Supporting Information

Palladium Hydride with High-Index Facets for Enhanced Methanol Oxidation

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Experimental Section

1. Materials synthesis

1.1 Chemicals and materials: Palladium chloride ($PdCl_2$), potassium hydroxide(KOH), L-ascorbic acid (AA) were purchased from Shanghai Aladdin Co. Ltd.; sodium chloride (NaCl), poly (vinyl pyrrolidone) (PVP, MW≈40000 and MW≈58000), potassium bromide (KBr; 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd.; N,N-dimethylformamide (DMF), ethanol, acetone were purchased from Tianjin Yuanli Chemical Co., Ltd.; Ar (99.999%) was purchased from Tianjin Huanyu High-Tech Gas Co. Ltd. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used for all the experiments. Nafion (5.0 wt%) solution was purchased from Sigma-Aldrich. All the chemicals were used as received without further purification.

1.2 Synthesis of Pd Nanocubes

The synthesis of Pd nanocubes used a modified method by Younan Xia et al[1]. Typically, L-ascorbic acid (60 mg), KBr (600 mg), and PVP (Mw≈40000) (80 mg) were dissolved in deionized water (8.0 mL) in a 25 mL round bottom flask, which was preheated at 80 °C under stirring at least for 10 min to obtain a homogeneous solution. Subsequently, 3 mL of aqueous solution containing $PdCl_2$ (34.4 mg) and NaCl (22.6 mg) was added into the vial. The sealed vial was kept in an oil bath at 80 °C under stirring for 3 h. The final product was collected by centrifugation and further purifed by water/ethanol mixture, and dispersed in 10 mL water to make a seed solution.

1.3 Synthesis of Pd concave nanocubes

The synthesis of Pd concave nanocubes used a modified method by Younan Xia et al[2]. In a typical synthesis, 7.7 mL of an aqueous solution containing PVP (Mw ≈ 58,000) (105 mg), AA (60 mg) and KBr (300 mg), and 0.3 mL of the Pd seeds were mixed in a glass vial. The mixture was heated to 60 °C under stirring. Then, 3.0 mL of aqueous solution containing $PdCl_2$ (8.8 mg) and NaCl (5.8 mg) was added to the mixture by pipette under stirring. The synthesis was allowed to proceed at 60 °C for 3 h. The resulting products were collected by centrifugation (10800 rpm, 10 min) and washed with water three times to remove excess PVP.

1.4 Synthesis of β-Palladium Hydride ($PdH_{0.43}$) concave nanocubes

Typically, the as-synthesized Pd nanocubes above were dispersed in 40 mL of DMF with the assistance of ultrasonic for 10 min. The obtained homogeneous solution was transferred to Teflon-lined stainless-steel autoclave and then heated to 160 °C for 2 h before it was cooled to room temperature. The resulting products were collected by centrifugation (10800 rpm, 10 min) and washed with water three times.

1.5 Preparation of Carbon-Supported Nanoparticles

Carbon powder (Vulcan XC-72R) and catalysts was dispersed in ethanol. The ethanol solutions of catalysts nanoparticles and the carbon powder were sonicated for 2 h. Then the carbon supported nanoparticles were collected by centrifugation. The final products were obtained with a Pd loading of ca. 20%.

2. Materials characterization

The morphology images of the products were taken on a JEOL-1230 transmission electron microscope (TEM) operated at 100 kV. High-resolution transmission electron microscopy (HR-TEM) were carried out on Talos F200X transmission electron microscope (Thermo Fisher Scientific). Powder X-ray diffraction (XRD) analysis was carried out on a D8-Focus diffractometer (Bruker AXS) using Cu Kα radiation ($\lambda = 1.5418$ Å) with a current of 40 mA and a voltage of 40 kV. X-ray photoelectron spectroscopy (XPS) data was collected utilizing an ESCALAB-250Xi spectrometer (Thermo Fisher Scientific) with Al Kα radiation as the X-ray source for excitation. The binding energy was calibrated against the carbon 1s line.

