Electronic supplementary information

Dealloying of Pt1Bi2 intermetallic toward optimization of electrocatalysis on Bi-continuous nanoporous core-shell structure

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Experimental

Chemicals Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99.9%), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99.0%), polyvinylpyrrolidone (PVP, K30, 99.9%), polyethylene glycol (PEG600, 99.0%), and nitric acid (HNO_3, 68%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Commercial Pt/C (Pt/C, 20 wt %) and Nafion 117 solution (5%) were obtained from Sigma Aldrich. Ultrapure water (18.2 MΩ cm) was used to prepare the solutions used in the experiments.

Synthesis of Pt–Bi intermetallic nanoparticles The synthesis of the PtBi/XC-72 intermetallic was performed using a microfluidics method, as reported in our previous work.[1] A typical synthesis of the PtBi intermetallic nanocrystals involved the addition of $Bi(NO_3)_3{\cdot}5H_2O$ (0.2 mmol), $H_2PtCl_6{\cdot}6H_2O$ (0.1 mmol), and PVP (30 mmol for monomer) to PEG600 (100 mL) in a flask. The reaction solution containing the precursor metal ions was introduced to a reaction microchannel (200 μm i.d.) by pressure-regulated nitrogen (N_2) gas, and the length of the reaction channel was ~120 cm. The collected products were separated by centrifugation and then washed with ethanol.

Preparation of bi-continuous nanoporous PtBi@Pt/C nanoparticles Chemical leaching of the PtBi intermetallic nanoparticles was conducted by immersing them in 1 M HNO_3 under magnetic stirring at 80 °C for 2 h. Following this dealloying step, the sample was then centrifuged and washed using deionised water and ethanol three times.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker diffractometer equipped with a Cu Kα radiation source (D8 Advance X-ray diffractometer, Cu Kα, λ = 1.5406 Å, 40 kV and 40 mA) to study the crystallographic information of the samples. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted using a JEOL JEM-2100 microscope operated at 200

kV with a nominal resolution. High-resolution scanning transmission electron microscopy-energy-dispersive X-ray microanalysis (HRSTEM-EDX) was performed on a JEOL ARM200F instrument at an accelerating voltage of 200 kV. The bulk composition of the prepared porous PtBi@Pt/C nanoparticles was measured using inductively coupled plasma-atomic emission spectrometry (ICP-MS).

Electrochemical measurements

A CHI 604E electrochemical analyzer was used to conduct electrochemical measurements. A glassy carbon rotating disk electrode (GC-RDE, 4 mm) was used as the working electrode, which was polished with 50 nm alumina to yield a mirror finish and then washed before conducting any experiments. A mercurous sulfate electrode (MSE) and Pt plate electrode were used as the reference and counter electrodes, respectively. Then, 10 μL ethanol suspensions of the as-prepared catalyst were transferred to the surface of the GC-RDE electrode. After that, 5 μL of Nafion (0.05 wt%) solution was dropped onto the electrode surface and dried at room temperature in air for 2 h.

Before measurements, the working electrode was electrochemically cleaned by continuous potential cycling between 0.0 and 1.2 V (*vs.* RHE) at 200 mV s^{-1} in N_2-saturated 0.10 mol L^{-1} $HClO_4$ solution until a stable cyclic voltammetry (CV) curve was obtained. The ORR polarization measurements were performed in O_2-saturated 0.1 mol L^{-1} $HClO_4$ solutions using the GC-RDE at a scan rate of 10 mV s^{-1} under different rotation rates.

