

Supplementary Materials

Chemically Controlled Surface Compositions of Ag-Pt Octahedral Catalysts

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Chemicals and Materials

Silver nitrate (AgNO_3 , 99.85%, ACROS); potassium tetrachloroplatinate (II) (K_2PtCl_4 , 46.4% Pt, Alfa Aesar); polyallylamine hydrochloride (PAH, Alfa Aesar); formaldehyde (HCHO , 37% in water, MACRON Fine Chemicals); ethanol (EtOH, 200 proof, Decon Lab); acetic acid (AA, >99.7%, Glacial, Fisher Scientific); ammonium hydroxide (NH_4OH , 28-30%, MACRON Chemicals); carbon black (Vulcan XC-72, Cabot); perchloric acid (70%, VERITAS double distilled, GFS Chemicals); formic acid (88%, GFS chemicals); propanol (LC-MS Reagent, J. T. Baker) and argon (Ar, UHP grade, Airgas) were used as received. Deionized water was generated using a Millipore Q-50 unit with a resistance reading equal to or above 18.2 $\text{M}\Omega$.

Preparation of Solutions

Stock solution of 0.05-M $\text{K}_2\text{PtCl}_{4(\text{aq})}$ was made by dissolving 103.77 mg of K_2PtCl_4 in 5 mL of deionized water. Similarly, solution of 0.05-M $\text{AgNO}_{3(\text{aq})}$ was prepared by dissolving 42.4 mg of AgNO_3 in 5 mL of deionized water, and 0.5-M PAH was prepared by dissolving 472.5 mg of PAH in 10 mL of deionized water.

Synthesis of Ag-Pt Octahedral Nanoparticles

Ag-Pt octahedral nanoparticles were prepared via a modified hydrothermal method reported elsewhere.^[1-2] In short, 0.5-mL aqueous solution of 0.05-M K_2PtCl_4 , 0.5 mL solution of 0.05-M AgNO_3 , and 1.0-mL solution of 0.5-M PAH were well mixed in a 25-mL Teflon liner by continuous stirring at 500 rpm for 15 min. The designed amounts of HCHO solution

was added into the mixture and stirred for another 1 min, while the total volume of solution was kept at 10 mL. The Teflon liner was then sealed, placed into a stainless-steel autoclave, and transferred into an oven that was preheated to 180 °C. After reaction for 4 h, the autoclave was cooled down under ambient conditions and the products were separated by centrifugation. The products were then washed with deionized (DI) water by sonication and separated by centrifugation for five times using 20 mL of aqueous acetic acid solution (5 vol%) as the solvent and 20 mL of aqueous ammonium hydroxide solution (10 vol%) as the antisolvent.

Characterization

Transmission electron microscope (TEM) characterization was performed using JEOL Cryo 2100 at an accelerating voltage of 200 kV. Powder X-ray diffraction (PXRD) patterns were acquired using a Bruker D8 Venture Duo diffractometer. The particle size was calculated using the full width half maximum (FWHM) of the diffraction peaks by the Scherrer equation. The instrument broadening was determined empirically using LaB₆ powder standards. The Rietveld refinement was carried out by a combined Lorentzian-Gaussian function for further calculations. X-ray-photonelectron spectroscopy (XPS) patterns were acquired using Kratos Axis ULTRA (Manchester UK) spectrometer with a monochromatic Al source. The XPS analysis was done using CasaXPS software with Shirley-type baseline.

Preparation of Carbon-Supported Catalysts

Carbon black was used as support for making silver-platinum catalysts (Ag-Pt/C). In a standard preparation, carbon black particles were dispersed in ethanol and sonicated for 1 h. A designed amount of Ag-Pt nanoparticles suspension in water was added to this dispersion of carbon black at the nanoparticle-to-carbon-black mass ratio of 20:80. This mixture was further sonicated for 30 min and stirred overnight. The resultant solids were precipitated out by centrifugation and vacuum dried at room temperature in a vacuum oven (VWR, Symphony series).

