Supporting information

SO$_2$ electrocatalytic oxidation properties of Pt-Ru/C bimetallic catalysts with different nanostructures

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Experimental details

1. Pretreatment of carbon carrier

A certain amount of carbon black (Carbot Corp., XC-72, BET: 237 m^2/g, CB for short) was weighed and placed in a beaker. Then acetone solution was added, which was about twice the volume of CB, stirred and ultrasonic for 3 h at room temperature. After filtration and washing with deionized water, the filter cake was vacuum-dried at room temperature. The dried sample was placed in a mixture of 10% HNO_3 and 30% H_2O_2 (volume ratio of HNO_3:H_2O_2 was 2:1) and reflux for 5 h at 60 ℃. Filter the sample with deionized water until neutral, then vacuum drying at room temperature.

2. Synthesis of Pt/C, Ru/C, PtRu/C and Ru@Pt/C catalysts

The preparation method of Ru@Pt/C shell-core catalyst is as follows. First, Ru nucleus was synthesized on CB support: $RuCl_2$/EG (0.1 mol/L) solution was mixed with sodium citrate in 25 ml EG with ultrasonic treatment. 10 mg CB support was added in above mixture and ultrasonic for 30 min to form a uniform slurry. Adjusting the mixture to about 10 with 1 M KOH/EG solution and then processing it with a microwave oven (G70F20CN1L-DG(B0), 700 W, Galanz) in heating mode of stopping 10 s for every 60 s, repeated twice. After cooling to room temperature, 10% HNO_3 was added to modulate the pH to below 3. The sample was washed with deionized water until no chloride ions were present in the filtrate and then vacuumized to dry at room temperature. Pt shells are then prepared on Ru cores in the same way, with microwave

treatment of 90 s in a heating mode of stopping 10 s for every 30 s. Because of the large surface energy of Ru nucleus, Pt salt will be nucleated and reduced on Ru nucleus first [1]. The low reduction temperature causes the Pt precursor to deposit on the Ru nanonucleus, avoiding the formation of single metal Pt nanoparticles [2]. The preparation method of Pt/C and PtRu alloy catalysts was the same as above. A certain amount of CB powder, sodium citrate and chloroplatinic acid (or the mixture of chloroplatinic acid and $RuCl_2$) were mixed evenly in ethylene glycol solution with ultrasonic treatment, and the PH was adjusted to 10 with KOH and then placed in microwave oven for 120 s, stopping 10 s for every 60 s. The total load of the metal was 50%, and the molar ratio of Pt/Ru in the bimetallic catalyst was 1:1. Commercial 50% Pt/C catalyst (Johnson Matthey Corp) was used for comparison.

3. Structure characterization of the catalysts

Transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN) was used to determine the morphology and microstructure of the as-prepared catalyst, carried out at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (XRD, X-pert Powder) using Cu-Kα radiation in the 2θ range of 10□-80. The surface structure and composition of the catalysts were characterized by X-ray photo-electron spectroscopy (XPS, VG ESCALAB) with a monochromic Cu-K source (λ = 0.15406 nm). The metal loading of Pt/RGO and Pt/C were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Thermo icap 6300).

