

Shape-controlled synthesis of planar PtPb nanoplates for high efficient methanol electro-oxidation reaction

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Experimental

Chemicals

Pt(II) acetylacetonate ($\text{Pt}(\text{acac})_2$, 99%), Pb(II) acetylacetonate ($\text{Pb}(\text{acac})_2$, 99%), polyvinylpyrrolidone (PVP, 40000, 99%), diethylene glycol (DEG, 98%) were purchased from Sigma-Aldrich. Nafion alcohol solution (5wt.%) was purchased from Alfa Aesar. Vulcan XC-72 carbon was purchased from Carbot Corporation. Commercial Pt/C (20 wt.% of Pt nanoparticles supported on Vulcan XC-72 carbon) was purchased from Johnson Matthey (JM). All chemicals were used as received without further purification.

Synthesis of PtPb nanoplates and nanospheres

All the synthesis was carried out in a standard Schlenk line. First, 1.554g PVP was dissolved in 12 mL DEG and then vacuumed at 55 °C for 30 min with stirring to remove impurities with low boiling point. Subsequently, 8 mL of DEG solution containing 10 mg $\text{Pt}(\text{acac})_2$ and 40 mg $\text{Pb}(\text{acac})_2$ was injected into the above DEG solution, and the mixture solution was heated up to 105 °C and kept for 5 h to ensure the complete reaction under a nitrogen flow. The black product was collected by centrifugation and washed by ethanol and acetone mixture (1:3) for three times. The final product was dried under vacuum at 80 °C. Different ratios of Pt/Pb nanocrystals were prepared by tuning the feeding molar ratios of Pt/Pb precursors (1:2, 1:3 and 1:6). For comparison,

PtPb nanosphers were prepared by the same method except for using 220 °C for 5 h to finish the reaction.

Characterization

Transmission electron microscope (TEM) images were collected by a LaB 6 TEM (TECNAI G2, FEI), operating at 200 kV. Scanning electron microscopy (SEM) was taken at 5 kV by using Supra55 from Carl Zeiss. X-ray diffraction (XRD) was performed on an Empyrean diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS Untraded ultrahigh vacuum (UHV) surface analysis system. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on 710-ES, Varian.

Electrochemical measurements

MOR measurements were carried out in a typical three-electrode cell on a CHI660E workstation. A glassy carbon electrode (3 mm in diameter), Pt gauze and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. The ink was prepared as following: 2.0 mg catalysts (including different ratios of Pt/Pb nanocrystals and PtPb nanospheres), 0.2 mg Vulcan XC-72 carbon and 6 μ L of 5 wt% Nafion solution were dispersed in a mixed solvent (H₂O:ethanol = 1:1), and vigorously ultrasonicated for 30 min to form a homogeneous ink. Then, 5 μ L suspension of the catalyst was loaded onto the glassy carbon electrode to achieve a loading

density of 0.14 mg cm^{-2} . The working electrode was first activated in N_2 -saturated 1.0 M KOH by CV at a range from -1.0 V to 0.2 V with a scan rate of 50 mV s^{-1} for 50 cycles, and then MOR tests were measured in 1.0 M KOH containing 1.0 M methanol solution. The CA measurements were held at -0.2 V in 1.0 M KOH containing 1.0 M methanol solution. For comparison, the commercial Pt/C was prepared and measured under the same conditions.

DFT calculation

Adsorption energies were computed by subtracting the energies of the gas-phase CO molecule and surface from the energy of the adsorption system. E_{ad} was defined as $E_{\text{ad}} = E(\text{CO/surface}) - E(\text{CO}) - E(\text{surface})$. With the definition, a negative E_{ad} corresponds to stable adsorption on the surface. A four-layer slab was used in the calculations. The atoms in the top two layers were fully relaxed while the rest of the atoms were fixed in their equilibrium positions. DFT calculation was performed with the program package DMol3 in Material Studio (version 7.0) of Accelrys Inc. on personal computers. We used the double numeric quality basis set with polarization functions (DNP). The basis file of DNP basis set was 4.4. The gradient-corrected GGA function developed by Perdew, Burke, and Ernzerh of (PBE), and $3 \times 3 \times 4$ k-point set was employed. The tolerance of energy, gradient, and displacement convergence were 1×10^{-5} hartree ($1 \text{ hartree} = 27.2114 \text{ eV}$), $2 \times 10^{-3} \text{ hartree/\AA}$, and $5 \times 10^{-3} \text{ \AA}$, respectively.