3. Electrochemical measurements

Electrochemical measurements were performed with electrochemical workstation (CHI660E, and CS-150H) with a standard three-electrode system at room temperature. A Hg/HgO electrode and a platinum foil electrode (1 cm × 1 cm) were used as reference and counter electrode, respectively. The catalyst ink was prepared by mixing the carbon-supported catalyst with 980 μl of ethanol, and 20 μl of Nafion (5.0 wt%) to form a suspension under ultrasonication. 8 μl of the catalyst ink of all the powder samples was drop-casted onto glassy carbon (GC) electrode and dried under room temperature to obtain the working electrode (a catalyst-modified glassy carbon electrode with a diameter of 4 mm). The total loading weights of metals were kept constant at around 64 μg cm^{-2} for the Pd and PdH catalysts. All potentials in this paper were measured against the Hg/HgO reference electrode and converted to the pH-independent RHE reference scale by $E \text{ (vs RHE)} = E \text{ (vs HgO)} + 0.098 + 0.059 \times \text{pH}$.

For every measurement, the fresh 1M KOH electrolyte filled in a clean electrochemical cell was deoxygenated with a steady stream of ultrahigh-purity Ar for at least 20 min. The working electrode was first electrochemically cleaned via potential cycling between 0.05 V and 0.9 V versus the RHE for 20 cycles at 200 mV s^{-1} until a stable cyclic voltammogram was recorded.

The CO stripping measurements were carried out in 1 M KOH solution by cycling between 0.05 V and 1.2 V versus RHE at 10 mV s^{-1} for the electrochemical surface area determination.

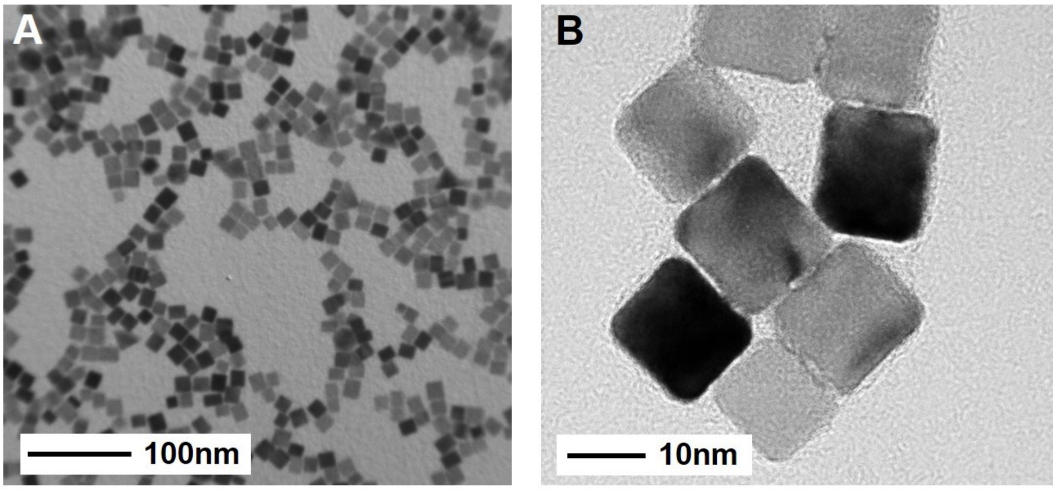

Figure S1. (A) TEM and (B) HRTEM images of Pd nanocubes that were used as seeds for the synthesis of concave Pd nanocubes.