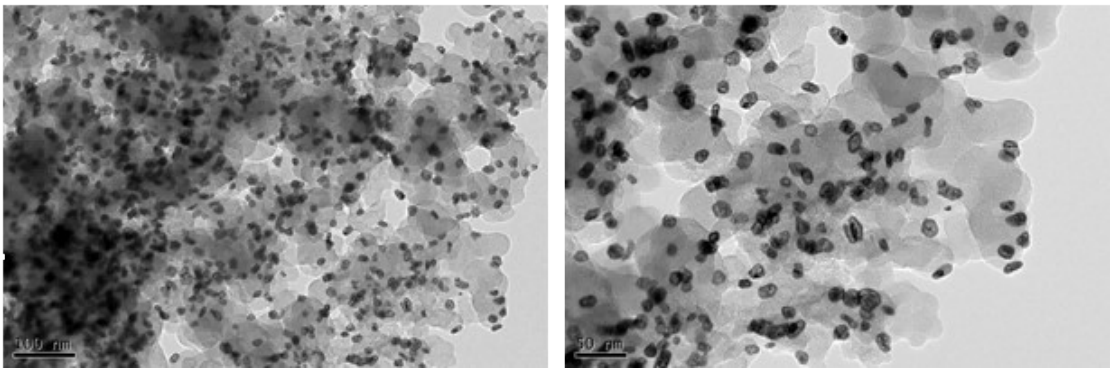

Figure S1. Low-magnification TEM images of the PtBi@Pt/C nanocrystals dealloyed in 1 M HNO_3 for 2 h.

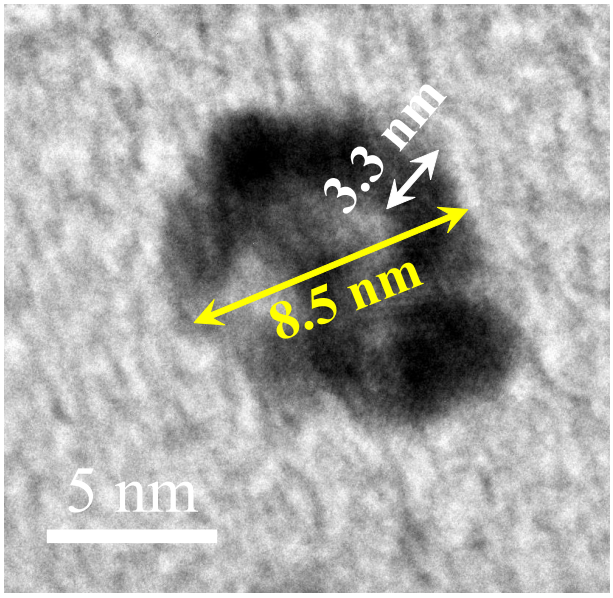

Figure S2. TEM image of the minimum PtBi@Pt nanoparticle size formed after dealloying process.

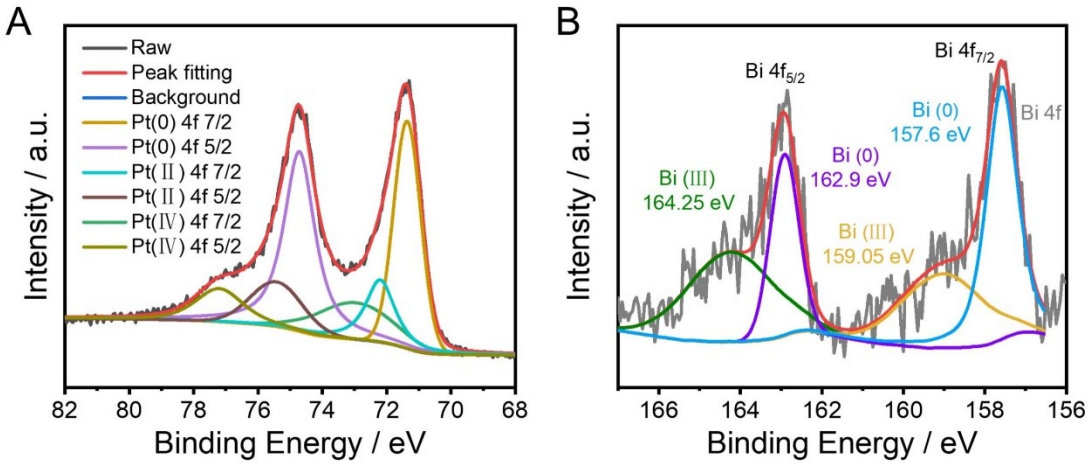

Figure S3. (A) Pt/4f and Bi/4f XPS spectra of PtBi/Pt core-shell nanoparticles.