4. Electrochemical measurement of the catalysts

Electrochemical measurements of the catalysts were carried out on three-electrode cell by a potentiostat (AUTOLAB PGSTAT302N, Metrohm Technology Ltd.). Figure S1 shows the electrochemical measurement facility. The working electrode was a glassy carbon (GC) electrode of 5 mm in diameter. 15 μl of the catalyst slurry was applied to the pre-polished GC electrode and allowing it to air dry. The catalyst slurry was obtained by mixing the catalysts (2 mg), Nafion aqueous solution (25 μL) and DI water (10 μL) in isopropyl alcohol (435 μL), followed by sonication for 30 min. An Ag/AgCl electrode was used as reference electrode and a spring-shaped Pt wire with diameter of 1 mm were used as the counter electrode. Prior to any electrochemical measurements, the working electrode was cyclic voltammetric treated at a potential range of 0-1.3 V at a scan rate of 50 mV/s to activate the catalyst. The catalytic activity of the catalysts for SO_2 oxidation in high acid environment was determined by cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) measurements. The electrolyte used in the experiment was 13 mol/kg_{H2O} H_2SO_4 solutions saturated with SO_2 which was determined by our previous studies [3]. SO_2 gas was fed into the electrolyte at a flow rate of 15 ml/min for 3 h before the experiment and continued to supply during the experiment to ensure SO_2 saturation. The CV test was measured in a scan range of 0.4-1.3 V with scan rate of 50 mV/s. The EIS test was conducted at 0.6 V, with the amplitude and frequency of the sinusoidal disturbance signal being 10 mV and 10 kHz-10 mHz, respectively. The electrochemical active surface area (*ECSA*) of the catalyst was obtained by cyclic

voltammetric investigation in 0.5 M sulfuric acid solution with scanning range of 0-1.2

V and scan rate of 50 mV/s. All the experiments were conducted at 20 ℃ and all the

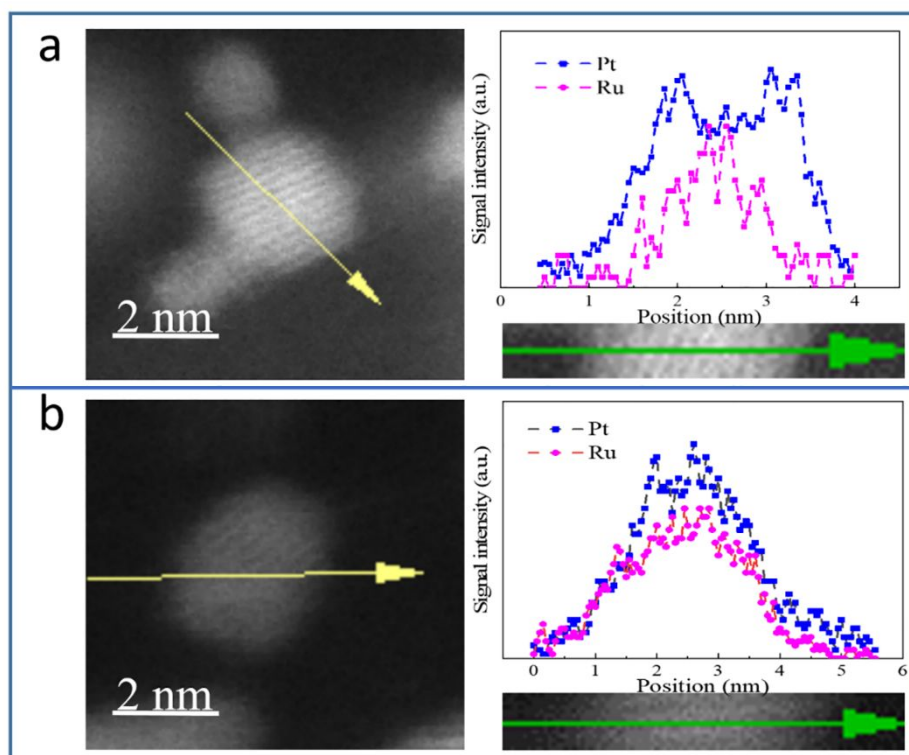potentials shown in this paper were converted to the reversible hydrogen electrode

