

Supporting Information

Strain Effect in Pd@PdAg Twinned Nanocrystals towards Ethanol Oxidation Electrocatalysis

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METHODS

Chemicals and materials

Sodium tetrachloropalladate (Na_2PdCl_4 , 99.99%), silver nitrate (AgNO_3 , 99.9999%), poly(vinylpyrrolidone) (PVP, MW \approx 40,000), potassium bromide (KBr), and ascorbic acid (AA) were all purchased from Sigma-Aldrich. Oleylamine (OAm, 80%-90%) and tert-butylamine (99%) were purchased from Aladdin. Ethylene glycol (EG), ethanol, acetone, cyclohexane, chloroform, methanol, and toluene were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pd/C (10 wt%) was purchased from Alfa Aesar. The resistivity of deionized (DI) water used in all the experiments was $18.2 \text{ M}\Omega \cdot \text{cm}$. All the chemicals were used as received.

Synthesis of Pd icosahedra and {111} truncated bi-pyramids

In a typical procedure for the synthesis of Pd icosahedra, 60 mg of AA, 111 mg of PVP, and 200 mg of KBr were dissolved in 6.0 mL of EG, which was subsequently added to a 20 mL glass vial heated to $160 \text{ }^\circ\text{C}$ under magnetic stirring for 5 min. Then, a 5.0 mL of EG solution with a concentration of Na_2PdCl_4 of 3.6 mg/mL was injected into the pre-heated EG solution at an injection rate of 3 mL/h through a syringe pump. The reaction was kept at $160 \text{ }^\circ\text{C}$ for 3 h. For the synthesis of Pd {111} truncated bi-pyramids, the quantity of KBr and the injection rate of precursor were changed to 300 mg and 2 mL/h, respectively. The reaction was kept at $118 \text{ }^\circ\text{C}$ for 3.5 h under otherwise identical experimental conditions. These products were collected by centrifugation, washed three times with ethanol and acetone and then re-dispersed in ethanol for the phase transformation.

Phase transfer of Pd icosahedra and {111} truncated bi-pyramids

In a typical procedure, 5 mL of ethanol solution containing Pd icosahedra or {111} truncated bi-pyramids was mixed with 1 mL of toluene and 5 mL of OAm in a 20 mL glass vial, which was subsequently heated to $80 \text{ }^\circ\text{C}$ for 12 h under magnetic stirring until the complete volatilization of ethanol. The Pd icosahedra or {111} truncated bi-pyramids in OAm was washed three times with a mixture of ethanol and cyclohexane, and then re-dispersed in OAm serving as the starting materials for the next synthesis.

Synthesis of Pd@PdAg nanocrystals

In a typical procedure, 4 mL of OAm solution containing 1.7 mg of Pd icosahedra or {111} truncated bi-pyramids and 0.34 mg of AgNO_3 was added to a 20 mL glass vial, and subsequently heated to $200 \text{ }^\circ\text{C}$ under magnetic stirring. The solution was kept at $200 \text{ }^\circ\text{C}$ for 3 h. The product was collected by centrifugation, washed with a mixture of cyclohexane and ethanol for three times.

Characterizations

Transmission electron microscopy (TEM) images were taken through a Hitachi microscope (HT-7700) operated at 100 kV. High-resolution transmission electron microscopy (HRTEM) images were taken through a FEI Tecnai F20 G2 microscope, which was operated at 200 kV. Energy dispersive X-ray (EDX) analyses were performed on a FEI Titan ChemiSTEM, which was equipped with a Super-X EDX detector system. The X-ray diffraction (XRD) patterns were performed on a Bruker D8 focus diffractometer in a scan range of $10\text{-}80^\circ$ at a scan rate of $2^\circ/\text{min}$. Inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, TJA Co., USA) was used to determine the compositions of Pd and Ag in the samples. X-

ray photoelectron spectrometer (XPS) analysis was taken on a scanning X-ray microprobe (Axis Supra, Kratos Inc.) with Al K α radiation.

