Supporting Information

Single-crystalline Pd square nanoplates enclosed by {100} facets on reduced graphene oxide for formic acid electro-oxidation

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Experimental Section

Chemicals and Materials. Graphite oxide powder was purchased from XFNANO at Nanjing. Na₂PdCl₄ (\geq 99.99%), ascorbic acid (AA, 99%), poly (vinyl pyrrolidone) (PVP, MW = 55000) and KBr (\geq 99%) were purchased from Sigma-Aldrich. KCl (99.5%) was purchased from Aladdin. All the chemicals and materials were used as received.

Preparation of Graphene oxide. Graphene oxide (GO) aqueous suspension was obtained by sonicating graphite oxide powder (prepared by Hummer's method) in deionized (DI) water for 2 h. After centrifugation, GO in the supernatant solution was collected by vacuum filtration and then annealed at 60 °C for 1 h. Other GO nanosheets were prepared by annealing in an Ar atmosphere at different temperatures including 100, 150, and 200 °C for 1 h. The annealed GO nanosheets were re-dispersed in DI water for further experiments.

Synthesis of Pd square nanoplates on reduced graphene oxide enclosed by {100} facets (denoted as {100} PdSP@rGO). In a standard procedure, 120 mg of KBr, 12 mg of AA and 50 mg of PVP were dissolved into 8 ml of DI water containing 12.96 mg of GO (annealed at 60 °C for 1 h) in a 25 mL flask. The mixed solution was preheated at 80 °C in the air with magnetic stirring for 10 min. After that, 12 mg of Na₂PdCl₄ was dissolved into 3 mL of DI water, which was quickly injected into the mixed solution in a 25 mL flask. The flask was tightly capped and kept at 80 °C for 3 h before cooled down in an ice water. The product was collected and washed by centrifugation with DI water and ethanol for at least 10 times. Finally, the catalyst powder was obtained by blow-drying with Ar gas at room temperature. Other Pd nanoplates or nanoparticles on GO were produced using GO annealed at 100, 150 and 200 °C as the templates, respectively.

Synthesis of Pd nanoplates on reduced graphene oxide enclosed by {111} facets (demoted as {111} PdNP@rGO). The synthesis of {111} PdNP@rGO followed up the standard procedure, except for replacing KBr with 74.55 mg of KCl.

Synthesis Pd nanocubes on rGO. Pd nanocube@rGO were prepared by the standard procedure, expect for using the fresh GO as the templates.

Synthesis of commercial Pd black on rGO. 11 mL of DI water containing 12.96 mg of GO and 12 mg AA were stirred at 80 °C for 3 h. The rGO was collected by centrifugation with ethanol and re-dispersed in 15 mL of isopropanol. After that, 4.3 mg of the commercial Pd black was added into the solution and dispersed by ultrasonic treatment for 15 min. After stirring for 10 h, rGO supported Pd black was obtained by centrifugation and washed with ethanol for three times.

Phase transfer of {100} PdSP@rGO. 1 mL of as-prepared {100} PdSP@rGO solution was re-dispersed in 6 mL of ethanol. After that, 3 mL of toluene and 6 mL of OAm were added and the mixed solution was heated at 80 °C for 6 h until ethanol and toluene were evaporated completely. The product was collected by centrifugation with ethanol and re-dispersed into cyclohexane for TEM characterization.

Morphological and structural characterizations. Transmission electron microscopy (TEM) images were obtained using a Hitachi HT-7700 microscope operated at 100 kV. High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) were performed using a FEI Tecnai G2 F20 microscope operated at 200 kV. The XRD patterns were recorded on a Bruker D8 focus diffractometer in a scan range of 10-80° at a scan rate of 1.0° min⁻¹. Raman spectroscopy was carried out by Bruker Optic GmbH, SENTERRA equipped with a charge coupled device array detector using a 532 nm excitation laser. Fourier transform infrared spectra (FTIR) were recorded by using a Tensor 27 FTIR spectrometer (Bruker Inc.). The samples were dropped on the surface of KBr pellets.

