

Supporting Information

Synthesis of “Clean” and Well-Dispersive Pd Nanoparticles with Excellent Electrocatalytic Property on Graphene Oxide

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Experimental Details

1. Reagents

K_2PdCl_4 was purchased from Wake Pure Chemicals, Co. Ltd. (Japan); the graphite powder was from Lvyin Co. (China); 5% Nafion ethanol solution and Pd/C catalyst (containing 10 wt% Pd) were from Aldrich Chem Co. (USA) and rod glassy carbon electrodes (GCEs) were from BAS Co. Ltd. (Japan). All other reagents were of analytical grade and used without further purification. The pure water for solution preparation was from a Millipore Autopure WR600A system (USA).

2. Instrumentation

Morphologies and crystal structures of PdNPs-GO observed by TEM and HRTEM was performed on a JEM-2100 transmission electron microscopy with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with carbon film. Electronic binding energies of C_{1s} and Pd_{3d} were measured by XPS analysis which was performed on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatised microfocused Al X-ray source. All the binding energies were calibrated by C_{1s} as reference energy ($C_{1s} = 284.6$ eV). Cyclic voltammetry (CV) measurements were performed with a CHI 660B Electrochemical Analyzer. A conventional three-electrode system included a GCE coated with catalyst film, a silver auxiliary electrode and a saturated calomel reference electrode (SCE). All potentials reported in this paper are referred to the SCE scale.

3. Procedures

Graphene oxide (GO) was prepared according to a modified Hummer's method. 50 mg as-synthesized GO was dispersed in 100 mL water to obtain a yellow-brown aqueous solution with the aid of ultrasonication. In a typical synthesis of PdNPs-GO, homogeneous GO suspension

(5 mL 0.5 mg mL⁻¹) and K₂PdCl₄ (0.5 mL 10 mM) aqueous solution was kept in a vial under vigorous stirring for 30 min in an ice bath. Then, the reaction mixture was washed with pure water and centrifuged to remove the remaining reagents. Before the preparation of the catalysts modified GCE, the GCE was polished with 1, 0.3 and 0.05 μm α-Al₂O₃, sequentially. Water dispersion of purified products were then deposited on the polished GC electrode and dried in the air for 4 h at room temperature.

Supplementary Results

1. Characterizations of PdNPs-GO

(1) XPS

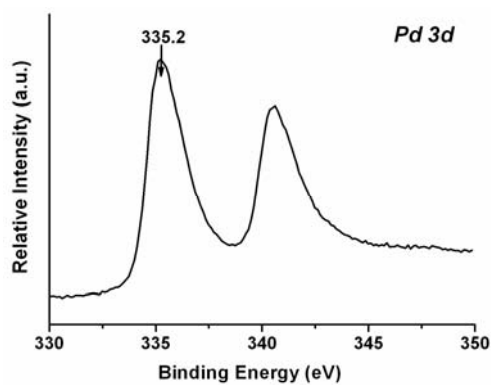


Figure S1. XPS spectrum of Pd_{3d} on PdNPs-GO.

(2) Stability

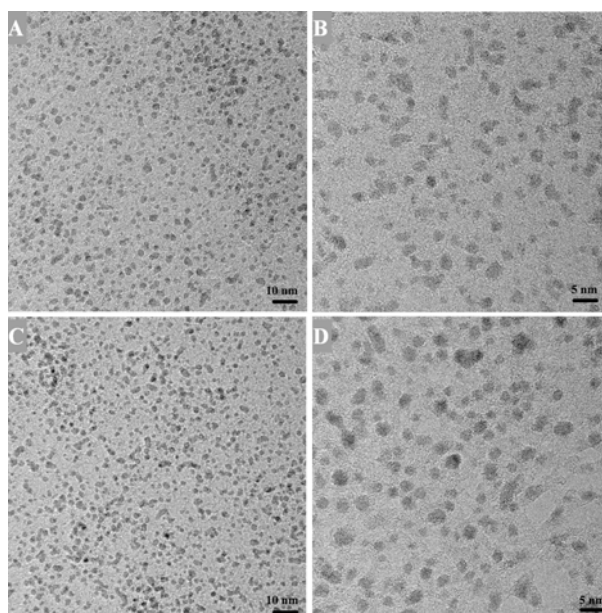


Figure S2. TEM images of PdNPs-GO synthesized at 0 °C: (A-B) fresh product (C-D) dispersed in aqueous solution after 2 months.

2. Effect of preparation conditions on the morphology of PdNPs-GO

(1) Time effect

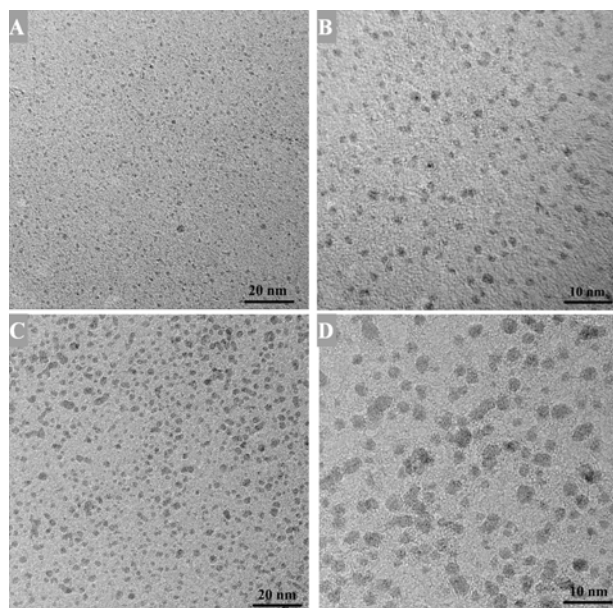


Figure S3. TEM images of the product after reaction for 5 min (A, B) and 30 min (C, D).