Electrocatalytic Performance Measurement

A three-electrode cell was used to measure the electrochemical properties of these alloy catalysts. The working electrode was a glassy-carbon rotating disk electrode (RDE) (area: 0.196 cm²). A 1-cm² platinum foil was used as the counter electrode and a HydroFlex hydrogen electrode was used as the reference, which was placed in a separate compartment. Hydrogen evolution reaction (HER) was used to calibrate this hydrogen electrode before the tests. All potentials were referenced to the reversible hydrogen electrode (RHE). The mass of metal in each Ag-Pt/C catalyst was determined by a bench top balance. To prepare the working electrode, 5 mg of the Ag-Pt/C catalyst was dispersed in 5 mL of a mixed solvent and sonicated for 5 min. This mixed solvent contained de-ionized water, isopropanol, and 5% Nafion at the volumetric ratio of 8:2:0.05. 40 μ L of the suspension was added onto the RDE by a pipette and dried in air. Cyclic voltammetry (CV) measurements was carried in argon-saturated 0.1-M HClO_{4(aq)} solution at room temperature with a scan rate of 50 mV/s. The

electrochemical active surface area (ECSA), based on adsorption of hydrogen on Pt surface, was determined by integrating the area accounted for proton adsorption in the potential range of 0.05-0.4 V (vs RHE) with the following formula:

$$\text{ECSA (cm}^2_{\text{Pt}}) = \text{area}/[0.05 \text{ (V/s)} \times 210 \text{ (\mu C/cm}^2\text{)}]$$

Formic acid oxidation (FAOR) activity was determined in a Ar saturated 0.1 M HClO_{4(aq)} and 0.5 M HCOOH_(aq) solution with a scan rate of 50 mV/s. Data were used without iR-drop correction.

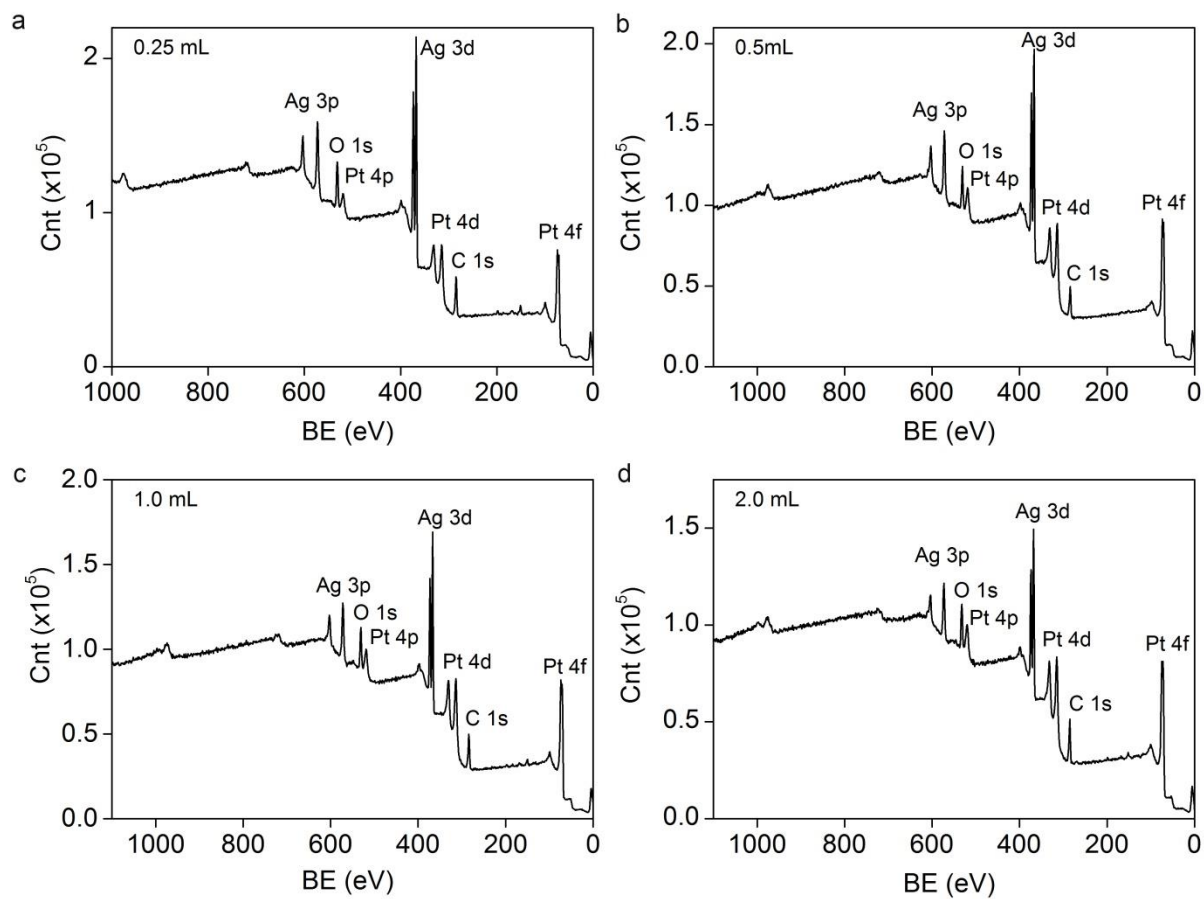


Figure S1. XPS survey spectrum of Ag-Pt nanoparticles using (a) 0.25, (b) 0.5, (c) 1.0, and (d) 2.0 mL HCHO in hydrothermal synthesis.