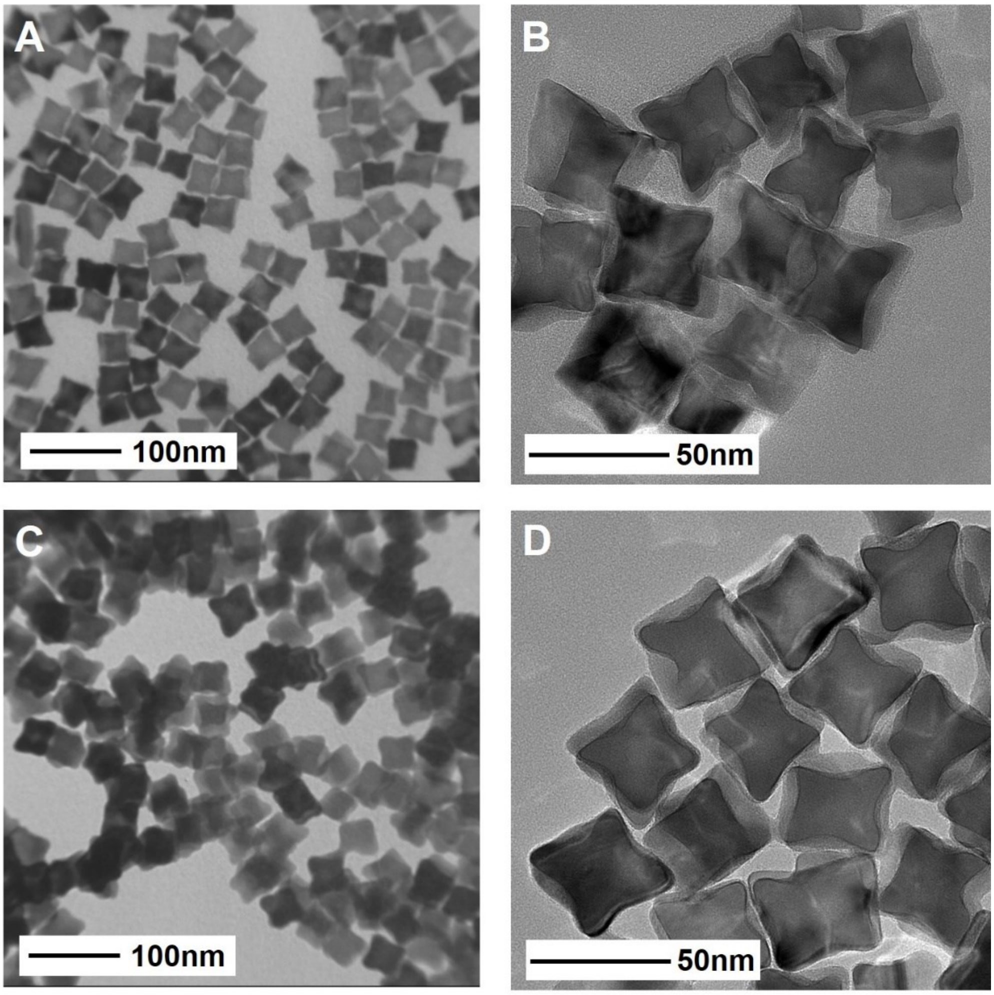

Figure S2. TEM images of (A) Pd concave cubes, (C) PdH concave cubes, and HRTEM images of (C) Pd concave cubes, (D) PdH concave cubes respectively.

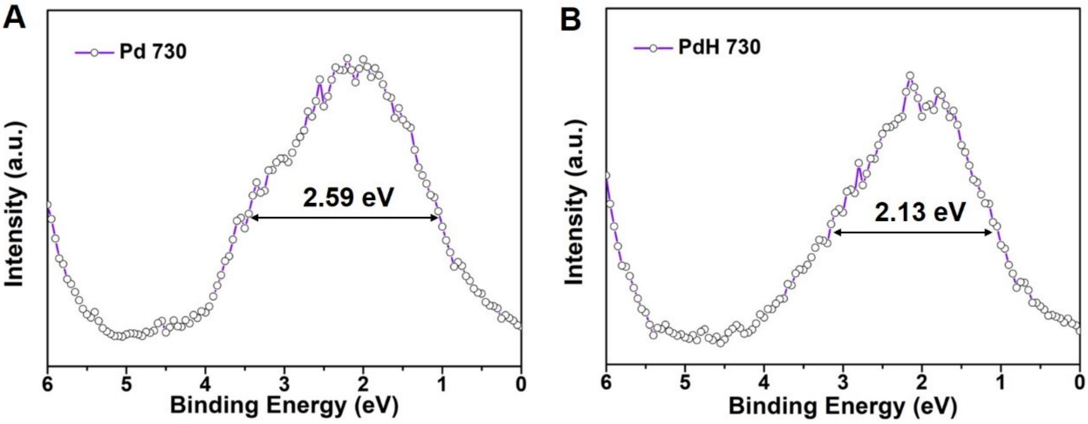

Figure S3. XPS valence band structure of (A) Pd concave cubes, and (B) PdH concave cubes.

