Supporting Information

Ternary PtRuCu Aerogels for Enhanced Methanol Electrooxidation

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Materials and Methods

Chemicals

Sodium borohydride ($NaBH_4$), Chloroplatinic acid (H_2PtCl_6), Nafion solution (5 wt %), Ruthenium chloride hydrate were all purchased from Sinopharm Chemical Reagent Co. Let (Shanghai, China). Copper chloride was purchased from Alfa Aesar. Platinum on graphitized carbon (20% Pt loading) was purchased from Alorich. KOH was obtained from China National Medicines Corporation Ltd. The water in all experiments was prepared in a three-stage Millipore Milli-Q plus 185 purification system and had a resistivity higher than 18.2 MΩ cm. Unless otherwise stated, other reagents were of analytical grade and were used as received.

Apparatus

X-ray Diffraction (XRD) characterization was carried out by a D8 ADVANCE (Bruker, Germany). Scanning electron microscope (SEM) image was obtained by a Quanta FEG250 field-emission environmental SEM (FEI, United States). Transmission electron microscope (TEM) images were from Titan G260-300 (Thermo Fisher, United States). X-ray photoelectron spectroscopy (XPS) measurements were performed by VG Multilab 2000 (Thermo Fisher, United States). Supercritical CO_2 drying was conducted using SPI-Dry™ critical point drying apparatus (SPI Supplies, USA). The content of each element in the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 8800).

Synthesis of PtRuCu hydrogels

In a typical synthesis of $Pt_4Ru_1Cu_5$ metallic hydrogels, 0.25 mM H_2PtCl_6, 0.05 mM $RuCl_3 \cdot 3H_2O$ and 0.25 mM $CuCl_2$ were added into the 35 mL H_2O, followed by adding 2 mL $NaBH_4$ (0.05 M) under stirring at 60 ℃ for 1 min. The resultant solution was allowed to settle still at 60 °C for 2 h. The as-synthesized $Pt_4Ru_1Cu_5$ hydrogels were washed with water for three times. $Pt_4Ru_1Cu_5$ aerogels could be obtained from supercritical fluid CO_2 drying technique. Pt_5Cu_5, Pt_5Ru_5 and other PtRuCu metallic hydrogels with different chemical compositions were synthesized by varying the mole proportion of Pt, Ru and Cu precursors with the same synthetic process of $Pt_4Ru_1Cu_5$ mentioned above.

Electrocatalytic experiments

All electrochemical measurements were in process with a standard three-electrode system by using electrochemical workstation (CHI-660) at room temperature. The catalyst-modified glassy carbon electrode (GCE, 3 mm diameter) as the working electrode, a $Hg/HgCl_2$ electrode filled with saturated potassium chloride aqueous solution as the reference electrode and Pt wire as the counter electrode. The GCE was prepared by polishing with 1.0 and 0.05 μm alumina powder, respectively, and rinsed with deionized water. For methanol oxidation reaction, 2.5 μL of the as-obtained aerogels (0.2 mg_N/mL) (N represents noble metal) or Pt/C catalyst (1 mg_{pt} /mL) aqueous solution were dropped on the surface of GCE and dried at 50°C, followed by dropping 1.5 μL of Nafion (0.05 %) and dried at 50 °C.

