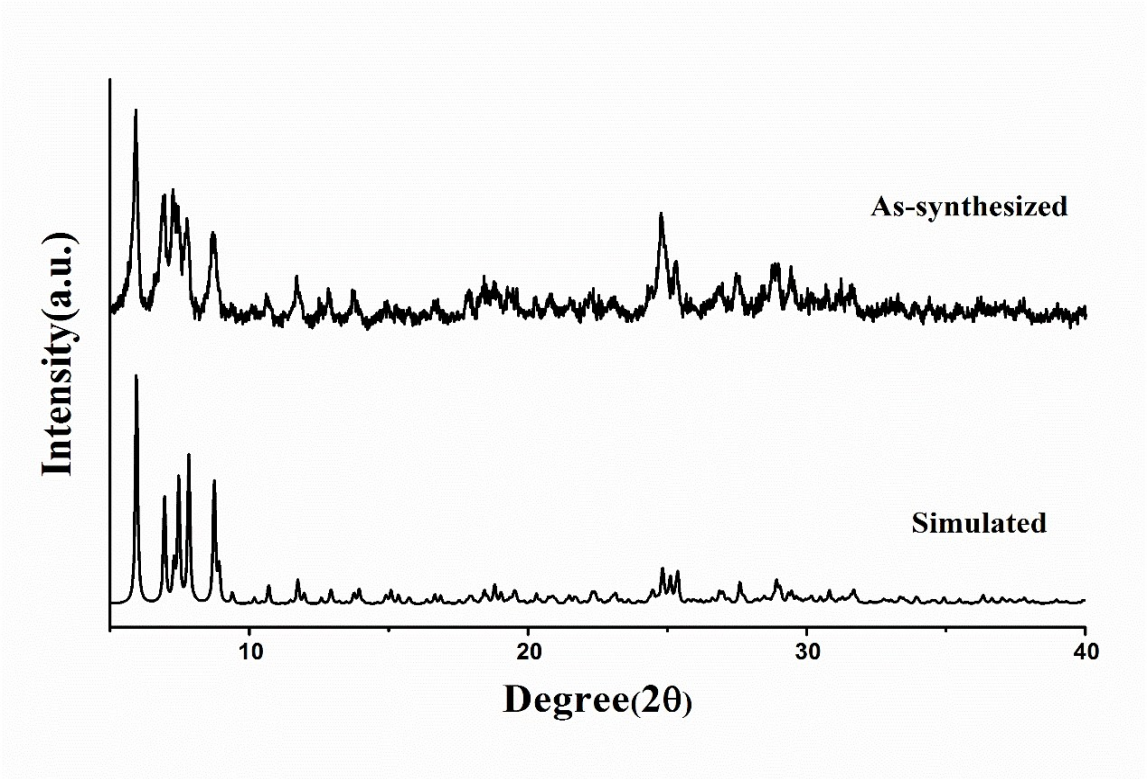


Fig. S2 The PXRD patterns of CPs **1** (a) and **2** (b).

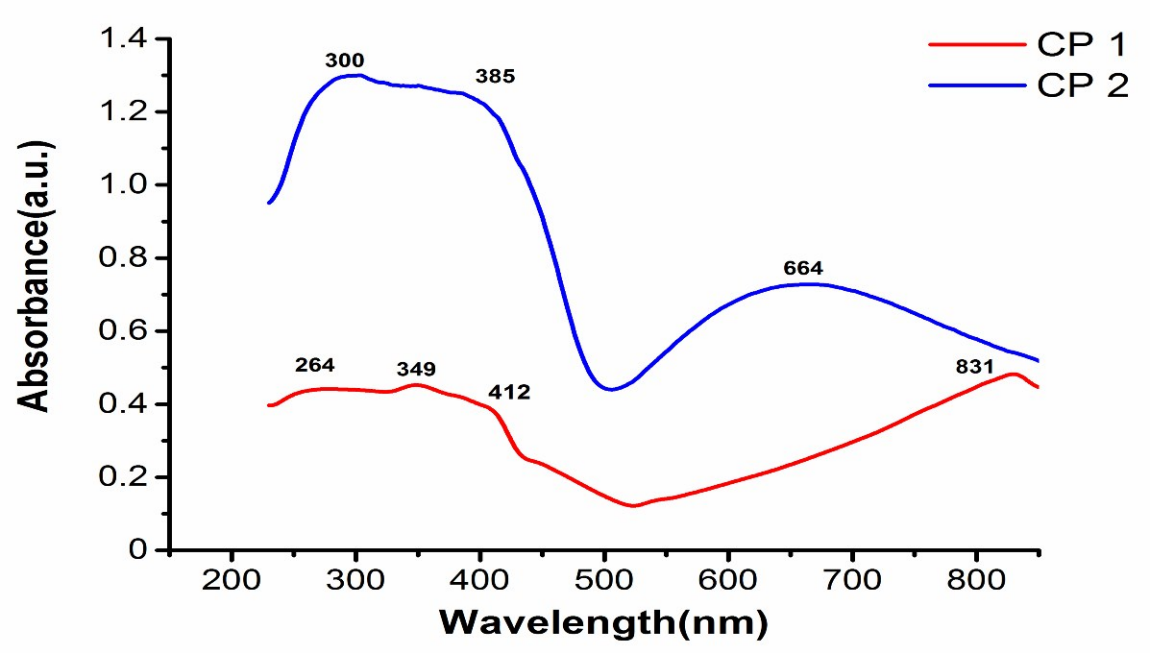


Fig. S3 UV-vis absorption spectra at room temperature for **CPs 1** (red) and **2** (blue)**.**