Preparation of carbon-supported catalysts

In a typical preparation, chloroform-dispersed Pd@PdAg icosahedra and {111} truncated bi-pyramids were deposited onto carbon black particles (Vulcan XC-72R) in chloroform sonicated for 30 min. Then, the mixture was precipitated by centrifugation and re-dispersed in tert-butylamine stirring for more than 72 h. Finally, as-prepared catalysts were centrifuged and washed many times with methanol and DI-water.

Electrochemical measurements

All the electrochemical measurements were carried out via a standard three electrode cell system using a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Factory, China) at room temperature under atmosphere. A glass carbon rotating disk electrode (RDE, 0.196 cm²) coated with catalysts was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and counter electrode, respectively. All potentials were measured against the SCE and converted to the reversible hydrogen electrode (RHE) reference scaled by E (vs. RHE) = E (vs. SCE) + 0.2438 V + 0.0592 \times pH. The mass of Pd loading on the RDE for all the catalysts was about 6 μ g. Before electrochemical ethanol oxidation measurements, catalysts were firstly activated in Ar-saturated 1 M KOH through a cyclic voltammetry (CV) process between 0.07 and 1.27 V versus RHE at a scan rate of 50 mV s⁻¹ for about 30 cycles. The EOR was conducted in a solution containing 1 M KOH and 1 M ethanol between 0.07 and 1.27 V versus RHE at a scan rate of 50 mV s⁻¹. The durability measurements were carried out under the same condition for an additional 1000 cycles. As for CO stripping measurements, the catalysts-coated RDE was firstly polarized in CO-bubbling 1 M KOH solution for more than 15 min to accomplish monolayer CO adsorption on the surface of catalysts. After that, the catalysts-coated RDE was transferred into Ar-saturated 1 M KOH solution with CV measurements conducted between 0.07 and 1.27 V versus RHE with a scan rate of 50 mV s⁻¹ for 3 cycles. The electrochemically active surface areas (ECSAs) of all catalysts were determined by integrating the CO oxidation charge in CV curves.

DFT Computational details

Density functional theory (DFT) calculations were performed using CASTEP package with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional.^{1,2} Four layers of 4 \times 4 Pd (111), 0.3% stretched Pd₃Ag (111) and 2.1% stretched Pd₃Ag (111), all of which contain 64 atoms were chosen as the slab model, and a vacuum region with 12 \AA was set to create a truly two-dimensional Pd (111) surface.

The Ultrasoft Pseudopotentials were used to describe the ionic core electrons, and a plane-wave basis set with a cutoff energy of 300 eV was adopted to treat the valence electrons. A threshold of self-consistent-field energy convergence was 1×10^{-5} eV/atom, and the maximum force and displacement of the convergence criterion for the structural optimizations were set to 0.03 eV/ \AA and 0.001 \AA , respectively. The Monkhorst-Pack scheme k-point meshes were set to be $3\times 3\times 1$.

The adsorption energy (E_{ads}) is calculated according to the formula:

$$E_{\text{ads}} = E_{\text{CH}_3\text{CO-catalyst}} - (E_{\text{CH}_3\text{CO}} + E_{\text{catalyst}}) \quad (1)$$

in which $E_{\text{CH}_3\text{CO-catalyst}}$ is the calculated total energy of the system with CH₃CO adsorbed on

various (111) surfaces; $E_{\text{CH}_3\text{CO}}$ represents the energy of isolated CH_3CO ; and E_{catalyst} is the energy of (111) faceted Pd or Pd_3Ag catalyst. A more negative E_{ads} in equation (1) implies that the adsorption is thermodynamically more favorable.

References

- 1 K. Gundersen, B. Hammer, K. W. Jacobsen, J. K. Nørskov, J. S. Lin and V. Milman, *Surf. Sci.*, 1993, **285**, 27-30.
- 2 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