(RHE) scale.
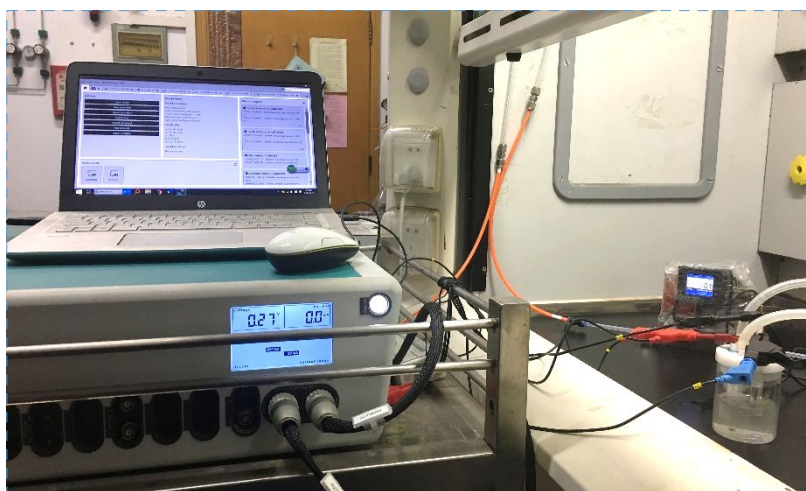
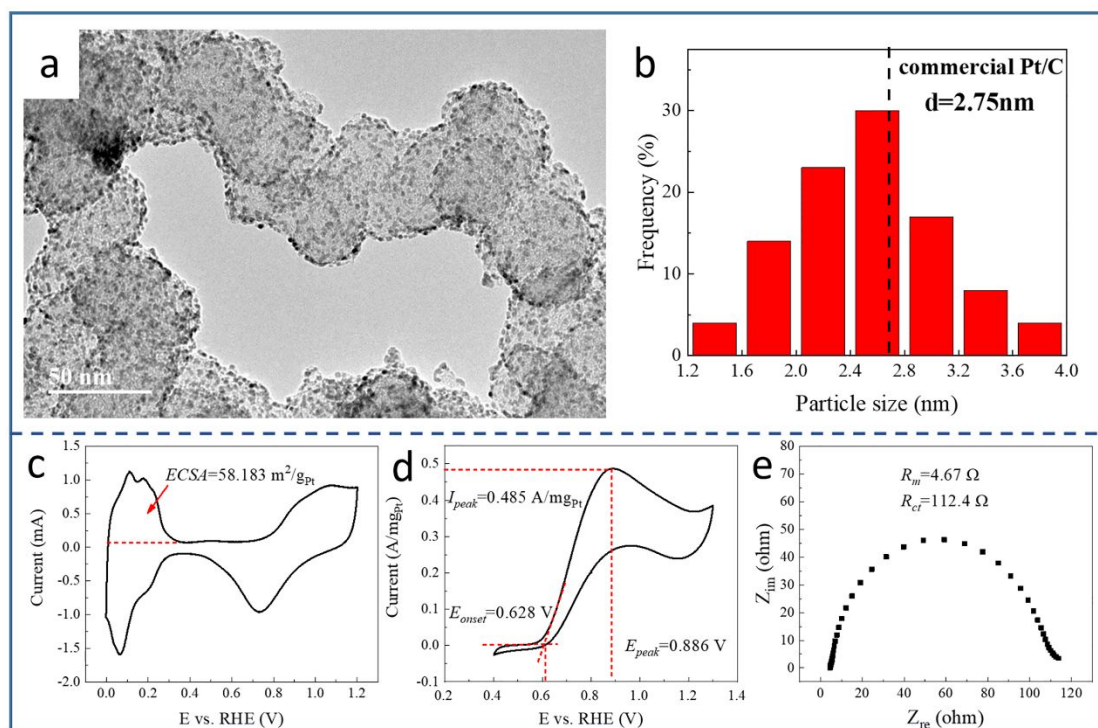**Figure S1.** The picture of electrochemical measurement facility.