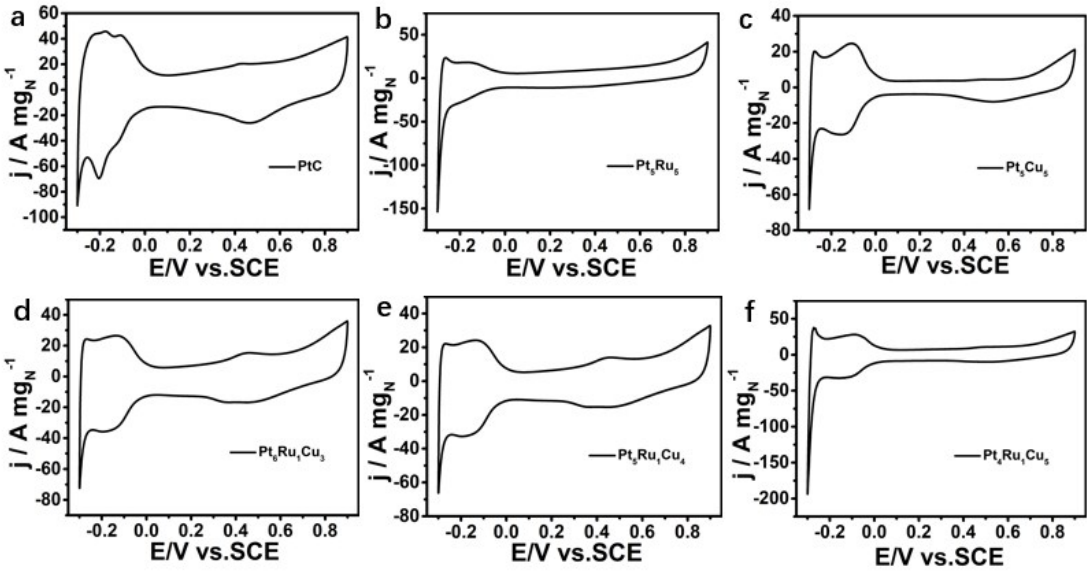

Figure S1. Seperate figures of PtRuCu aerogels with different compositions, Pt_5Ru_5, Pt_5Cu_5 and commercial Pt/C in aqueous nitrogen-saturated 0.1 M $HClO_4$.

Table S1. The composition of the $Pt_6Ru_1Cu_3$、$Pt_5Ru_1Cu_4$、$Pt_4Ru_1Cu_5$、Pt_5Ru_5 and Pt_5Cu_5 aerogels by ICP-OES.

samples	Pt (%)	Ru (%)	Cu (%)
$Pt_6Ru_1Cu_3$	45.10	8.82	44.12
$Pt_5Ru_1Cu_4$	56.86	8.82	34.31
$Pt_4Ru_1Cu_5$	36.00	8.00	56.00
Pt_5Ru_5	45.00	55.00	--
Pt_5Cu_5	48.00	--	52.00

Table S2. XPS peaks for $Pt_4Ru_1Cu_5$、Pt_5Ru_5 and Pt_5Cu_5 aerogels in different regions.

	$Pt_4Ru_1Cu_5$	Pt_5Ru_5	Pt_5Cu_5
Pt (0) $4f_{7/2}$	71.1 eV	71.4 eV	71.3 eV
Pt (0) $4f_{5/2}$	74.6 eV	74.9 eV	74.7 eV
Pt (II) $4f_{7/2}$	72.0 eV	72.3 eV	72.1 eV
Pt (II) $4f_{5/2}$	77.0 eV	77.4 eV	77.3 eV

Table S3. ECSA, onset potentials, mass activities and specific activities for $Pt_6Ru_1Cu_3$, $Pt_5Ru_1Cu_4$, $Pt_4Ru_1Cu_5$, Pt_5Ru_5 and Pt_5Cu_5 aerogels and commercial Pt/C.

samples	ECSA ($m^2\ g^{-1}$)	Onset potentials (vs. SCE)	Mass activities ($A\ mg_N^{-1}$)	Specific activities ($mA\ cm^{-2}$)
$Pt_6Ru_1Cu_3$	47.87	-0.434	1.55	3.52
$Pt_5Ru_1Cu_4$	43.54	-0.419	1.34	3.43
$Pt_4Ru_1Cu_5$	56.47	-0.421	2.07	4.10
Pt_5Ru_5	41.34	-0.486	0.32	1.26
Pt_5Cu_5	42.62	-0.421	1.21	2.85
commercial Pt/C	69.99	-0.418	0.74	1.06

Table S4. The composition of the $Pt_4Ru_1Cu_5$、Pt_5Ru_5 and Pt_5Cu_5 aerogels before and after chronoamperometric experiments by ICP-OES.

samples	Pt (%)	Ru (%)	Cu (%)
$Pt_4Ru_1Cu_5$	36.00	8.00	56.00
	35.00	5.00	60.00
Pt_5Ru_5	45.00	55.00	--
	55.00	45.00	--
Pt_5Cu_5	48.00	--	52.00
	50.00	--	50.00