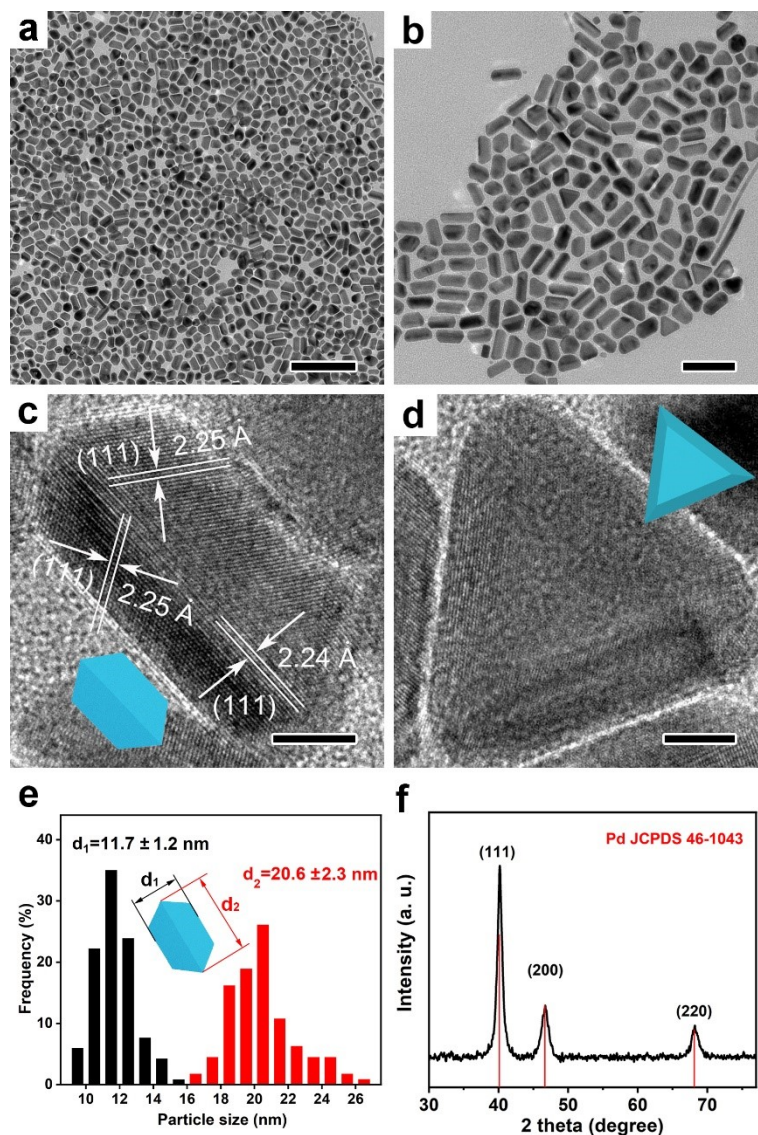


Figure S1 Morphological, structural, and size characterizations of Pd {111} truncated bi-pyramids. (a, b) TEM images, scale bar in (a) is 100 nm and in (b) is 50 nm, (c, d) HRTEM images, scale bars are 5 nm, (e) histogram of size distributions, and (f) XRD pattern. Inset models in (c, d) show the orientations of the corresponding nanoparticles. The short side of {111} truncated bi-pyramids is defined as d_1 and long side defined as d_2 .