Figures
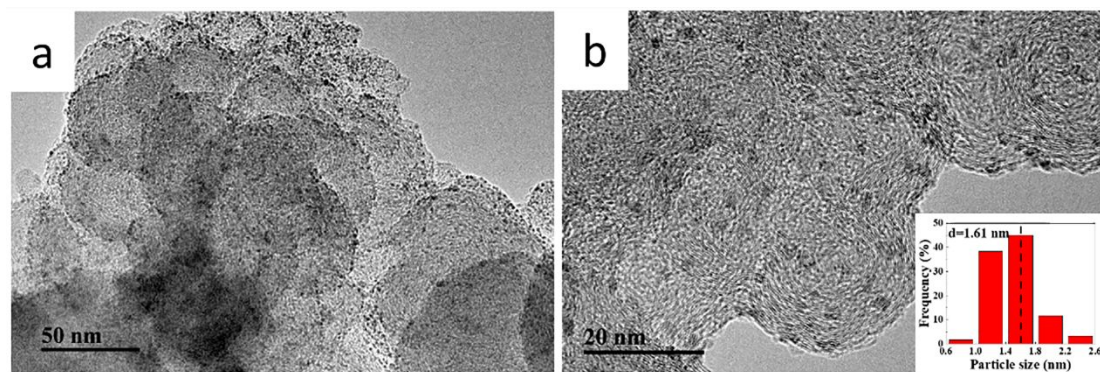
Figure S2. TEM pictures of Ru$_{core}$/C with scale of (a) 50 nm and (b) 20 nm, and the inset is
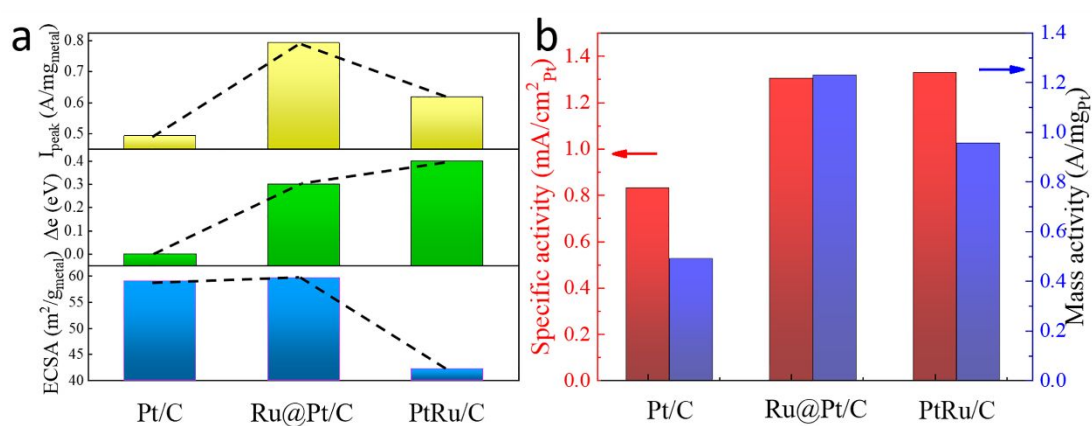
size distribution of Ru.