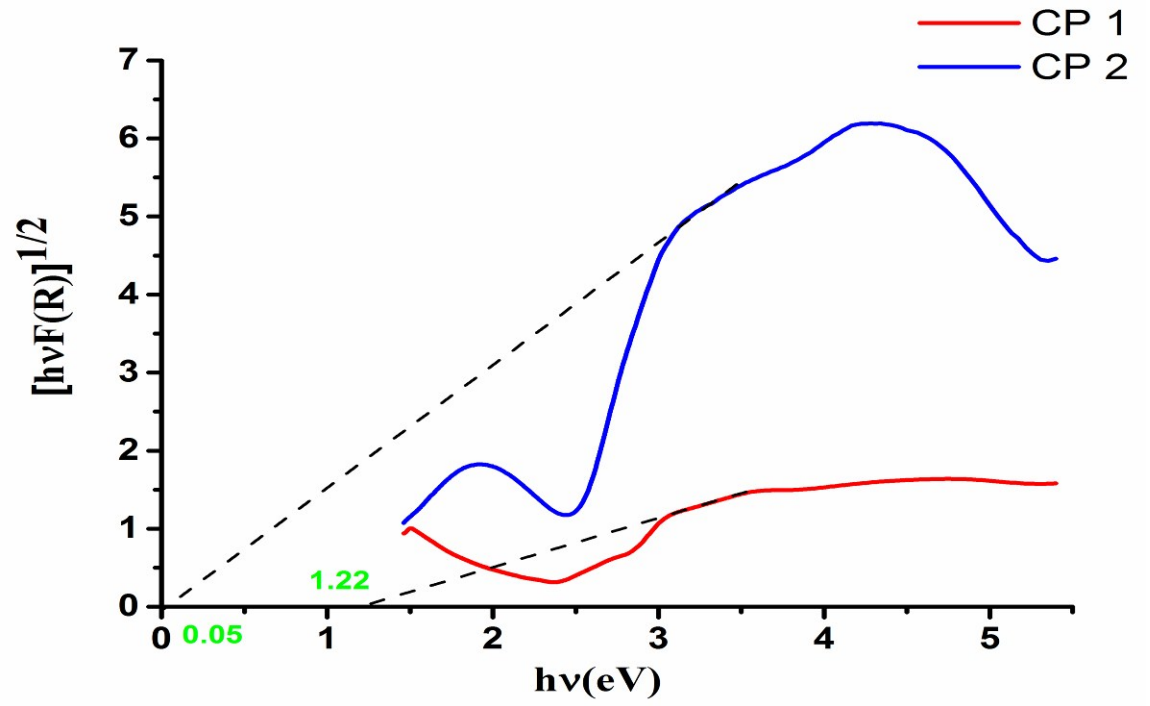
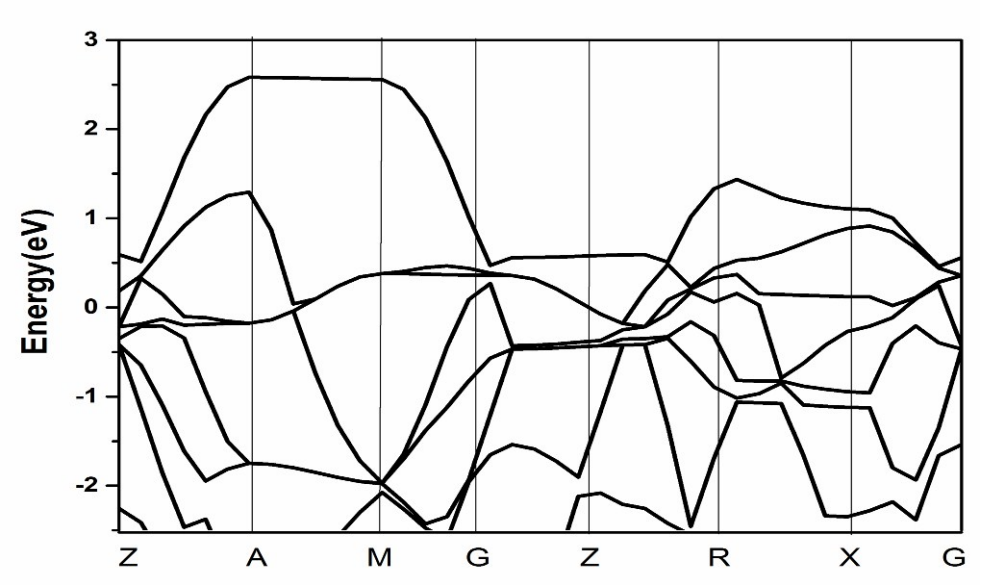


Fig. S4 The diffuse reflectance spectra (DRS) for CPs **1** and **2** in the transformed Kubelka–Munk functions.

(a)



(b)

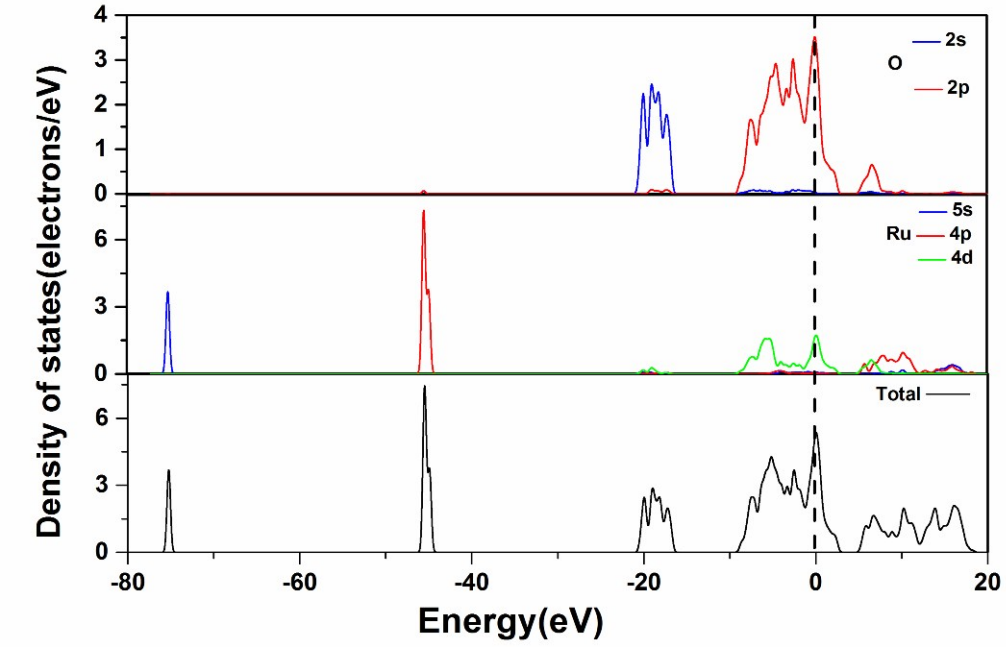


Fig. S5 Band structure (a), and TDOS and PDOS of RuO_2 (b). In the PDOS, blue, red and green lines represent s, p and d orbits, respectively.