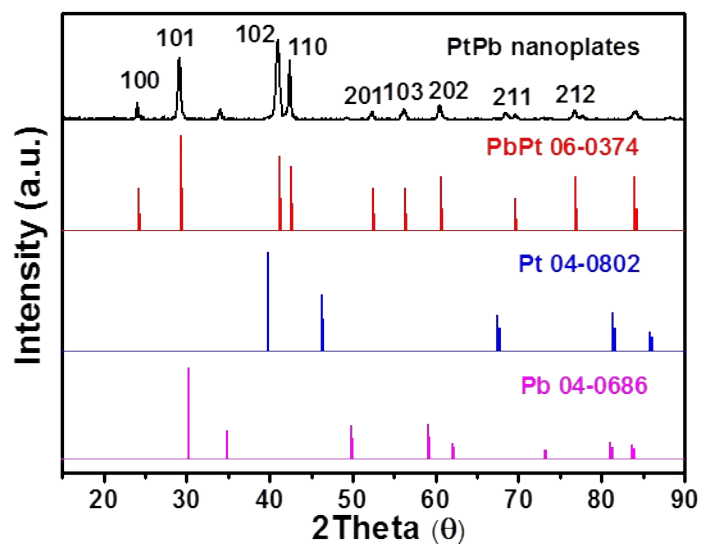


Fig. S1 XRD pattern of PtPb nanoplates.

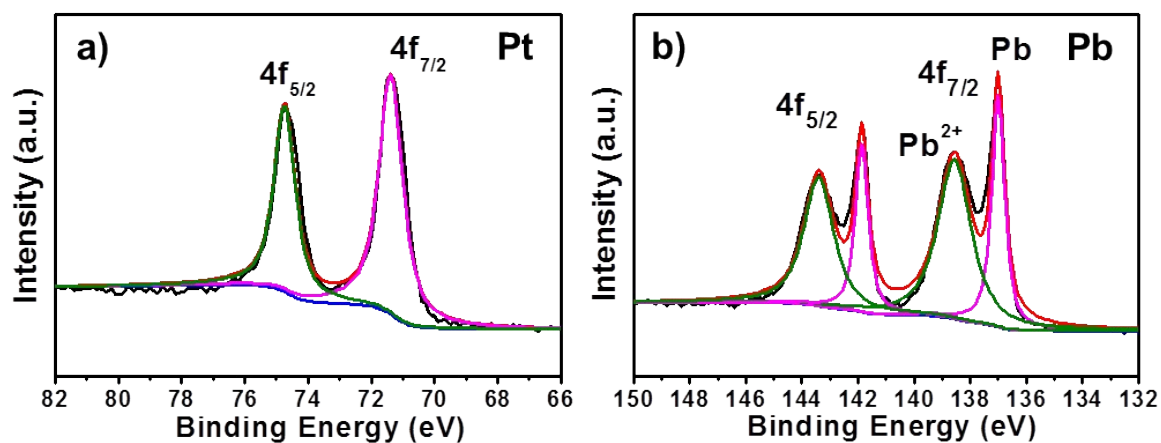


Fig. S2 XPS spectra of PtPb nanoplates: (a) Pt 4f, (b) Pb 4f.

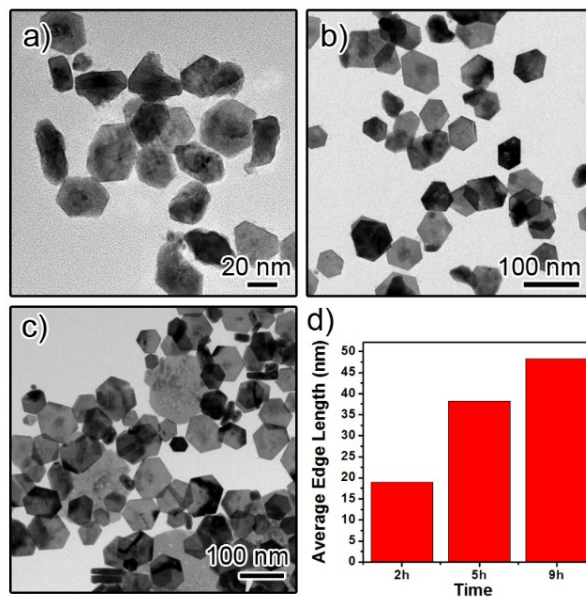


Fig. S3 Time-dependent experiments: (a) 2 h, (b) 5 h, and (c) 9 h. (d) Size diagram of the samples taken from different time.