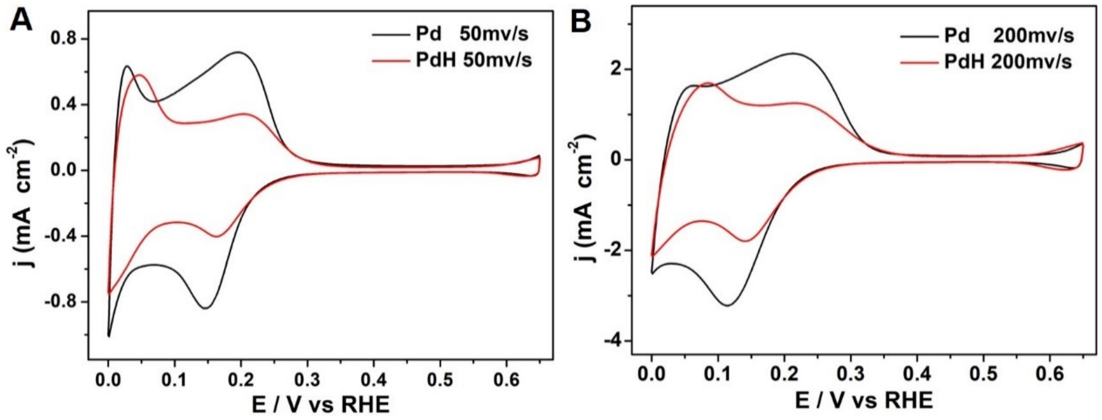

Figure S4. Cyclic voltamograms of (A) Pd concave cubes, and (B) PdH concave cubes in Ar-saturated 0.1 M $HClO_4$ electrolyte with a scan rate of 50 mV s^{-1}.

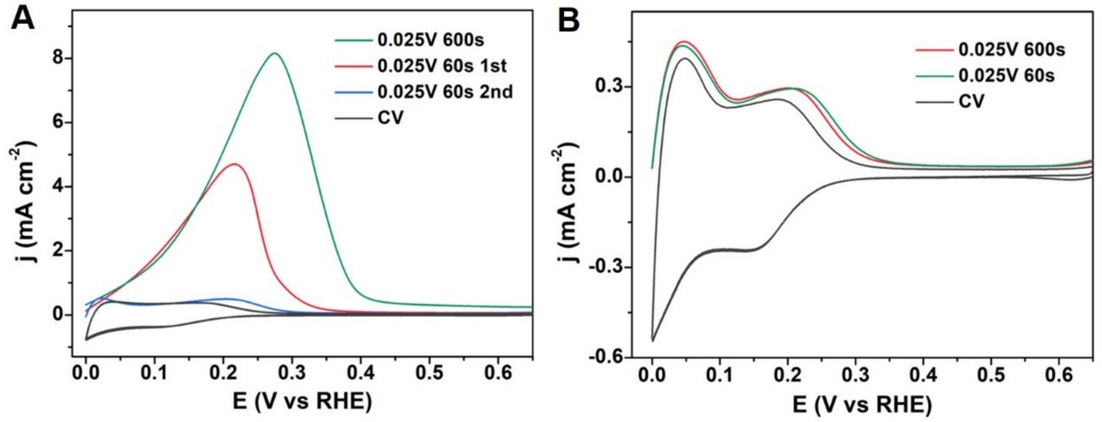

Figure S5. H stripping of (A) Pd, and (B) PdH concave nanocubes in Ar-saturated 0.1 M $HClO_4$ electrolyte (scan rate = 50 mV s−1) after the potential was held at 0.025V vs RHE for different holding time.