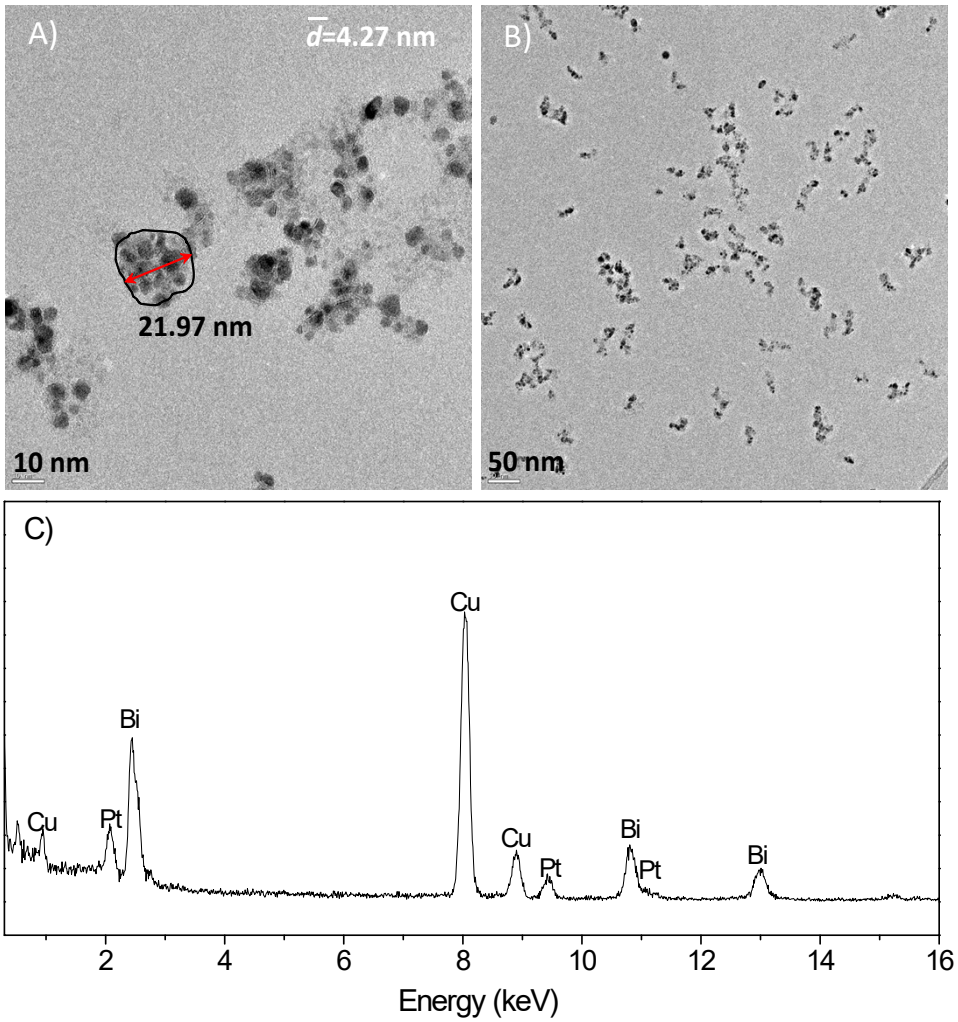

Figure S4. (A, B) TEM images and (C) EDS data of the product prepared at 350 °C with microchannels of 10 cm.