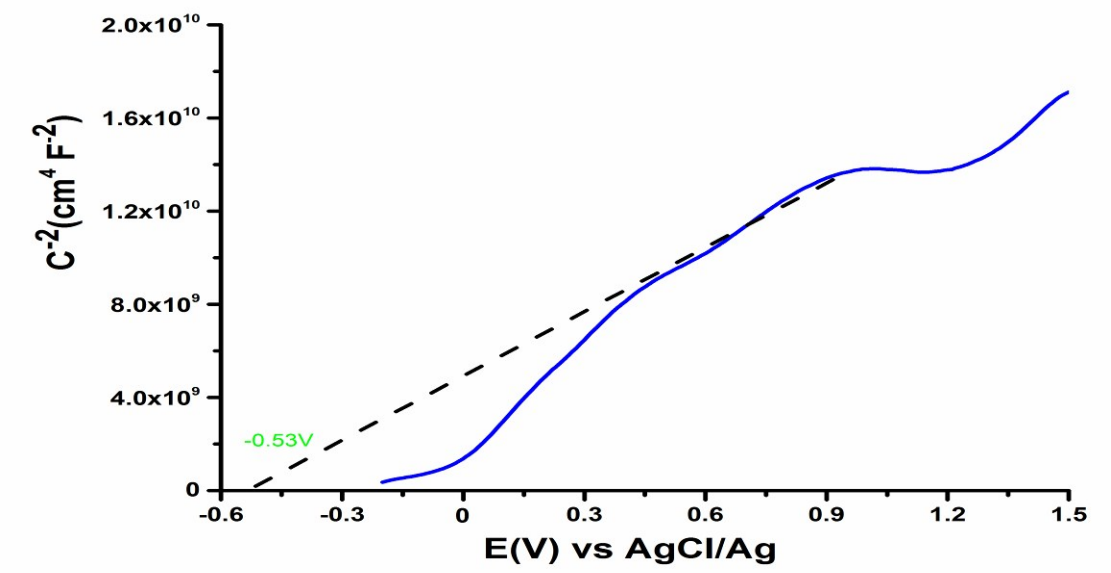


Fig. S6 Mott–Schottky plot of CP **1** in Na_2SO_4 aqueous solution (0.2 M, 50 mL) at the frequency of 1000 Hz in a potential range of -0.6 ~ 1.5 V vs AgCl/Ag (the amplitude of the potential perturbation was 5 mV).

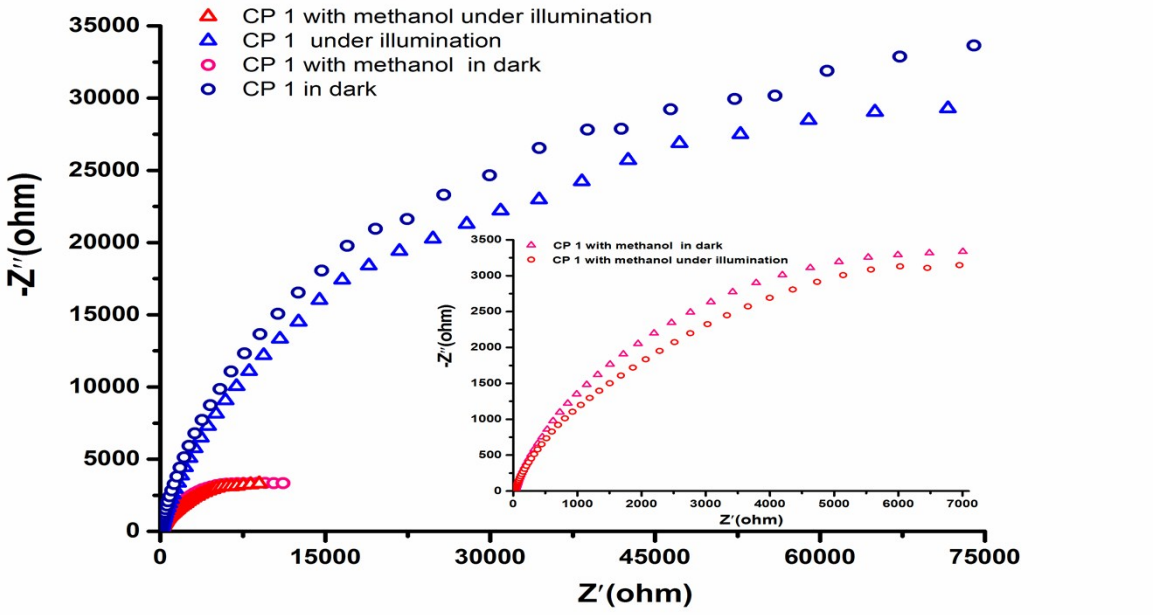
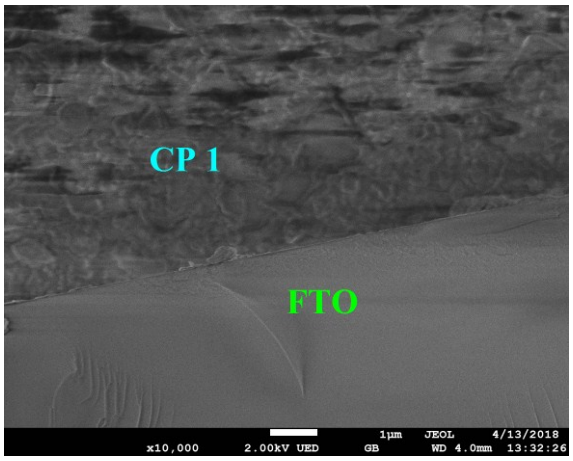
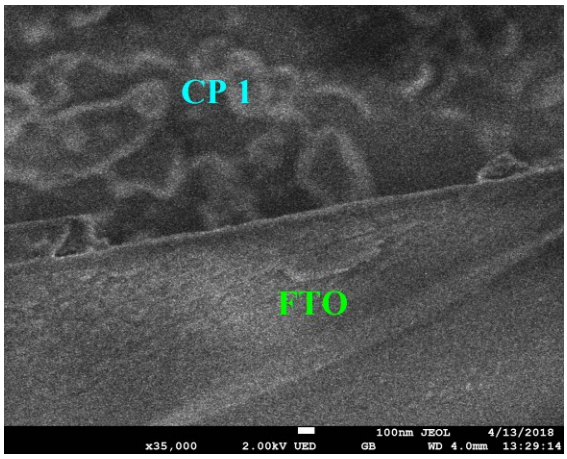


Fig. S7 Nyquist plots (Z' vs. $-Z''$) of CP **1** at 0 V vs AgCl/Ag in Na_2SO_4 aqueous solution with and without methanol in the absence and presence of visible light illumination ($\lambda >$ 420 nm, 100 mW cm^{-2}).