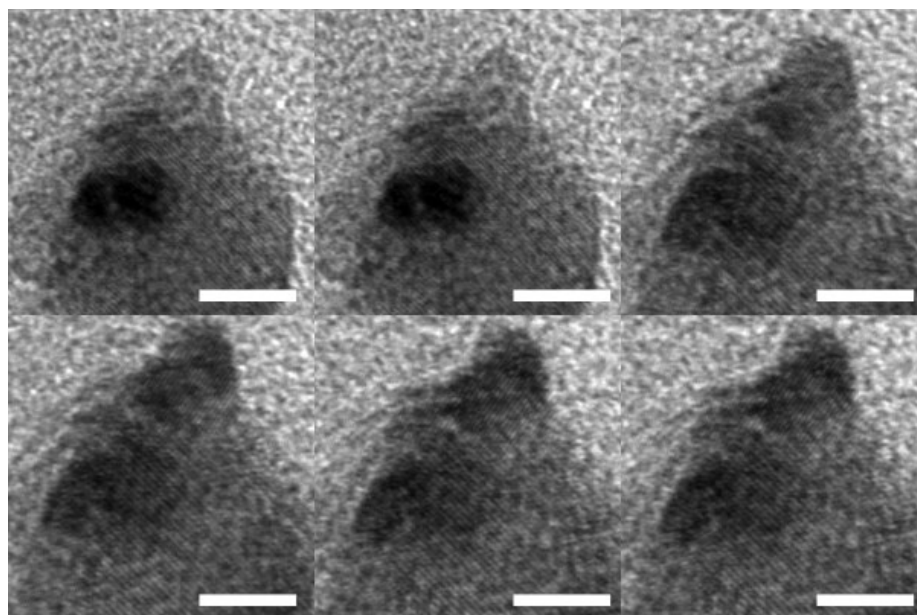


Fig. S4 *In-situ* crystallization of PtPb nanoplates. Scale bars: 5 nm.

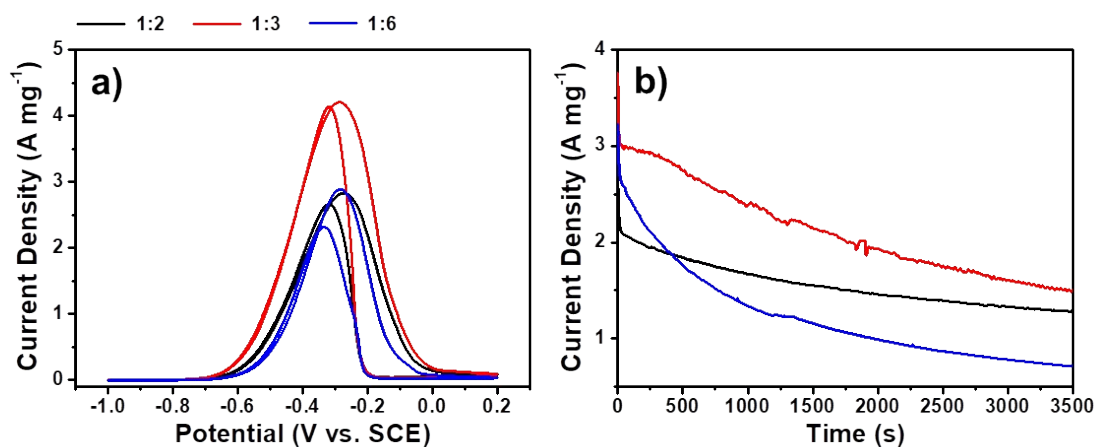


Fig. S5 (a) CV curves of different samples in N₂-saturated 1 M KOH containing 1 M methanol solution at a scan of 50 mV s⁻¹. (b) CA curves of different samples measured in N₂-saturated 1 M KOH solution containing 1 M methanol, recorded at -0.2 V vs. SCE.

