Supporting information

Preparation and properties of polypyrrole-modified carbon black supported Pt_3Cu alloy catalyst

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Characterization

Transmission electron microscope (TEM) and JEOL JEM ARM200F scanning electron microscope (SEM) were used to observe the morphology and surface microstructure of the modified carbon carrier. The surface element composition and electronic properties of the catalyst were characterized by Al Kα radiation source in XPS, LAB250 ESCA System, Thermo Fisher, USA. Using (ASP-2460-4N) N_2 adsorption-desorption isotherms to test the pore size distribution and specific surface area on carrier and catalyst. The structural defects of the modified carbon carrier were characterized by Renishaumann microscope with laser at 633 nm.

Electrochemical measurements

Electrochemistry workstation in ZAHNER ENNIUM was used for electrochemical tests using a three-electrode system with Pt filament used as reverse electrode and Ag/AgCl used as reference electrode. 50% Nafion solution (mixed solution of isopropanol and deionized water) is prepared for catalyst dispersion, and the dispersed mixed liquid drops are added to the rotating disk electrode (RDE, 0.196 cm^2) as the working electrode, with a load of 17 ug cm^{-2}. Test in 0.1 M N_2 saturated $HClO_4$ with a scanning rate of 50 mV s^{-1} and a cyclic potential of 0.05–1.1 V by cyclic voltammetry (CV). Linear sweep voltammetry (LSV) was set at a scan rate of 10 mV s^{-1} and a speed of 1600 rmp in 0.1 M $HClO_4$ at saturation O_2. Electrochemical Active Surface Area (ECSA) depends on the charge of the integral hydrogen desorption peak of 0.06–0.4 V in the CV curve. The durability test was conducted in 0.1 M $HClO_4$ solution saturated with O_2 at a scanning rate of 100 mV s^{-1} for 10000 cycles.

Using Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{i_k} + \frac{1}{i_d}$$

The catalyst with dynamic flow density (i_k) of 0.9 V (relative to RHE) was obtained. j represents the measured current density at 0.9 V (relative to RHE), where i_d is the diffusion limiting current density at 0.4 V (relative to RHE). From this, we can obtain the mass activity (MA) and specific activity (SA) of the catalyst, respectively, by normalizing the sum of Pt load and Pt Electrochemical Active Surface Area (ECSA) at the working electrode. The rotating ring-disk electrode (RRDE) test was performed on PARSTAT MC electrochemical workstation (USA) with the formula:

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}}$$

The electron transfer number (n) is calculated by the formula, where D is the current disk, I_R is the ring current, and N (0.40) is the current collection efficiency of RRDE.

The actual application effect of the catalyst is reflected in the performance of single cell. Nafion 211 membrane is used for spraying. The anode is JM Pt/C catalyst, the cathode is JM Pt/C and Pt_3Cu/C@PPy catalyst. The spraying area was 2×2 cm, the anode load was 0.2 mgpt cm^{-2} and the cathode load was 0.1 mgpt cm^{-2}. With the equipment HS330 HEPHAS ENERGY and the operating temperature of 80℃, the prepared membrane electrode assembly MEA (made of CCM, carbon paper and plastic film) is tested in H_2 and O_2 with a flow rate of 300 mL min^{-1} after the cathode and anode are completely humidified.