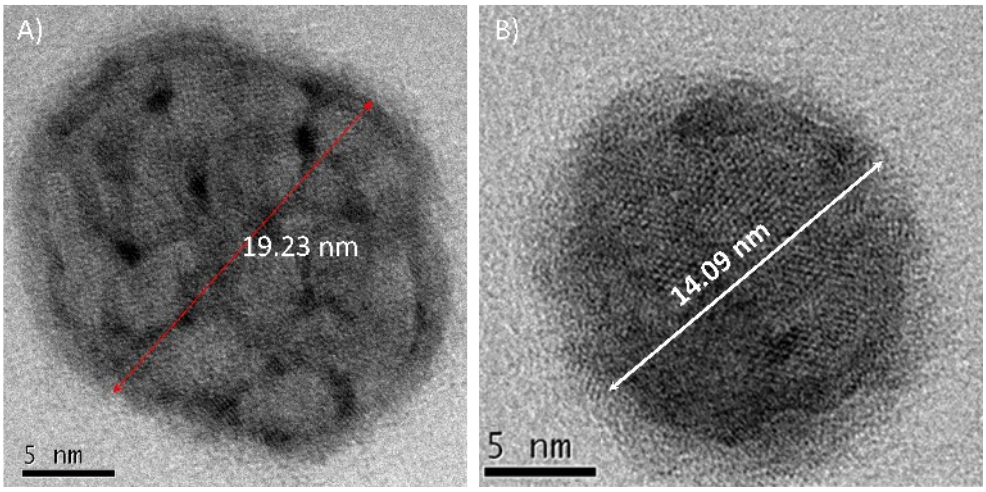

Figure S5. HRTEM images of the PtBi prepared at 350 °C with microchannels of (A) 40 cm and (B) 90 cm.

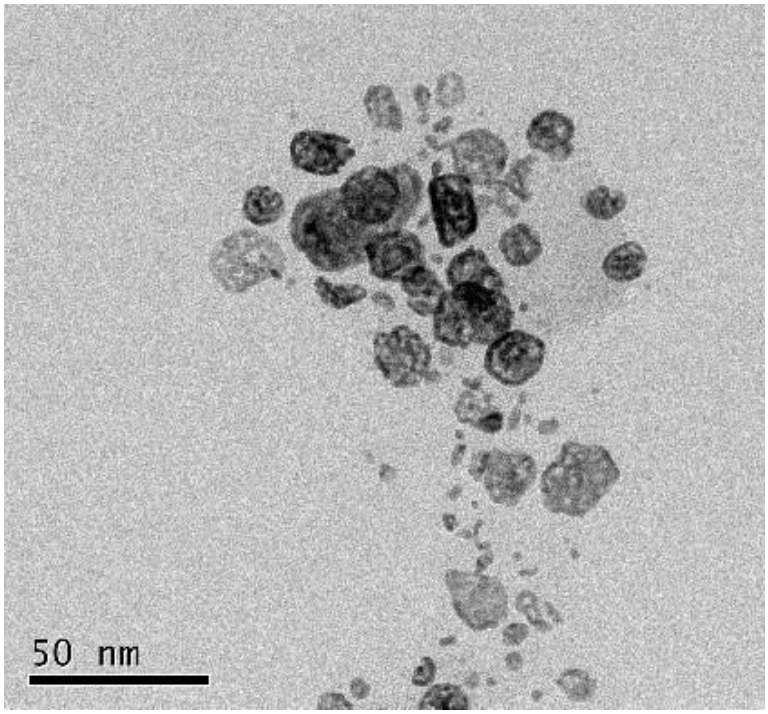

Figure S6. TEM images of the product prepared at the etching condition of 5 mol L^{-1} HNO_3 for 1 h at 80 °C.

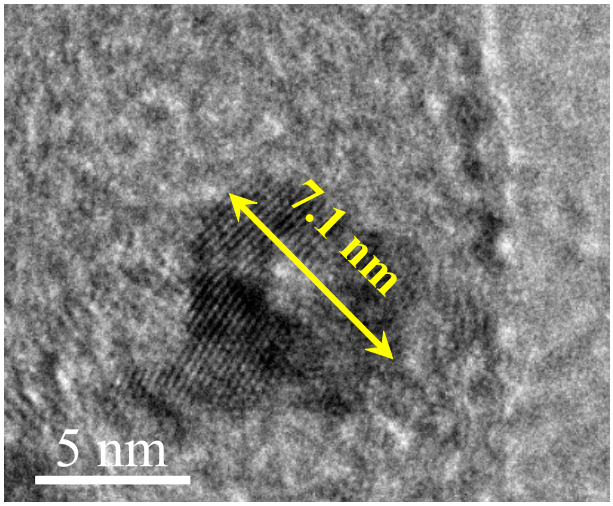

Figure S7. TEM images of dealloyed PtNi nanoporous particles.