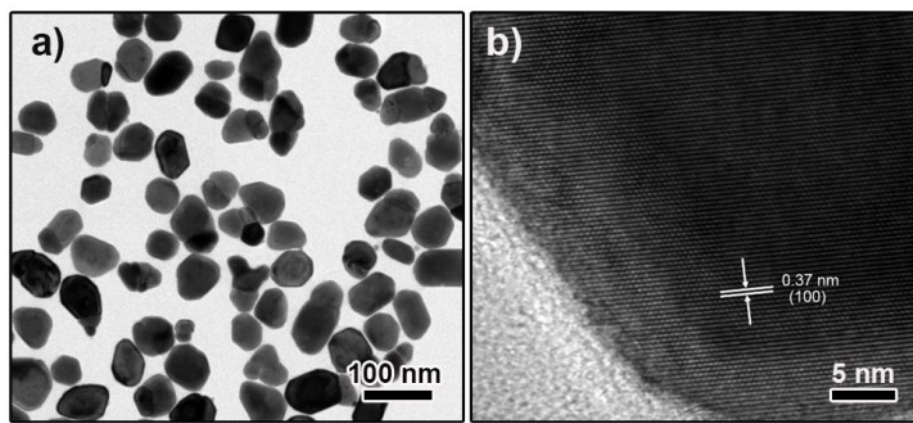


Fig. S6 (a) TEM and (b) HRTEM images of PtPb nanospheres.

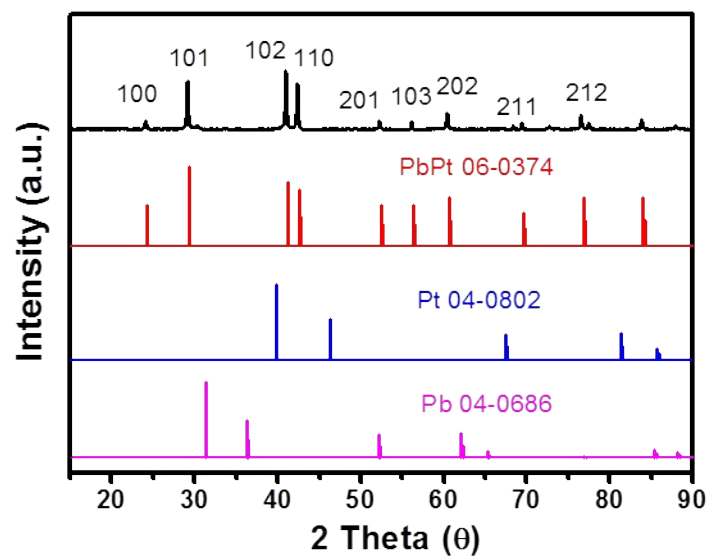


Fig. S7 XRD pattern of PtPb nanospheres.

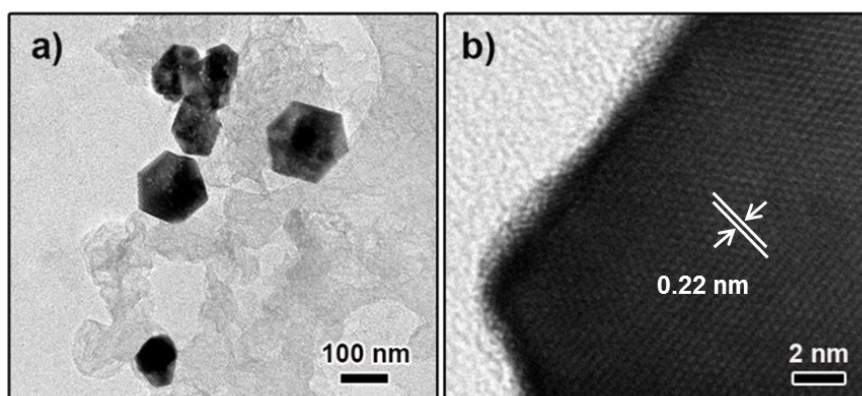


Fig. S8 (a) TEM and (b) HRTEM images of PtPb nanoplates after the CA test for 3600 s.