Figure S3. HAADF-STEM (left) and EDX line-scan (right) of (a) Ru@Pt/C and (b) PtRu/C
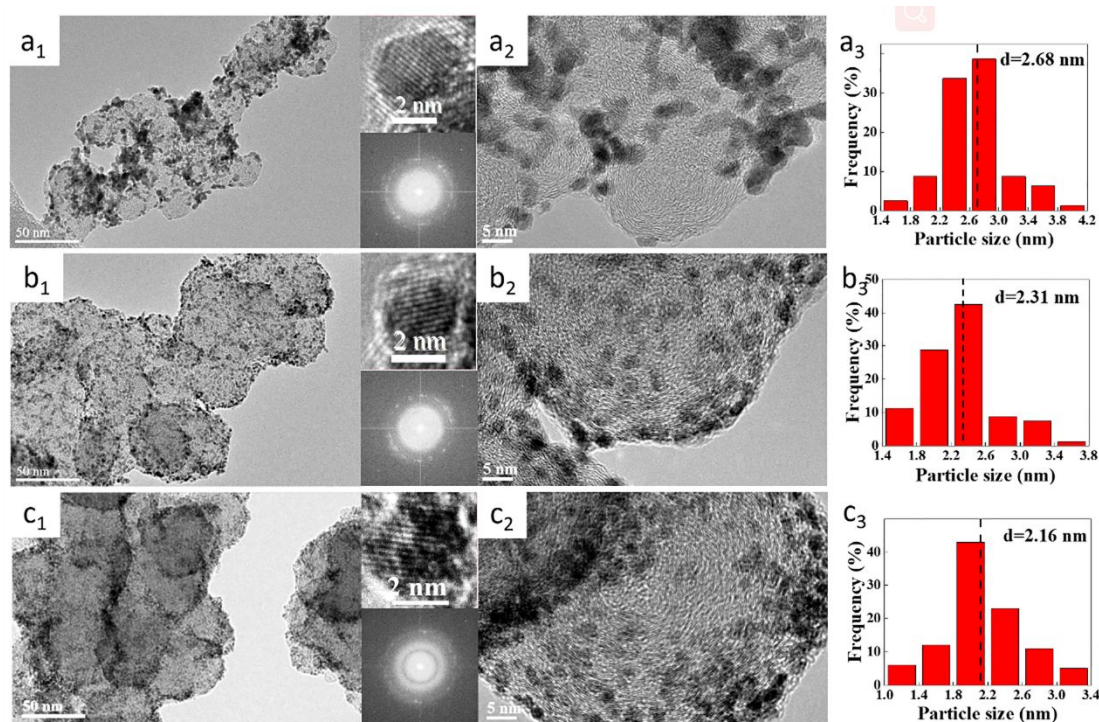
samples.

Figure S4. (a) TEM pictures, (b) particle size distribution, (c) ECSA measurement, (d) CV curve of SO$_2$OR and (e) Nyquist graph of commercial Pt/C catalyst.

Figure S5. (a) Relationship between influencing factors and catalytic activity; (b) activity comparison among the samples.

Figure S6. TEM characterization of (a) Pt/C, (b) Ru@Pt/C and (c) PtRu/C catalysts after stability test, left: scale of 50 nm, middle: scale of 5 nm, and right: particle size distribution.

Tables

Table S1. Content of Pt and Ru in catalysts evaluated by ICP-AES and EDX.

Catalyst	Ru/Pt mass ratio by ICP	Metal loading by ICP	Ru/Pt mass ratio by EDX	Metal loadion by EDX
Pt/C	0:100	53.5	0:100	53.2

Ru@Pt/C	33:67	47.2	37:63	46.6
PtRu/C	44:56	48.6	43:57	45.3

Table S2. XPS analysis data of peak attribution, position and element abundance.

Attribution	Pt $4f_{5/2}$	Pt $4f_{7/2}$	Pt^{2+}	Pt^{2+}	Ru	RuO_2	RuO_xH_y
Pt/C	74.61	71.41	76.23	72.51			
	36.34%	24.64%	26.55%	12.47%			
Ru@Pt/C	75.03	71.72	76.88	73.35	460.75	462.71	465.24
	35.77%	30.13%	17.71%	16.39%	41.55%	28.79%	29.66%
PtRu/C	75.10	71.81	76.73	73.22	459.78	461.21	463.6
	36.11%	22.91%	25.80%	15.18%	49.02%	22.91%	28.07%
Ru/C	-	-	-	-	459.3	461.44	463.78
	-	-	-	-	50.13%	34.64%	15.23%

Table S3. Impedance value obtained by fitting with the equivalent circuit

Catalyst	R_m (Ω)	R_{ct} (Ω)
Pt/C	4.67	114.6
Ru@Pt/C	4.64	40.26
PtRu/C	4.65	74.69

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