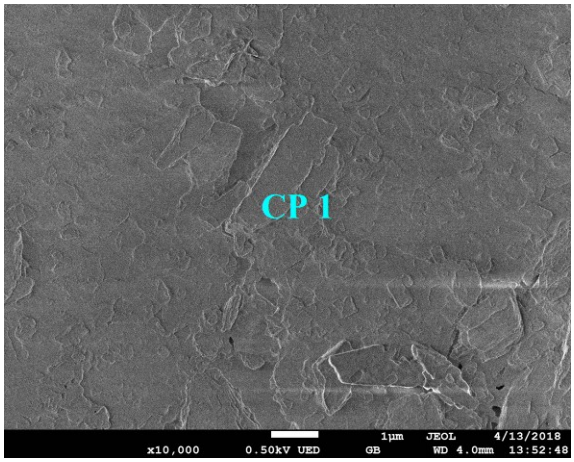
(a)


CP 1
FTO
x10,000 2.00kV UED GB 1μm JEOL WD 4.0mm 4/13/2018 13:32:26

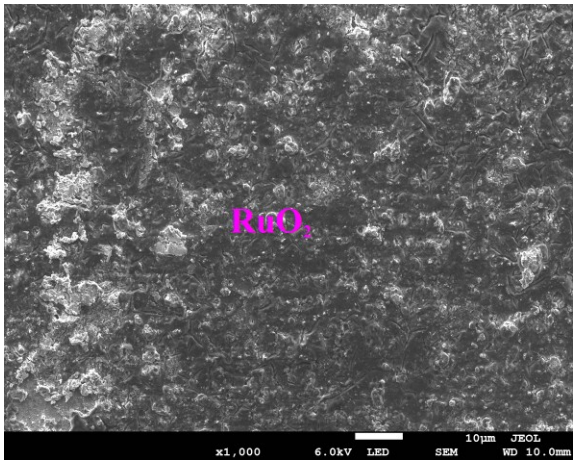
(b)


CP 1
FTO
x35,000 2.00kV UED GB 100nm JEOL WD 4.0mm 4/13/2018 13:29:14

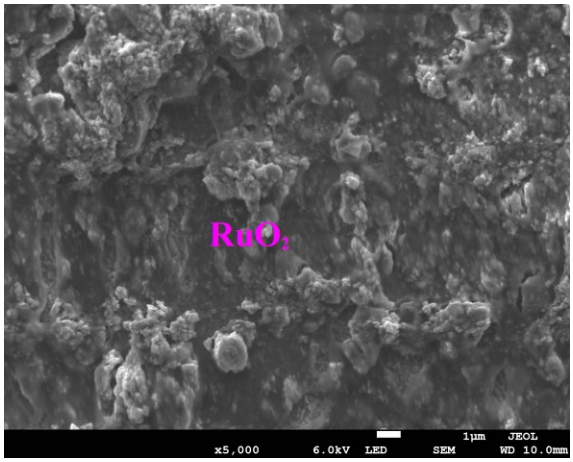
(c)


CP 1
x10,000 0.50kV UED GB 1μm JEOL WD 4.0mm 4/13/2018 13:52:48

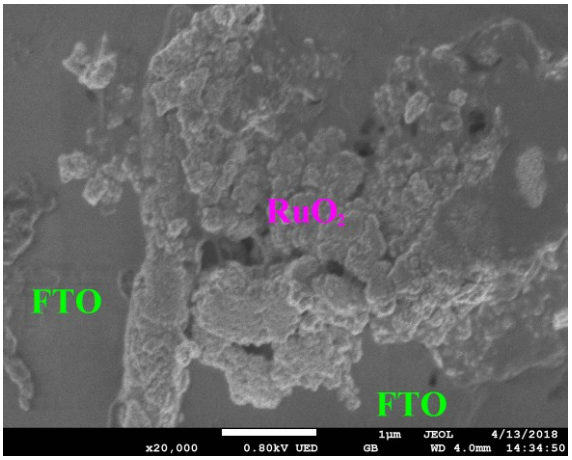
(d)


RuO2
x1,000 6.0kV LED SEM 10μm JEOL WD 10.0mm

(e)


RuO2
x5,000 6.0kV LED SEM 1μm JEOL WD 10.0mm

(f)


RuO2
FTO
FTO
x20,000 0.80kV UED GB 1μm JEOL WD 4.0mm 4/13/2018 14:34:50

(g)

(h)

