Electronic supplementary information for:

Trimetallic PtCuCo hollow nanospheres with dendritic shell for enhanced electrocatalytic activity toward ethylene glycol electrooxidation

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1. Experimental Section

1.1. Materials

Trisodium citrate (TSC) and $CuCl_2$ was obtained from Beijing Chemical Corp (China). Chloroplatinic acid and $CoCl_2$ were obtained from Sinopharm (Shanghai, China). Nafion ethanol solution (5 wt.%) and sodium borohydride were obtained from Aldrich. Commercial Pt catalyst was purchased from Alfa Aesar (A Johnson Matthey Company). Water used through the experiments was Milli-Q ultrapure water (Millipore, $\geqslant$ 18.2 MΩ cm). All chemicals used in this experiment were of analytical grade and used as received without any further purify steps.

1.2. Synthesis of PtCuCo HDNPs

Firstly, 0.5 mL of $CoCl_2$ (0.2 mol L^{-1}) and 1 mL of TSC (0.2 mol L^{-1}) were added into 100 mL of water, and purged with highly purified N_2 for at least 30 min. Then 10 mL of aqueous solution containing 19 mg of sodium borohydride were added slowly to the above mixture. After aged for 15 min, a mixture containing 172 μL of H_2PtCl_6 (0.193 mol L^{-1}) and 340 μL of $CuCl_2$ (0.1 mol L^{-1}) was dropped to the above solution with a pipette. Another two kinds of PtCuCo HDNPs were also synthesized just by tuned the volume of precursors, 208 μL of H_2PtCl_6 (0.193 mol L^{-1}) and 200 μL $CuCl_2$ (0.1 mol L^{-1}), 130 μL of H_2PtCl_6 (0.193 mol L^{-1}) and 500 μL $CuCl_2$ (0.1 mol L^{-1}), respectively. The products were collected via centrifugation at 8000 rpm for 15 min and washed several times with water, finally the products were concentrated for the further characterizations.

1.3. Material structural and compositional characterizations

TEM and high-resolution transmission electron microscopy (HRTEM), HAADF-STEM, elemental mapping, EDS and cross-sectional compositional line profiles measurements of PtCuCo HDNPs were made on a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. The compositions of PtCuCo HDNPs were determined by ICP-MS (X Series 2, Thermo Scientific USA). Low resolution TEM images were recorded by HITACHI H-600 Analytical TEM with an accelerating voltage of 100 kV. XRD patterns of PtCuCo HDNPs were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu−Kα radiation with a Ni filter (λ = 0.154059 nm at 30 kV and 15 mA). XPS measurements of PtCuCo HDNPs were performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al Kα X-ray radiation as the X-ray source for excitation.

1.4. Ethylene glycol electrocatalytic oxidation measurements

The catalytic performance measurements of PtCuCo HDNPs for the EGORs were carried out on a CHI 832B electrochemical workstation (Chenhua Instruments Corp, Shanghai, China), the system containing a three-electrode cell that composed of an Ag/AgCl (saturated KCl) electrode, a platinum wire electrode and modified glassy carbon electrode (GCE) as reference electrode, counter electrode and working electrode respectively. Prior to each catalytic test, the GCE was polished carefully by alumina powder and further cleaned by sonication in ethanol and water. Then, commercial Pt catalyst or the prepared PtCuCo HDNPs catalyst solution (the loading weight of Pt is 53.2 μg cm^{-2}) was deposited on GCE and dried by using an infrared

lamp carefully. Then, 5 μL of Nafion (0.5%) was deposited on the above GCE and dried before measurements.

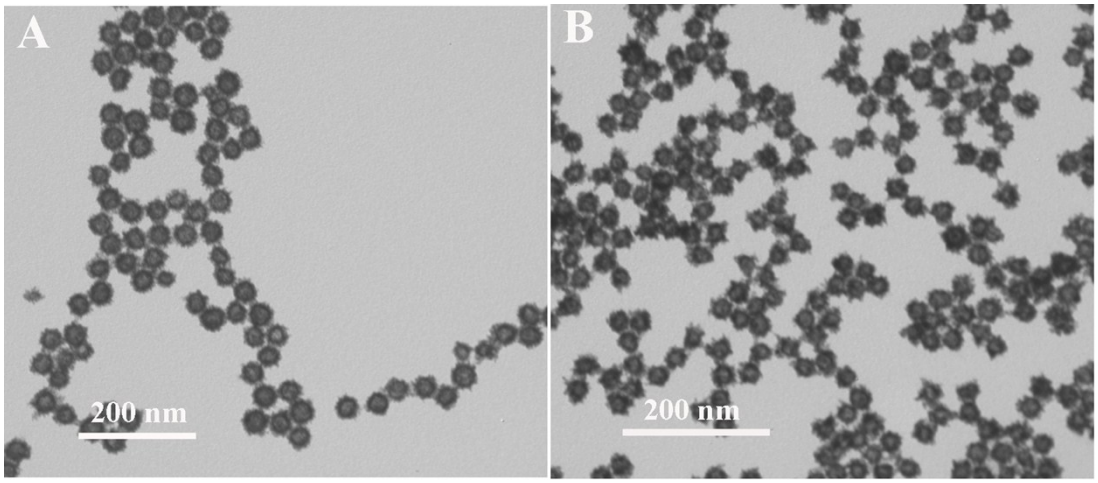

Figure S1 Typical TEM images of the another types of PtCuCo HDNPs, $Pt_{54}Cu_{23}Co_{14}$ (A) and $Pt_{81}Cu_{19}Co_{23}$ (B).

Table S1 Element content of the three types of PtCuCo HDNPs measured by different methods.

	Type 1	Type 2	Type 3
ICP-MS	$Pt_{77}Cu_{54}Co_{23}$	$Pt_{81}Cu_{19}Co_{23}$	$Pt_{54}Cu_{23}Co_{14}$
EDS	$Pt_{80}Cu_{49}Co_{23}$	$Pt_{77}Cu_{14}Co_{19}$	$Pt_{57}Cu_{21}Co_{13}$
XPS	$Pt_{79}Cu_{59}Co_{25}$	$Pt_{78}Cu_{16}Co_{18}$	$Pt_{56}Cu_{19}Co_{14}$