Electrochemical Measurement. To make catalyst ink, 5 mg of {100} PdSP@rGO powder (29.38 wt.% Pd) was ultrasonically dispersed into 5 mL mixed solution containing 4 mL of DI water (millipore, 18.2 M Ω), 1 mL of isopropanol, and 25 µL of Nafion 117 (Aldrich). For preparation of working electrodes, 10 µL of this ink was pipetted on the surface of glassy carbon (GC) electrode, and then blow-dried under atmospheric conditions. The electrochemical measurements were carried out in the three-electrode system at room temperature using a rotating disk electrode (RDE, Pine Research Instrumentation, United States) connected to an electrochemical workstation (CHI 760E). A Pt wire and a reversible hydrogen electrode (RHE) were used as the counter electrode and reference electrode, respectively. Before electrochemical measurement, the working electrode was cleaned in the Arsaturated 0.1 M HClO₄ solution with a steady-state cyclic voltammograms (CV) scan in the range of 0-1 V *vs* RHE at a rate of 50 mV/s. The electrochemical active surface area (ECSA) was determined by integrating the carbon monoxide oxidation charge via CO stripping measurements. The CO stripping measurements were conducted in CO-saturated 0.1 M HClO₄ solution at a scan rate of 50 mV/s in the range of 0.1-1.2 V vs RHE. Formic acid oxidation reaction (FAOR) was performed in a mixture solution containing 0.5 M H₂SO₄ and 0.5 M HCOOH at a scan rate of 50 mV/s in the range of 0.1-1.1 V *vs* RHE. The chronoamperometry (I-t) curves were measured at 0.35 V (vs RHE) for 1500 s.



Fig. S1 (A) Raman spectrum and (B) TEM image of GO annealed at 60 °C for 1 h.



Fig. S2 (A) Selected area electron diffraction (SAED) pattern of {100} PdSP@rGO prepared using the standard procedure with reaction time of 3 h. (B) XRD patterns of {100} PdSP@rGO by reacting for 1 min and 30 mins, respectively.



Fig. S3 TEM of Pd nanoplate@rGO prepared using the standard procedure, except for different temperature or concentration of Na_2PdCl_4 : (A) 60 °C, 12 mg of Na_2PdCl_4 and (B) 80 °C, 24 mg of Na_2PdCl_4 .



Fig. S4 TEM and HRTEM images of {100} PdSP@rGO prepared for different reaction times: (A, B) 1 min and (C, D) 30 mins.



Fig. S5 A set of TEM images showing the thickness of {100} PdSP@rGO prepared at a reaction time of 1 min. The scale bar is 20 nm.



Fig. S6 A set of TEM image showing the thickness of {100} PdSP@rGO prepared at a reaction time of 3 h. The scale bar is 20 nm.



Fig. S7 TEM image of the Pd nanocubes prepared in the absence of GO with other conditions being the same as in the standard procedure.



Fig. S8 TEM images of the products prepared using the standard procedure, except for using GO annealed at different temperatures as the templates: (A) fresh GO, (B) 100 °C, (C) 150 °C, and (D) 200 °C.



Fig. S9 FTIR spectrum of fresh GO at a higher magnification.



Fig. S10 Schematic illustration for the formation of {100} PdSP@rGO.



Fig. S11 (A) TEM and (B) HRTEM of Pd nanoplates@rGO prepared using the standard procedure in the absence of KBr and KCl.



Fig. S12 Electrochemical measurements of the Pd black@rGO, Pd nanocubes@rGO, $\{111\}$ PdNP@rGO and $\{100\}$ PdSP@rGO. (A) CO stripping curves. The solid and dotted lines represent the first and second cycles, respectively. (B) Cyclic voltammograms (CV) of these four catalysts in 0.5 M HCOOH and 0.5 M H₂SO₄ solution with a sweep rate of 50 mV/s recorded at room temperature. (C) Current–time (I–t) curves for the FAOR at 0.35 V (vs. RHE) for 1500 s.



Fig. S13 TEM images of (A) 18 nm Pd nanocubes@rGO, (B) {111} PdNP@rGO, and (C) {100} PdSP@rGO after electrochemical measurements.