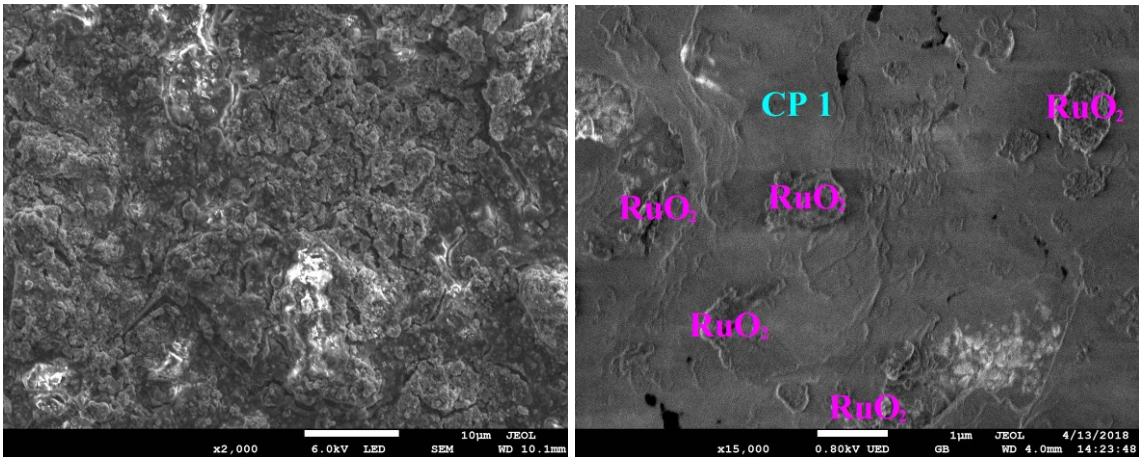
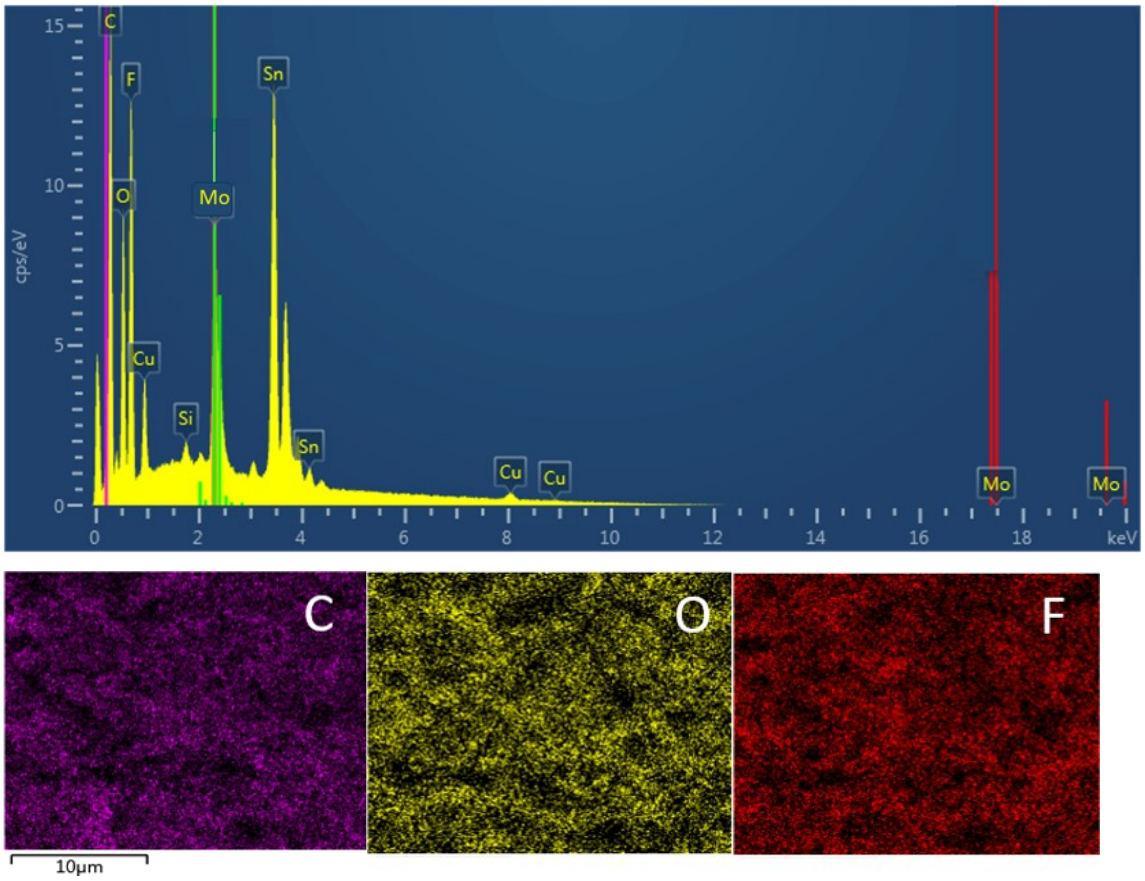
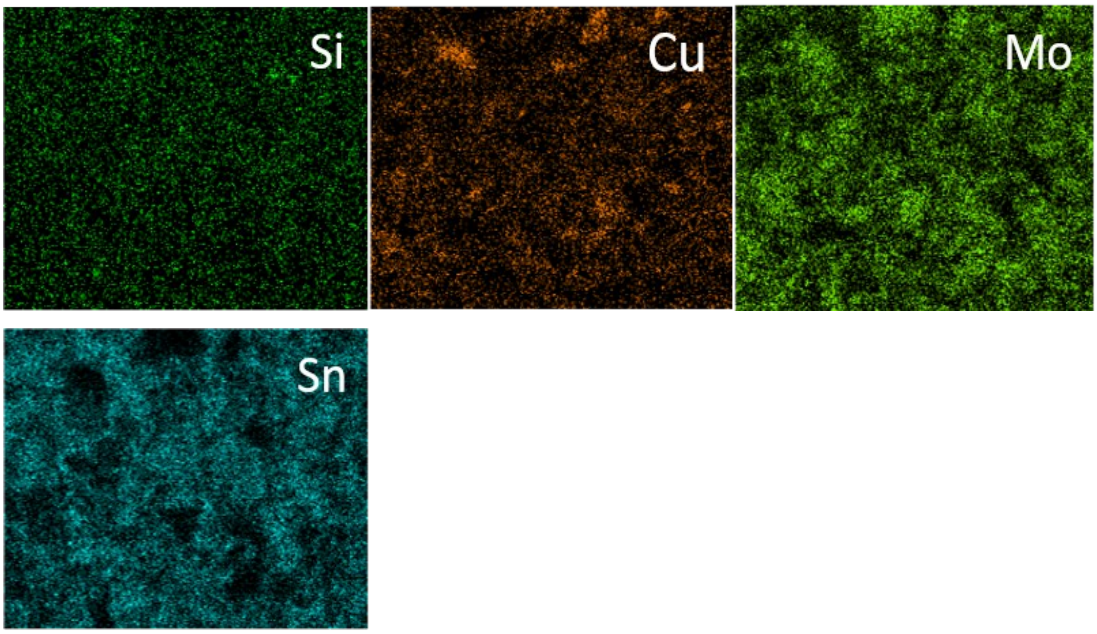