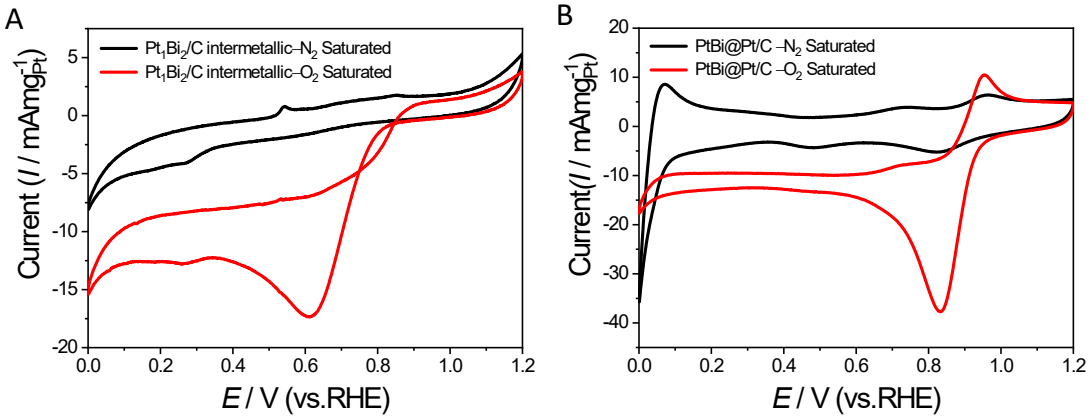

Figure S8. CV curves of (A) the Pt_1Bi_2/C intermetallic and (B) PtBi@Pt/C in an aqueous solution of KOH (0.1 M) at room temperature recorded at a scan rate of 50 mVs^{-1}. The current densities were normalized against the mass of Pt loaded on the electrodes.

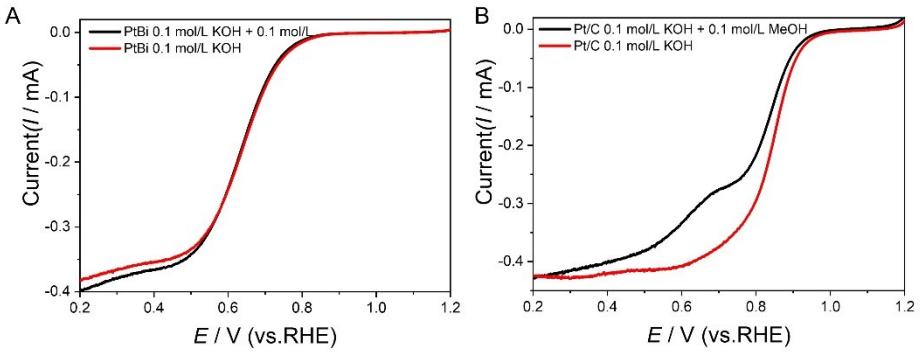

Figure S9. Polarization curves for the ORR. (A) PtBi@Pt/XC-72 catalyst; (B)Pt/C NPs. Conditions: in O_2-saturated 0.1 mol/L KOH that contained 0 and 0.1 mol/L methanol at a rotation rate of 900 rpm. Sweep rate: 10 mV/s.