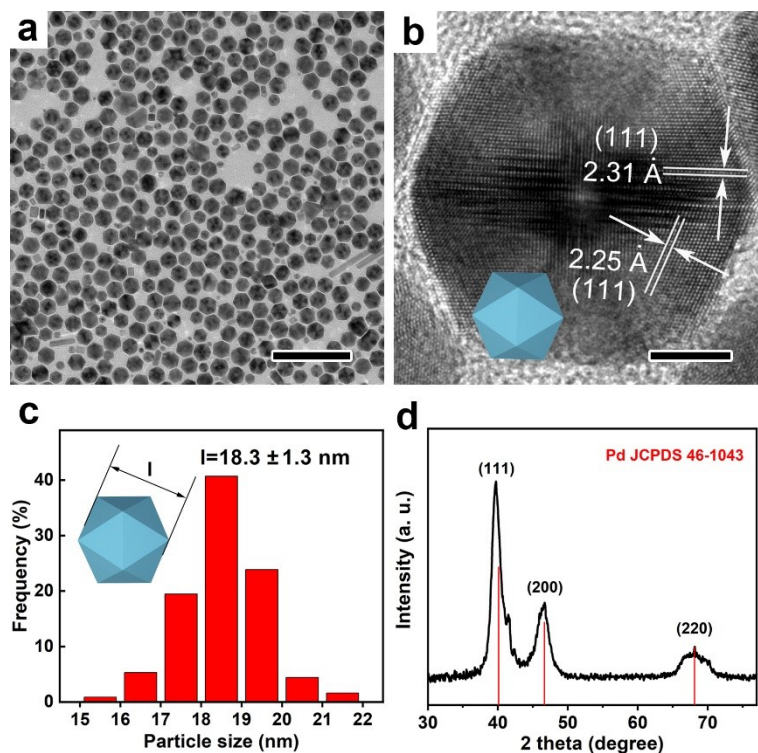


Figure S2 Morphological, structural, and size characterizations of Pd icosahedra. (a) TEM image, scale bar is 100 nm, (b) HRTEM image, scale bar is 5 nm, (c) histogram of size distribution, and (d) XRD pattern. Inset model in (b) shows the orientation of the icosahedron. The size of icosahedra is defined as the distance between two opposite faces.

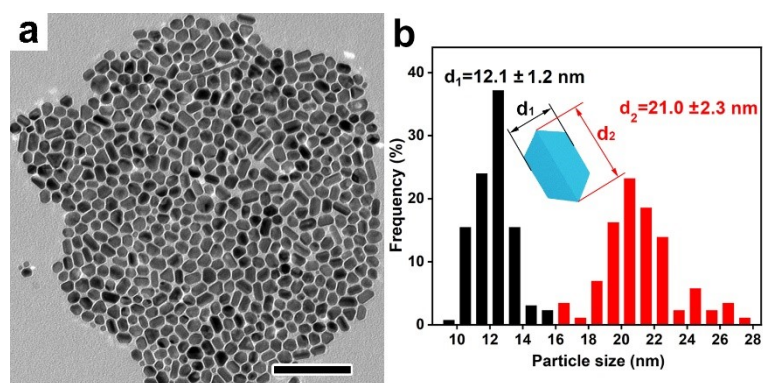


Figure S3 Morphological and size characterizations of Pd@PdAg {111} truncated bi-pyramids. (a) TEM image, scale bar is 100 nm and (b) histogram of size distributions. The short side of {111} truncated bi-pyramids is defined as d_1 and long side defined as d_2 .

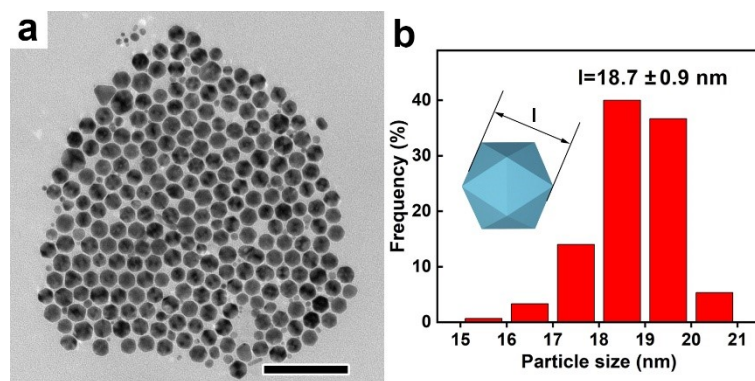


Figure S4 Morphological and size characterizations of Pd@PdAg icosahedra. (a) TEM image, scale bar is 100 nm and (b) histogram of size distribution. The size of icosahedra is defined as the distance between two opposite faces.