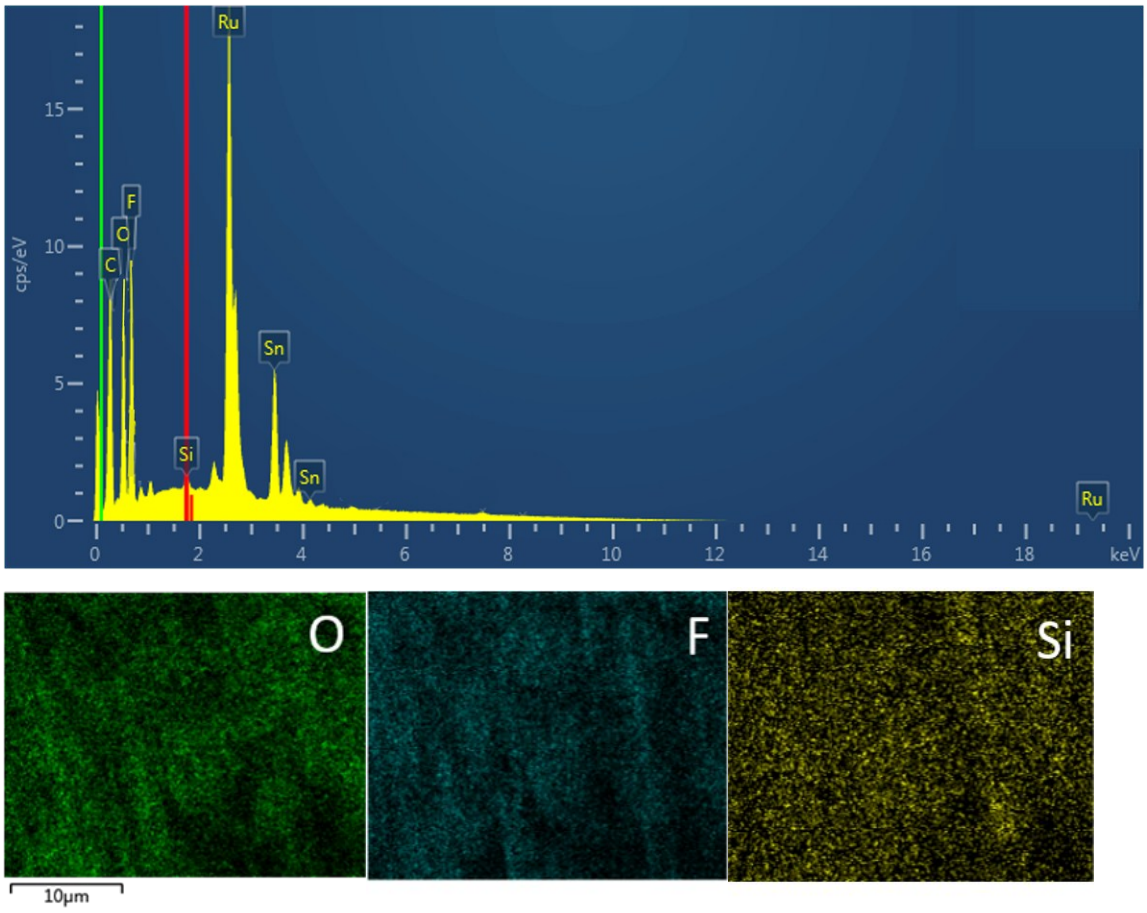
Fig. S8 SEM images of CP **1**-modified FTO (FTO/CP **1**) (a-c), RuO_2-modified FTO (FTO/RuO_2) (d-f) and FTO/CP **1**/RuO_2 (g, h).

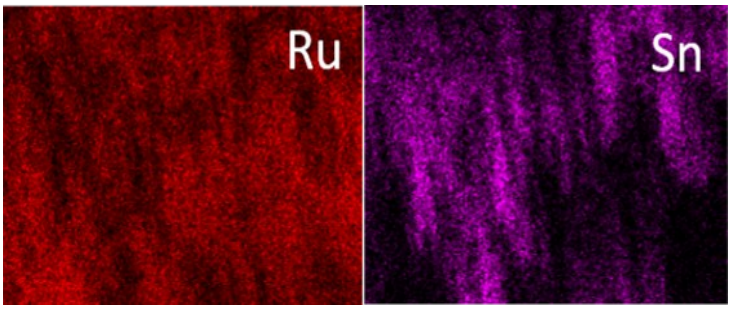
(a)