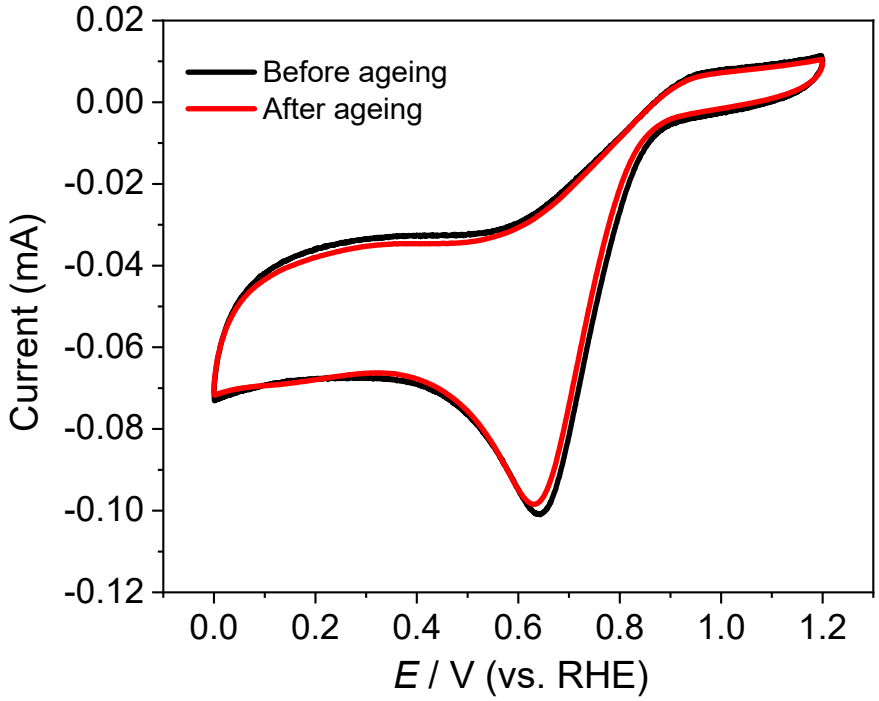

Figure S10. Stability test for PtBi@Pt/C. Before and after aging for 1000 cycles in O_2-saturated 0.1 mol/L KOH that contained 0 and 0.1 mol/L methanol. Sweep rate: 50 mV/s.

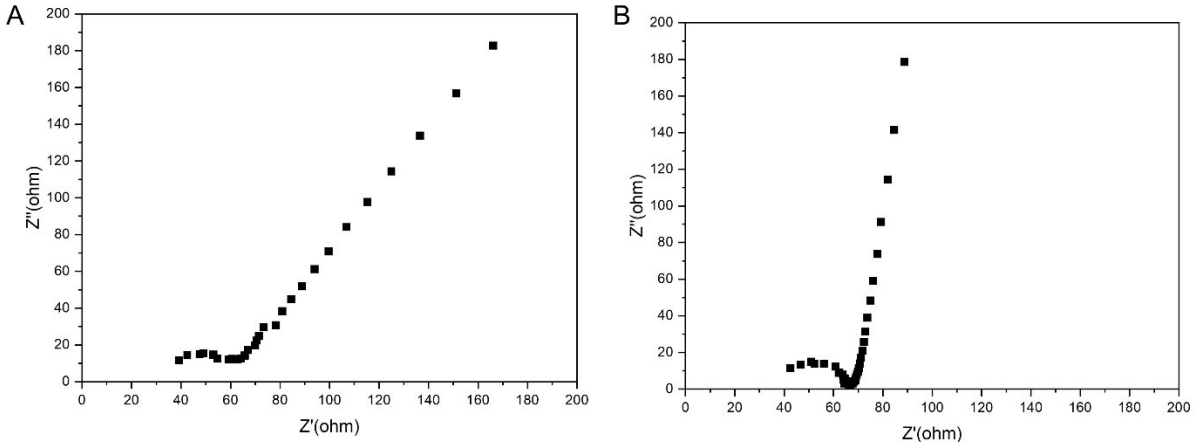

Figure S11. Nyquist plots of the corresponding catalysts of PtBi@Pt/C (A) and Pt/C (B).

1 D. Zhang, F. Wu, M. Peng, X. Wang, D. Xia and G. Guo, *J. Am. Chem. Soc.*, 2015, **137**, 6263-6269.