Supporting Information Available

Facile synthesis of corallite-like Pt-Pd alloy nanostructures and their enhanced catalytic activity and stability for ethanol oxidation

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Experimental section

Reagents and chemicals

Potassium tetrachloropalladite(II) (K_2PdCl_4), potassium tetracyanoplatinate(II) ($K_2Pt(CN)_4$), and sodium borohydride (NaBH₄) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Commercial Pt black and Pd black were purchased from Johnson Matthey Corporation. All the reagents were of analytical reagent grade and used without further purification.

Synthesis of corallite-like Pt-Pd alloy nanostructures (Pt-Pd CANs)

In a typical synthesis, 4 mL of 50 mM K_2PdCl_4 , 2 mL of 50 mM $K_2Pt(CN)_4$ aqueous solutions were added into a 25-mL beaker, and put in a room temperature for no more than 10 min to generate the $K_2PdCl_4/K_2Pt(CN)_4$ cyanogel. Then 6 mL of 0.1 g mL⁻¹ NaBH₄ solution was added into the $K_2PdCl_4/K_2Pt(CN)_4$ cyanogel and the solution was hold for 2 h. After reduction, the obtained Pt-Pd CANs were collected by centrifugation at 15000 rpm for 5 min, washed with both 0.1 M NaOH and 0.1 M HClO₄ solution twice successively, and then washed with Millipore water and ethanol, dried at 40 °C in a vacuum dryer for 12 h. The base wash process aimed to dissolve the CN⁻ ions and the unreduced cyanogel while the acid wash process could ensure the removal of base.

Electrochemical tests

All electrochemical experiments were performed by using a CHI 660 C electrochemical analyzer (CH Instruments, Shanghai, Chenghua Co.). A standard three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as the auxiliary electrode, a saturated calomel reference electrode (SCE), and a catalyst modified glassy carbon electrode as the working electrode. All potentials in this study were reported with respect RHE All electrochemical measurements were carried out at 30 ± 1 °C.

For preparation of working electrode, a previously reported procedure was used.^{1, 2} An evenly distributed suspension of catalyst was prepared by ultrasonic the mixture of 4.2 mg catalyst and 3 mL H₂O for 30 min, and 4 μ L of the resulting suspension was laid on the surface of the glassy carbon electrode (3 mm diameter, 0.07 cm²). After drying at 40 °C, 2 μ L of Nafion solution (5 wt. %) was covered on the surface of the modified electrode and allowed drying again. Thus, the working electrode was obtained, and the specific loading of metal on the electrode surface was about 80 μ g cm⁻². Cyclic voltammetry (CV) measurements were conducted in N₂-saturated 0.1 M KOH solution.

For CO-stripping measurements, the working electrode surface with catalyst was firstly saturated with CO by bubbling CO through 0.5 M H₂SO₄ solution while holding the working electrode at 0 V for 15 min.³ The remaining CO was purged by flowing N₂ for 30 min before measurements were made. The electrochemically active surface area (ECSA) of catalysts was calculated from the following equation (*eq* 1) by measuring the charge collected in CO adsorption oxidation region and assuming a value of 420 μ C cm⁻² for the adsorption of a CO monolayer.

$$ECSA = \frac{Q}{m \times C}$$
eq 1

where Q was the charge in the CO adsorption oxidation region, m was the loading amount of Pt and Pd metal, and C (420 μ C cm⁻²) was the charge required for monolayer adsorption of CO on Pt and Pd surface.

Instruments

Scanning electron microscopy (SEM) images were captured on a JSM-2010 scanning electron microscopy at an accelerating voltage of 20 kV. The composition of the catalysts was determined using the energy dispersive spectrum (EDX) technique. Transmission electron microscopy (TEM) measurements were made on a JEOL JEM-2100F transmission electron microscopy operated at an accelerating voltage of 200 kV. High-resolution X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K α radiator, and the vacuum in the analysis chamber was maintained at about 10⁻⁹ mbar. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. X-ray diffraction (XRD) patterns of the Pt catalysts were obtained with Model D/max-rC

X-ray diffractometer using Cu K_a radiation source (λ =1.5406 Å) and operating at 40 kV and 100 mA.

Experimental data



Fig. S1. EDX pattern of the Pt-Pd CANs.



Fig. S2. XRD pattern of the Pt-Pd CANs.



Fig. S3. XPS spectrum of the Pt-Pd CANs.



Fig. S4. (A) XPS spectra of the Pt-Pd CANs and Pt black in the Pt 4f region. (B) XPS spectra of the Pt-Pd CANs and Pd black in the Pd 3d region.



Fig. S5. Cyclic voltammograms of preadsorbed CO at the Pt-Pd CANs, commercial Pd black and commercial Pt black modified electrodes in $0.5 \text{ M H}_2\text{SO}_4$ solution at the rate of 50 mV s⁻¹.



Fig. S6. TEM image of (A) Pd black and (B) Pt black.



Fig. S7. CV curves for (A) the Pt-Pd CANs, (B) commercial Pd black and (C) commercial Pt black in N₂-saturated 0.1 M KOH solution before and after 1000 cycles at a scan rate of 50 mV s⁻¹.



Fig. S8. ECSA-normalized cyclic voltammograms for the Pt-Pd CANs, Pd black and Pt black in solution of 1.0 M ethanol + 0.5 M KOH at a scan rate of 50 mV s⁻¹.



Fig. S9. Chronoamperometry curves for the Pt-Pd CANs, Pd black and Pt black in solution of 1.0 M ethanol + 0.5 M KOH for 2000 s at 0.75 V potential.



Fig. S10. CV curves of the Pt-Pd CANs, Pd black and Pt black in N_2 -saturated 0.1 M KOH solution at 50 mV s⁻¹.

References

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