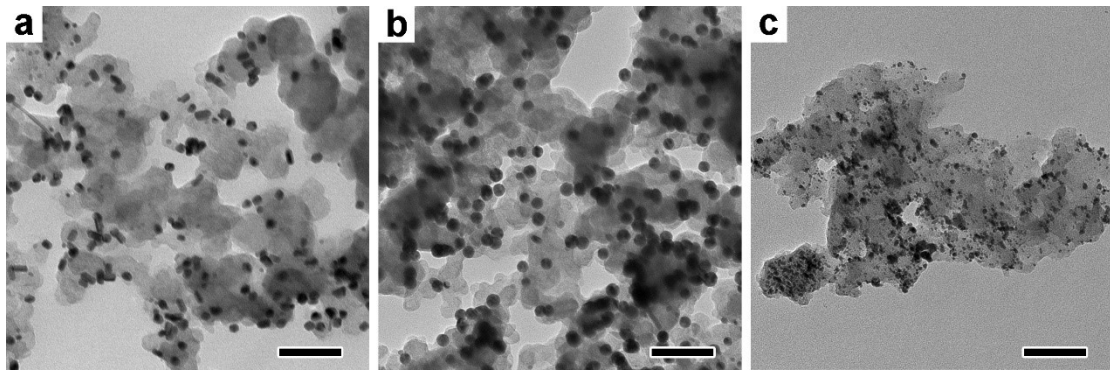


Figure S5 TEM images of carbon-loaded (a) Pd@PdAg {111} truncated bi-pyramids, (b) Pd@PdAg icosahedra, and (c) commercial Pd/C before CV measurement.

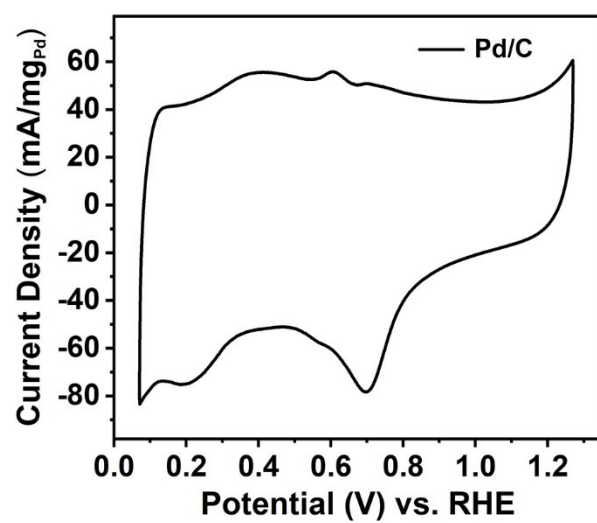


Figure S6 CV curve of commercial Pd/C in 1 M KOH solution normalized to the mass of Pd.

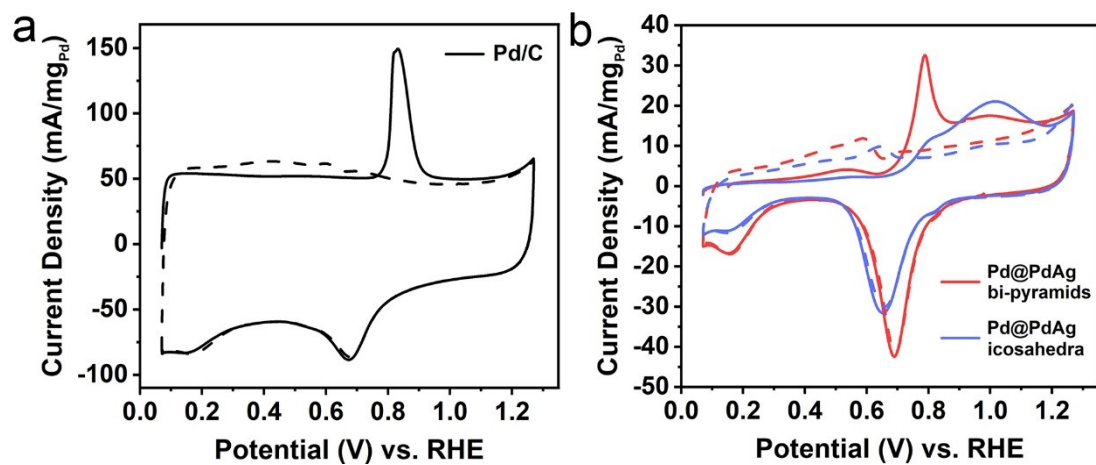


Figure S7 CO stripping voltammograms of (a) commercial Pd/C and (b) carbon-loaded Pd@PdAg nanocrystals in 1 M KOH solution normalized to the mass of Pd.

