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Supporting Information

One-step seed-less wet-chemical synthesis of gold@palladium nanoflowers supported on reduced graphene oxide with enhanced electrocatalytic properties

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Experimental section

Chemicals

Natural graphite powder (99.95%, 8000 mesh), melamine, poly(vinylpyrrolidone) (PVP, K-30), formic acid (HCOOH, 88%), chloroauric acid (HAuCl₄), palladium chloride (PdCl₂), and commercial Pd black were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). The other chemicals were of analytical grade and used as received. All of the aqueous solutions were prepared with twice-distilled water.

Synthesis

Graphene oxide (GO) was prepared from natural graphite powder by a modified Hummers' method.^{1, 2} Next, 5 mg of GO was dispersed in 50 mL of water by ultrasonication to obtain a brownish-yellow aqueous suspension.

For typical synthesis of Au@Pd nanoflowers supported on reduced graphene oxide (AuPd@Pd/rGO), 5 mL of 0.1 mg mL⁻¹ GO suspension was mixed with 250 µL of 10 mM HAuCl₄, 250 µL of 10 mM PdCl₂, 2 mL of 50 mM melamine, and 1 mL of 5 mg mL⁻¹ PVP. After homogeneous mixing, 2 mL of formic acid was drop-wisely added to the mixed solution under vigorous stirring. Afterward, the mixture was heated in a water-bath at 60 °C for 1 h under stirring. The resulting products were collected by centrifugation and thoroughly washed with water and ethanol, and finally dried at 60 °C in vacuum for further characterization. Control experiments were performed by varying the precursor, as well as without melamine, PVP, or GO, while other conditions were kept unchanged. Additionally, N-doped rGO was modified by melamine.

Characterization

Transmission electron microscopy (TEM) images were taken on a JEOL-2100F transmission electron microscope operated at 200 kV equipped with selective area electron diffraction (SAED). Energy dispersive spectroscopy (EDS) line scans were acquired on the scanning transmission electron microscope (STEM) with a high-angle annular dark-field (HAADF) detector operating at 30 kV (HITACHI S-5500). The powder X-ray diffraction (XRD) patterns were collected by using a Philips PW3040/60 diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) was performed by using a Themo SCIENTIFIC ESCALAB 250 with Al K α X-ray radiation (1486.6 eV). Fourier transform infrared

(FT-IR) analysis was conducted on a Nicolet NEXUS670 Fourier transform infrared spectrometer in the wave-number range of 500~4000 cm⁻¹. Thermogravimetric analysis (TGA) was performed under air by using a simultaneous thermogravimetric analyzer (NETZSCH STA 449C) from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

Electrochemical measuremants

All the electrochemical experiments were performed on a CHI 832B electrochemical workstation (CHI Instruments, Chenhua Co., Shanghai, China). A conventional three electrode system include a glass carbon rotating disk electrode (RDE, d = 4 mm, geometric area of 0.1256 cm²) or a glass carbon electrode (GCE, d = 3 mm, geometric area of 0.0706 cm²) as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

The preparation of the Au@Pd/rGO modified electrode is as follows: 1 mg of the sample was dispersed in 1 mL water by ultrasonication to form a homogeneous suspension. Then, 6 and 20 μ L of the suspension were casted on the GCE and RDE, dried in air at room temperature. Next, 6 and 10 μ L of Nafion (0.05 %) was coated on the electrode surface and dried naturally. The loading of the catalyst on the electrode surface is around 0.08 and 0.16 mg cm⁻². For comparison, Pd black, Pd/rGO, and Au/rGO modified electrodes were prepared with the similar procedure.

The ORR polarization curves were recorded by linear sweep voltammetry (LSV)

in O₂ saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹ by varying the rotation rates from 100 to 2500 rpm. Koutecky-Levich plots (*j*⁻¹ vs. $\omega^{-1/2}$) were analyzed at different electrode potentials. The corresponding slopes from the fitting lines are employed to calculate the electron transfer number according to the Koutecky-Levich equation (1-2):^{3, 4}

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$
(1)

$$B = 0.2nFC_0 D_0^{2/3} v^{-1/6}$$
⁽²⁾

where *j* is the measured current density, j_k is the kinetics-limited current density, ω is the electrode rotation rate, *n* is the electron transfer number, *F* is the Faraday constant (96485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.2 × 10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm² s⁻¹), and *v* is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹).

The specific and mass current densities were normalized in terms of the geometric area of RDE and GCE, along with the loading amount of metal, respectively. Stability tests were carried out by chronoamperometry at the applied potential of -0.4 V for 6000 s at a rotation rate of 1600 rpm. And the repeated ORR polarization curves were recorded in O₂ saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. For EG oxidation, cyclic voltammetry and chronoamperometry experiments were conducted in 0.1 M KOH containing 0.5 M EG. All the experiments were performed at room temperature, if not stated otherwise.



Fig. S1 Representative TEM images of Au/rGO (A) and Pd/rGO (B).



Fig. S2 TGA curves of Au@Pd/rGO (curve a), Pd/rGO (curve b), and Au/rGO (curve

c).



Fig. S3 High-resolution XPS spectra of C 1s for GO (A), Au 4f for Au/rGO (B), Pd 3d for Pd/rGO (C).



Fig. S4 FT-IR spectra of Au@Pd/rGO (curve a), Pd/rGO (curve b), Au/rGO (curve c), and GO (curve d).



Fig. S5 Representative TEM images of Au@Pd/rGO obtained in absence of melamine (A), PVP (B), and GO (C).



Fig. S6 Representative TEM images of Au@Pd/rGO obtained at the reaction temperature of 25 °C (A), 40 °C (B), and 80 °C (C).



Fig. S7 Representative TEM image of Pd black.



Fig. S8 ORR polarization curves (A) and CV curves (B) of N-doped rGO (curve a) and blank rGO (curve b).

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