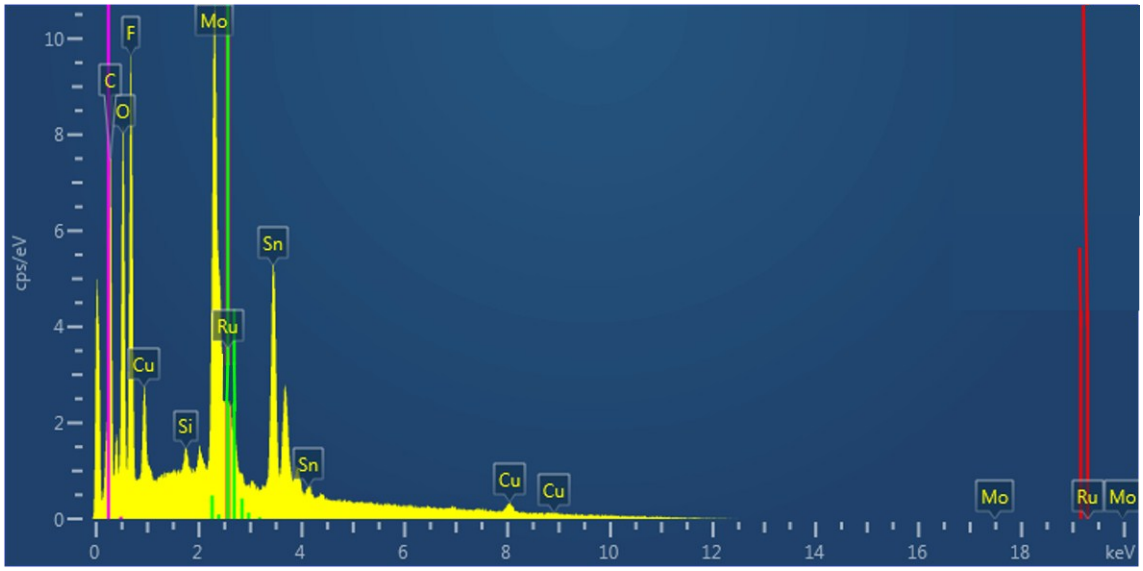

Si
Cu
Mo
Sn

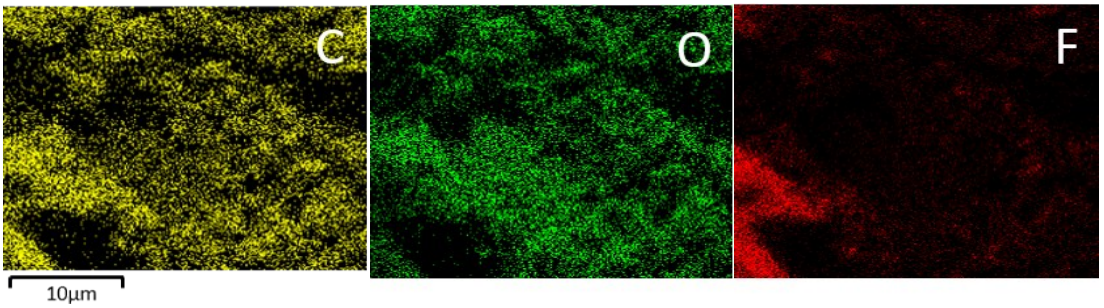
(b)

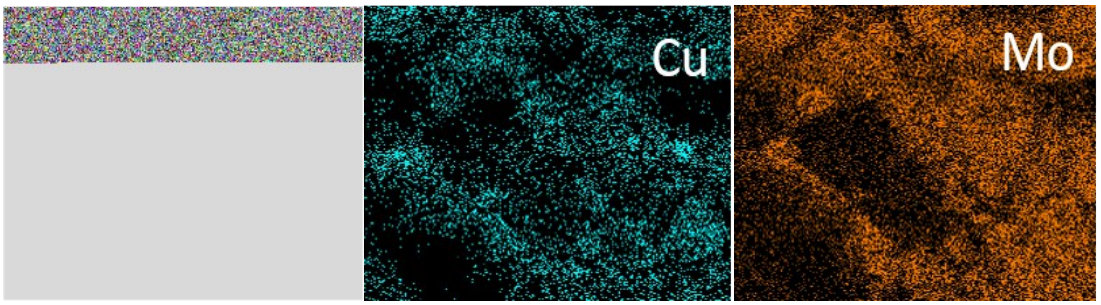

Ru
F
O
C
Sn
Si
Sn
Ru
cps/eV
0
5
10
15
0
2
4
6
8
10
12
14
16
18
keV
O
F
Si
10µm



(c)







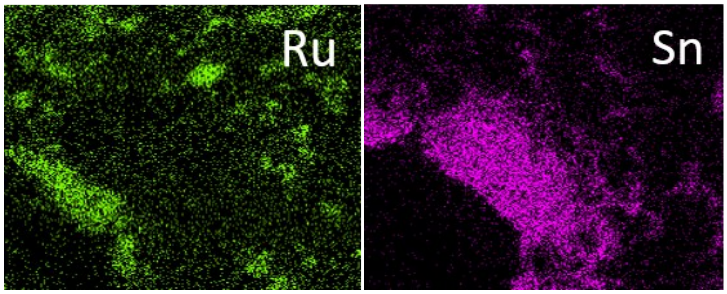
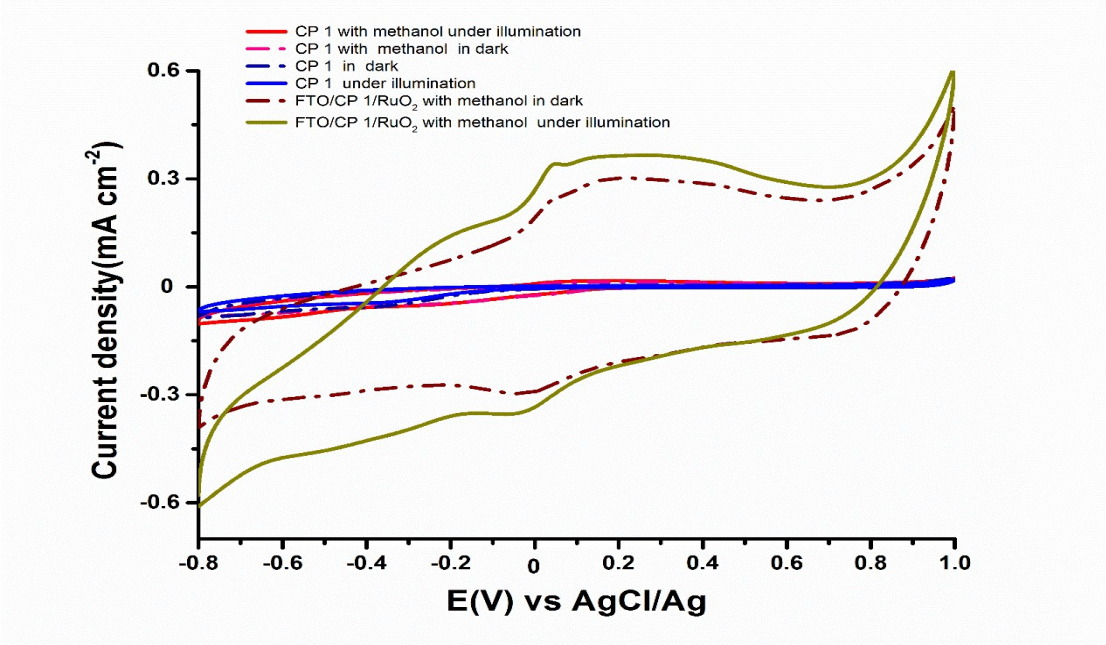


Fig. S9 EDS and elemental mappings for CP **1**-modified FTO (FTO/CP **1**) (a), RuO_2-modified FTO (FTO/RuO_2) (b) and FTO/CP **1**/RuO_2 (c).