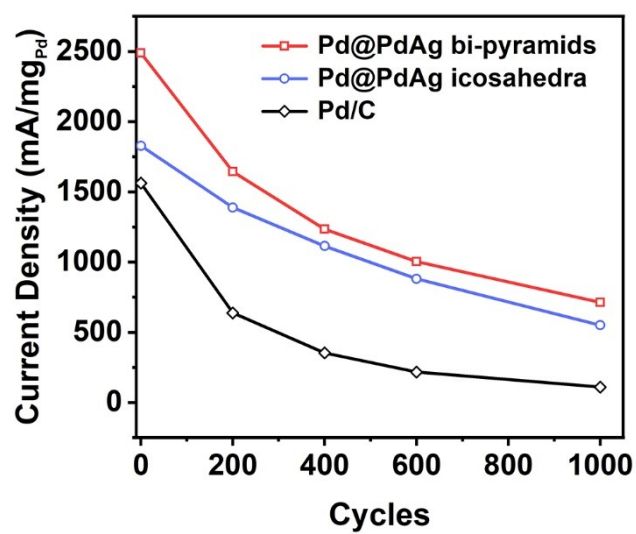


Figure S8 EOR cycling stability curves of carbon-loaded Pd@PdAg nanocrystals and commercial Pd/C normalized to the mass of Pd.

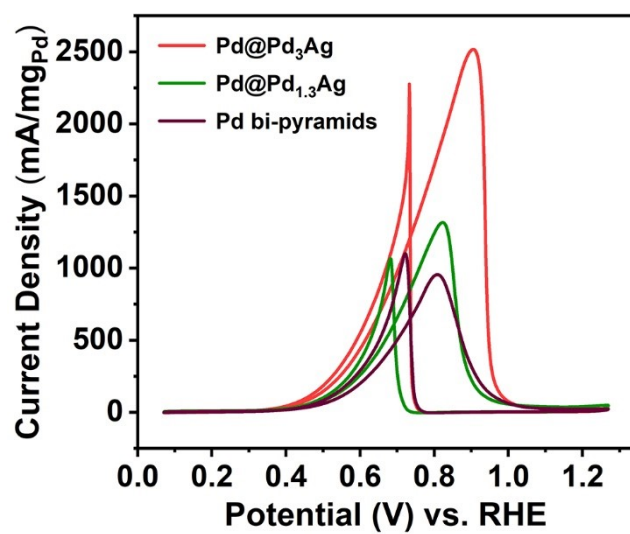


Figure S9 CV curves of carbon-loaded Pd@Pd₃Ag, Pd@Pd_{1.3}Ag, and Pd {111} truncated bi-pyramids nanocrystals normalized to the mass of Pd.

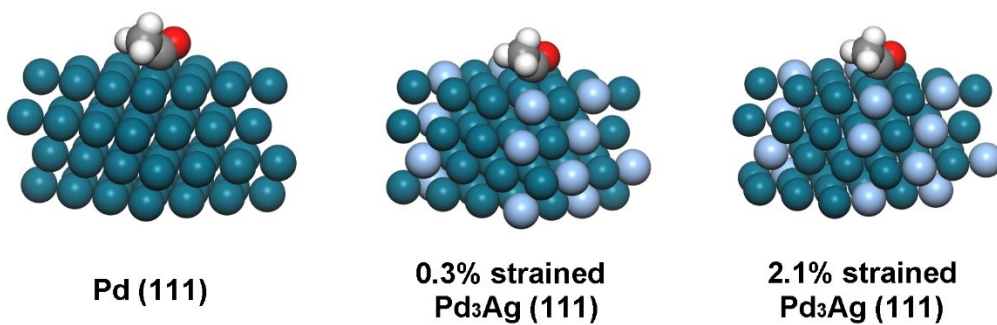


Figure S10 Structural models of Pd (111), 0.3% strained Pd₃Ag (111), and 2.1% strained Pd₃Ag (111) planes and configurations of *CH₃CO. The dark cyan, light cyan, red, gray, and white balls are corresponding to Pd, Ag, O, C, and H atoms, respectively.