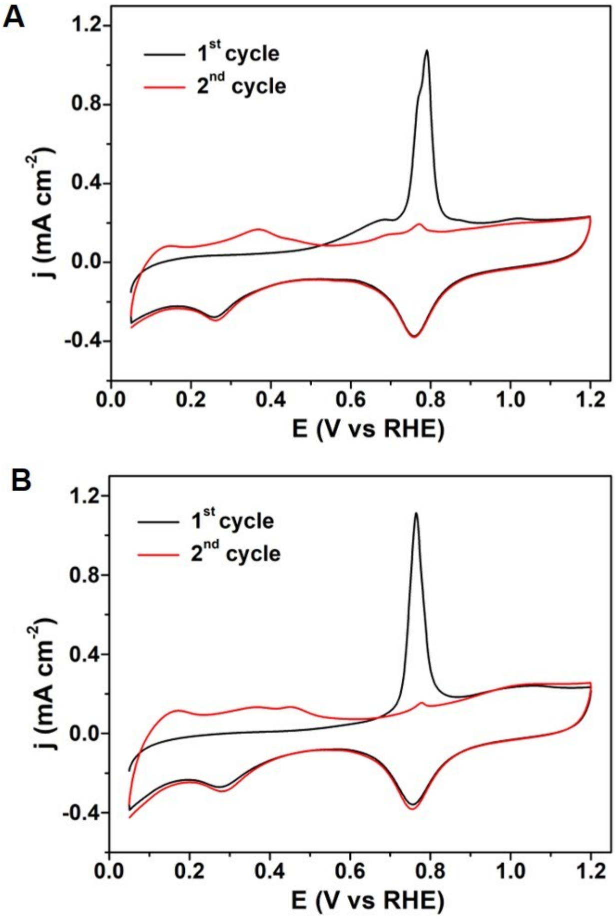

Figure S6. CO stripping voltammograms of (A) Pd concave cubes/C and (B) β-PdH concave cubes/C, respectively in a 1 M KOH solution with a scan rate of 10 mV s^{-1}.

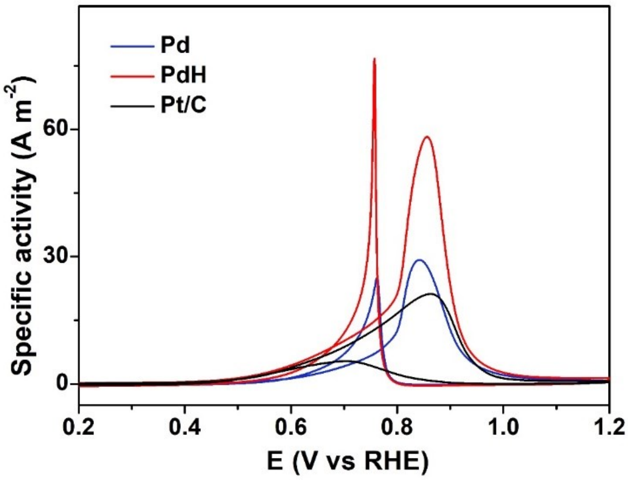

Figure S7 Cyclic voltamograms of Pd concave cubes, β-PdH concave cubes, and Pt/C in an Ar-saturated 1 M methanol + 1 M KOH electrolyte (scan rate = 50 mVs^{-1}) for methanol oxidation.

Table S1. The mass activity of recently reported Pd-based nanomaterials for MOR in CV measurements at 50 mV s^{-1}.

Catalysts	Electrolyte	Mass activity at peak potential [A g^{-1}_{metal}]	Ref.
Pd-PdO PNTs-260	1.0 M KOH + 1.0 M methanol	1111.3	2020[3]
Pd/C	1.0 M KOH + 1.0 M methanol	550	2019[4]
PdCo nanowires	1.0 M KOH + 1.0 M methanol	1080	2018[5]
Pd_2Cu_2/rGO	1.0 M KOH + 1.0 M methanol	916	2018[6]
PdAg@Pd nanoparticles	0.5 M NaOH + 1.0 M methanol	690	2018[7]
PdAuCu (50%)/rGO	1.0 M KOH + 1.0 M methanol	1046	2017[8]
Pd_2P_1 porous network	1.0 M KOH + 1.0 M methanol	870	2016[9]
$Pd_{72}Cu_{14}Co_{14}$/rGO	1.0 M KOH + 1.0 M methanol	1062	2019[10]
$Pd_{0.52}Ag$ on carbon nanotubes	0.5 M NaOH + 1.0 M methanol	720	2019[11]
Cu_2O/Pd networks	0.5 M NaOH + 1.0 M methanol	1030	2016[12]
Pd nanoparticles on N,S-doped graphene	0.5 M NaOH + 1.0 M methanol	399.3	2016[13]

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