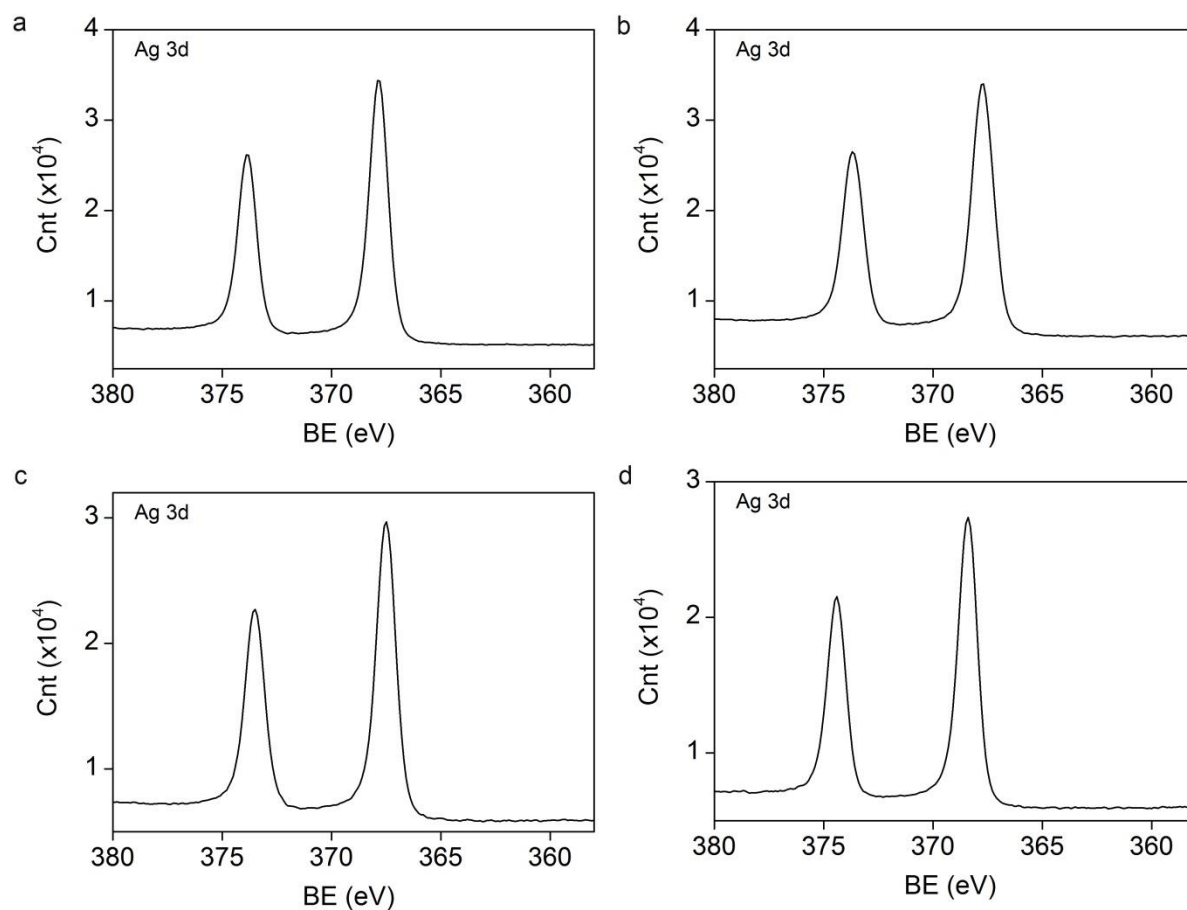


Figure S2. XPS Ag 3d high-resolution scan of Ag-Pt nanoparticles using (a) 0.25, (b) 0.5, (c) 1.0, and (d) 2.0 mL HCHO in hydrothermal synthesis.