(2) Temperature effect

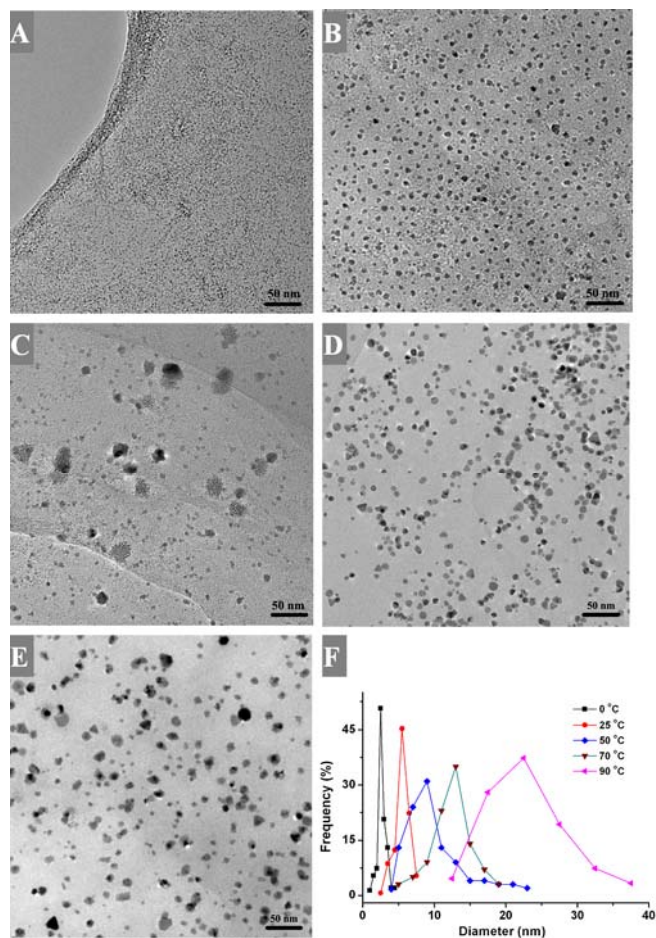


Figure S4. TEM images of PdNPs-GO synthesized at (A) 0 °C, (B) 25 °C, (C) 50 °C, (D) 70 °C and (E) 90 °C. (F) Summary curve of the temperature-dependent size of each sample.

3. CVs results of catalysis

Before electrocatalytic activity test, two cycles of potential sweeps between -0.20 V and 1.2 V at 100 mV s⁻¹ were applied on the GC electrode modified with catalysts. The electrochemical active surface areas (ECSAs) of catalysts were determined by electric charge of hydrogen desorption (Q_H), by adapting the assumption of 212 μC cm⁻². Figure S5 shows the CVs of our PdNPs-GO catalyst and commercial Pd/C catalyst recorded in 0.5 M H₂SO₄. The electric charge of the hydrogen desorption on PdNPs-GO and Pd/C are measured to be 37.2 μC and 32.4 μC, respectively. After adapting the assumption of 212 μC cm⁻², the ECSAs of PdNPs-GO and Pd/C are 0.175 cm² and 0.153 cm², respectively. The oxidation currents were normalized to the ECSAs for further comparing the activities of different catalysts.

(1) ECSAs

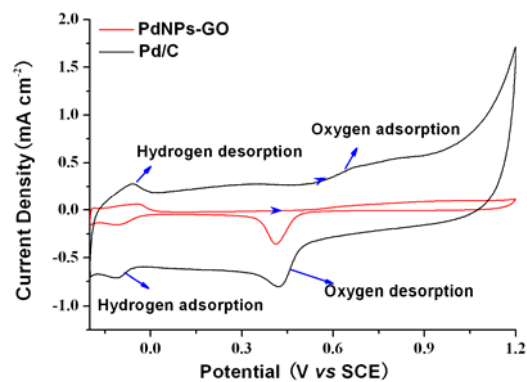


Figure S5. CVs of PdNPs-GO and commercial Pd/C catalyst recorded

in 0.5 M H₂SO₄ at 50 mV s⁻¹.

(2) Electrocatalytic stability

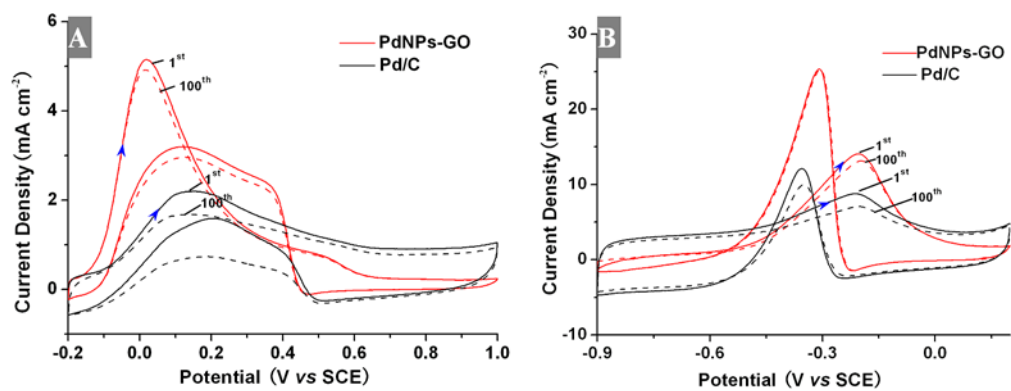


Figure S6. Electrocatalytic stability test of PdNPs-GO and commercial Pd/C catalyst in (A) 0.5 M

H₂SO₄ with 0.25 M formic acid and (B) 1.0 M NaOH with 0.5 M ethanol.