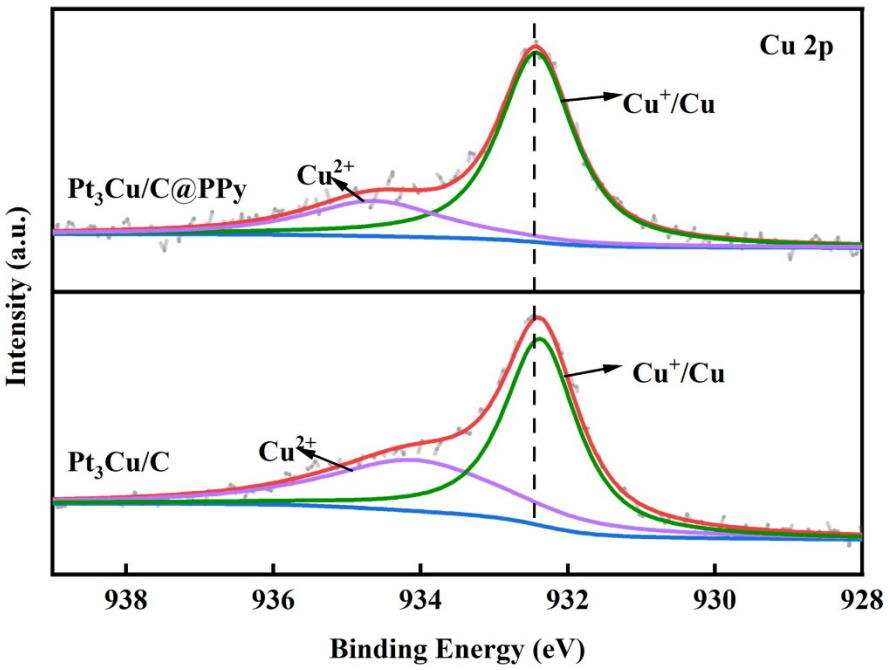

Fig. S1. Cu 2p XPS peak plot of Pt_3Cu/C@PPy and Pt_3Cu/C

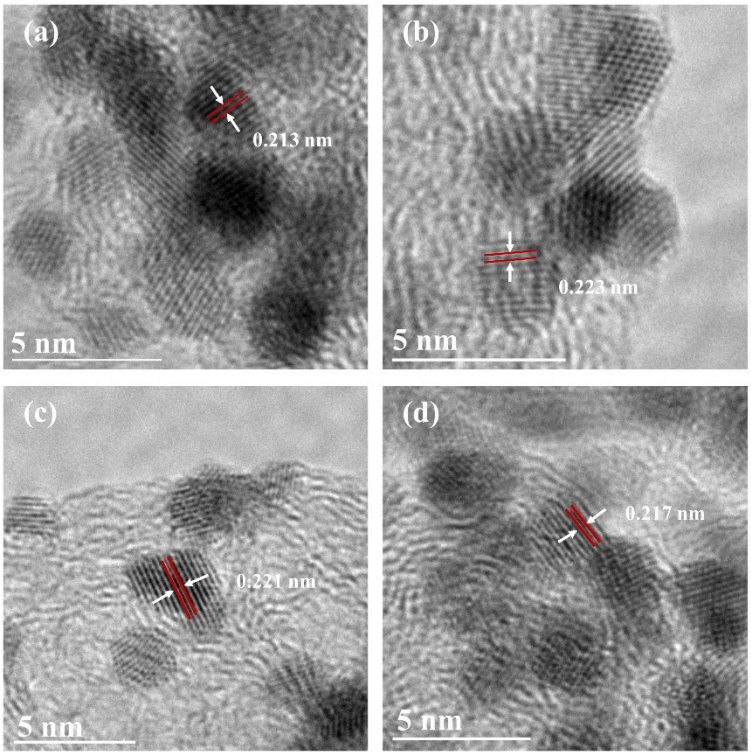

Fig. S2. HR-TEM images of (a) Pt_3Cu/C@0.4-PPy, (b) Pt_3Cu/C@0.2-PPy, (c) Pt_3Cu/C@0.3-PPy, (d) Pt_3Cu/C@0.5-PPy

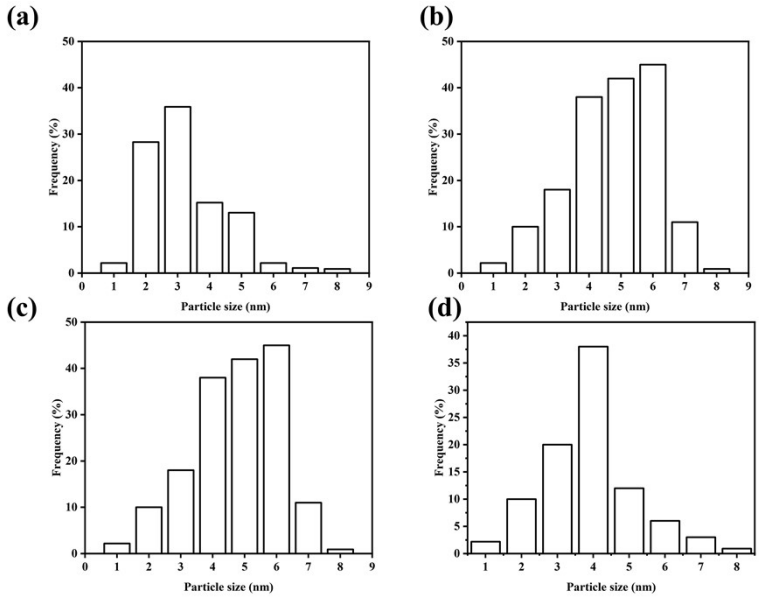

Fig. S3. Particle-size histograms of (a) Pt_3Cu/C@0.4-PPy, (b) Pt_3Cu/C@0.2-PPy, (c) Pt_3Cu/C@0.3-PPy, (d) Pt_3Cu/C@0.5-PPy

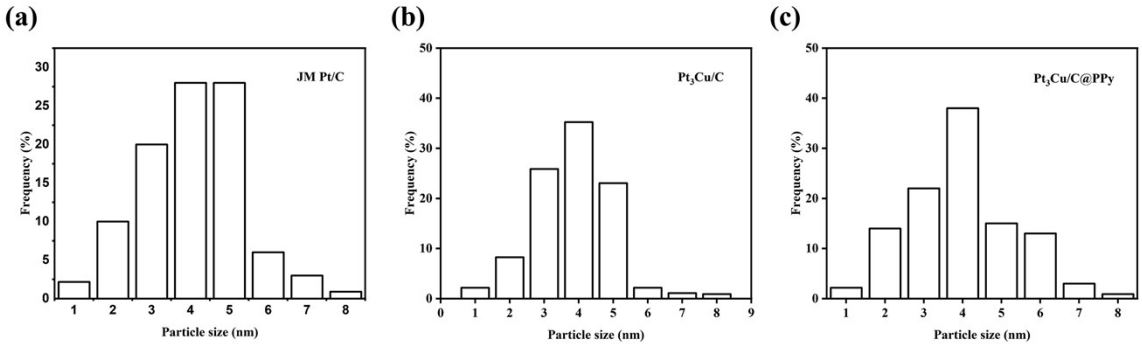

Fig. S4. Particle-size histograms of (a) JM Pt/C, (b) Pt_3Cu/C and (c) Pt_3Cu/C@0.4-PPy after ADT test