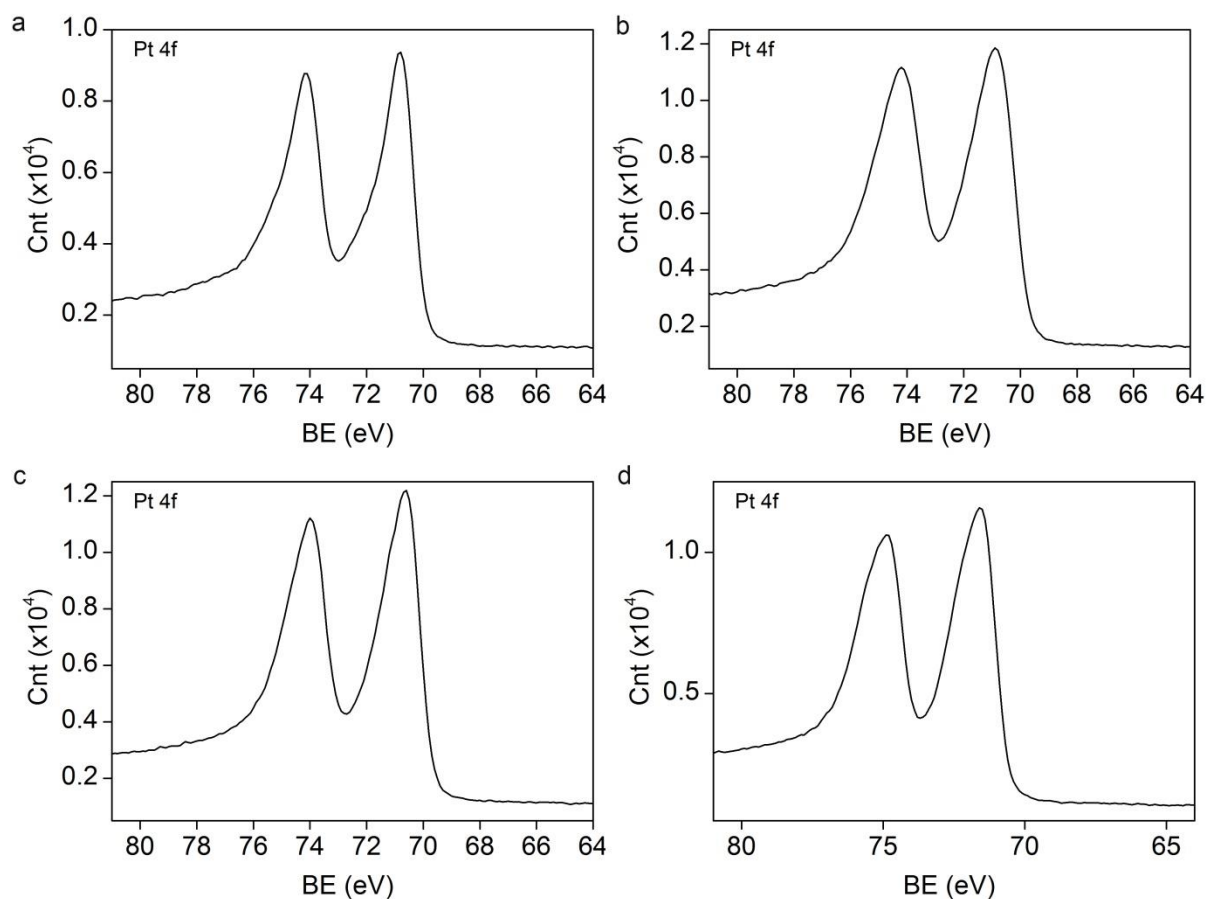


Figure S3. XPS Pt 4f high resolution scan of Ag-Pt nanoparticles using (a) 0.25, (b) 0.5, (c) 1.0, and (d) 2.0 mL HCHO in hydrothermal synthesis.

References

1. G.-T. Fu, R.-G. Ma, X.-Q. Gao, Y. Chen, Y.-W. Tang, T.-H. Lu, and J.-M. Lee: Hydrothermal synthesis of Pt-Ag alloy nano-octahedra and their enhanced electrocatalytic activity for the methanol oxidation reaction. *Nanoscale* **6**, 12310-12314 (2014).
2. Y.-T. Pan, L. Yan, Y.-T. Shao, J.-M. Zuo, and H. Yang: Regioselective Atomic Rearrangement of Ag-Pt Octahedral Catalysts by Chemical Vapor-Assisted Treatment. *Nano Lett.* **16**, 7988-7992 (2016).