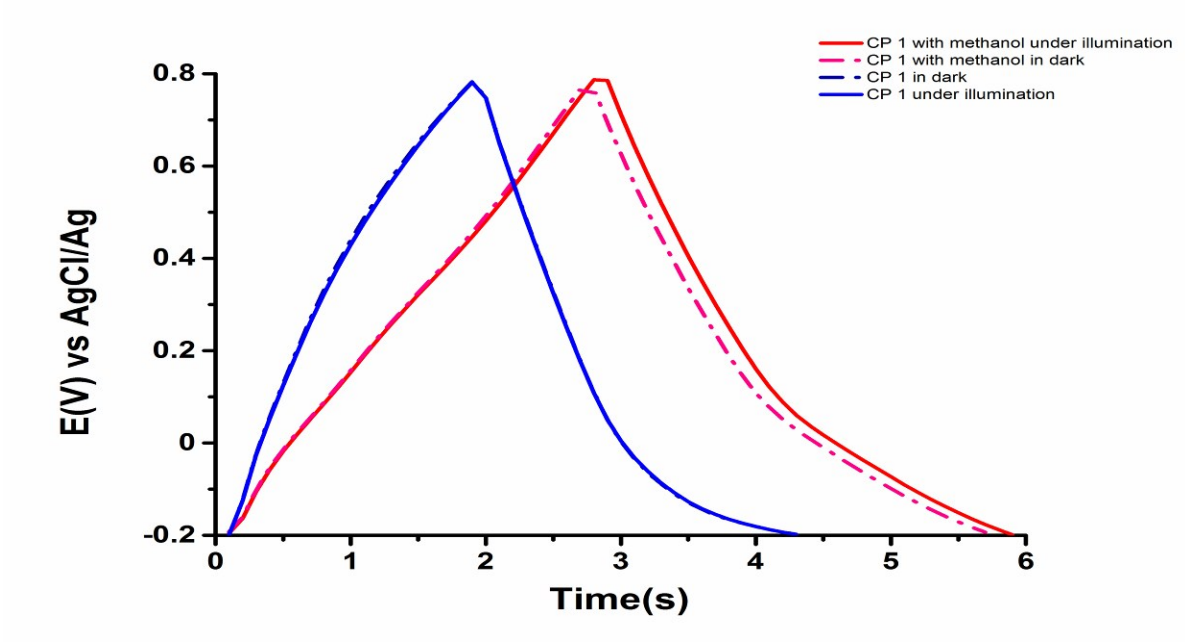
Table S3 The values of the parameters in the equivalent circuits

	R_S/Ω	R_{ct}/Ω	L/H	C/F	Q
RuO_2 with methanol under illumination	30.44	8.66	1.96×10^{-6}	6.11×10^{-6}	4.78×10^{-3}
FTO/CP 1/RuO_2 in dark	25.25	45.47	1.62×10^{-17}	4.85×10^{-5}	4.38×10^{-3}
FTO/CP 1/RuO_2 under illumination	25.26	39.72	1.97×10^{-15}	4.59×10^{-5}	4.36×10^{-3}
FTO/CP 1/RuO_2 with methanol in dark	22.58	19.79	1.86×10^{-15}	3.70×10^{-5}	4.69×10^{-3}
FTO/CP 1/RuO_2 with methanol under illumination	24.27	18.75	3.01×10^{-23}	4.05×10^{-5}	4.77×10^{-3}

(a)



(b)



(c)

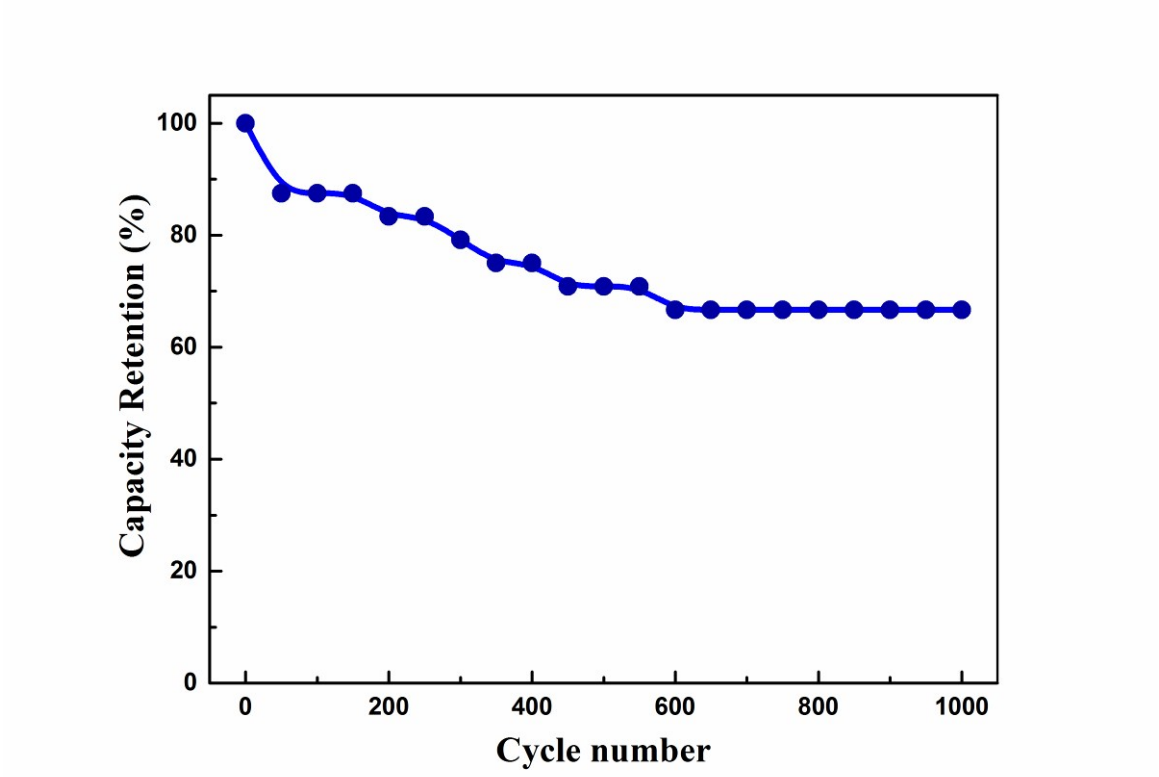


Fig. S10 Comparison of CVs for FTO/CP **1** and FTO/CP **1**/RuO_2 at 0.01 V s^{-1} (a) and GCD curves of FTO/CP **1** at 0.1 A g^{-1} (b) in the Na_2SO_4 solution in the absence and presence of methanol with (solid line) and without (dotted line) visible light illumination

($\lambda > 420$ nm, 100 mW cm^{-2}); 1000 GCD cycles of GCD curves of FTO/CP **1** at 0.1 A g^{-1} in the Na_2SO_4 solution in dark (c).