

## Supporting Information

### **Facile synthesis of hierarchical dendritic PtPd nanogarlands supported on reduced graphene oxide with enhanced electrocatalytic property**

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## **Experimental section**

### **1. Materials**

Natural graphite powder (99.95%, 8000 mesh), octylphenoxypolye thoxyethanol (NP-40, C<sub>33</sub>H<sub>60</sub>O<sub>10</sub>), ascorbic acid (AA), chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), palladium chloride (PdCl<sub>2</sub>), commercial 10% Pt/C and 10% Pd/C catalysts were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). All the other chemicals were of analytical grade and used without further purification. All the solutions were prepared with twice-distilled water in the whole experiments.

### **2. Preparation of graphene oxide (GO)**

Graphene oxide (GO) was prepared from natural graphite powder via acid-oxidation according to the modified Hummers' method.<sup>1,2</sup> After the removal of residual salts and acids, the resultant dispersion was subjected to ultrasonic treatment to obtain exfoliated GO.

### **3. Preparation of the PtPd/RGO**

Typical synthesis of the PtPd/RGO was described as follows. Prior to use, the GO suspension was ultrasonicated for at least 30 min. Then, 5.0 mL GO suspension (0.5 mg mL<sup>-1</sup>), 1.5 mL H<sub>2</sub>PtCl<sub>6</sub> (10 mM), 1.5 mL PdCl<sub>2</sub> (10 mM), and 0.5 mL NP-40 (0.5 mg mL<sup>-1</sup>) were mixed together by gentle agitation, followed by slow addition of 0.5 mL freshly prepared AA solution (0.1 M) under mild stirring. Next, the mixture was kept at room temperature without agitation for 12 h. The color of the reaction solution was changed from transparent brownish-yellow to dark brownish-red, and finally to opaque black. The resulting black precipitate was collected by centrifugation and thoroughly washed with water and ethanol. The collected product was dried in vacuum at 50 °C for further characterization. For comparison, Pt/RGO and Pd/RGO nanocomposites were prepared in a similar way, only using H<sub>2</sub>PtCl<sub>6</sub> or PdCl<sub>2</sub> as

precursors, and the common PtPd nanoparticles/RGO was prepared without using NP-40, while the other conditions were kept unchanged.

#### **4. Instrumental characterization**

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were taken on a JEOL-2100F transmission electron microscope operated at 200 kV equipped with selective area electron diffraction (SAED) and energy dispersive X-ray spectrometer (EDS). The samples for TEM and HRTEM measurements were prepared by depositing a drop of the diluted sample on a carbon-coated copper grid and dried at room temperature. The elemental mappings were carried out on the scanning transmission electron microscope (STEM) with a high-angle annular dark-field (HAADF) detector operating at 30 kV (HITACHI S-5500). X-ray diffraction (XRD) patterns were obtained by a Philips PW3040/60 diffractometer with Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm). UV-vis absorption spectra were recorded by using a Thermo Nicolet Evolution 500 spectrometer. Fourier transform infrared (FT-IR) analysis was conducted on a Nicolet NEXUS670 Fourier transform infrared spectrometer in the wave-number range of 500 ~ 4000  $\text{cm}^{-1}$  and X-ray photoelectron spectrometer (XPS) experiments were performed by using a Thermo SCIENTIFIC ESCALAB 250 with Al K $\alpha$  X-ray radiation (1486.6 eV) for excitation. Raman spectra were recorded by using a Renishaw RM1000 spectrometer with a He/Ne laser at a wavelength of 633 nm. Thermo gravimetric analysis (TGA) was carried out in air by using a simultaneous thermo gravimetric analyzer (Netzsch STA 449C) from room temperature to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$ .

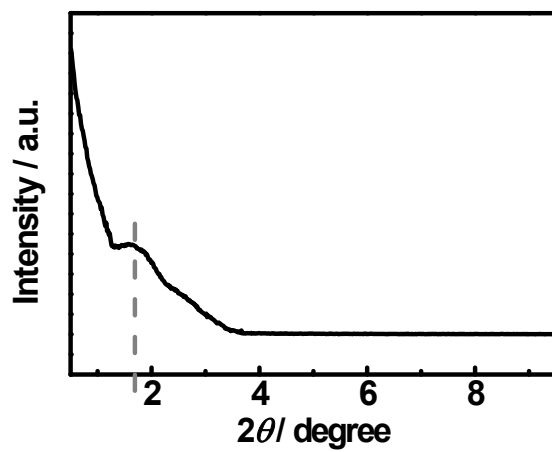
#### **5. Electrochemical measurements**

Cyclic voltammetry, CO-stripping voltammetry, chronoamperometry, and accelerated durability test (ADT) experiments were performed on a CHI 660D electrochemical analyzer (CHI Instrument, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a Pt wire as counter electrode, and a bare or modified glassy carbon electrode (GCE,  $d = 3$  mm) as working electrode. The modified GCE was coated with the PtPd/RGO, Pt/RGO, Pd/RGO, commercial 10% Pt/C, commercial 10% Pd/C, and PtPd nanoparticles/RGO catalysts, respectively, and dried in air, followed by casting 5  $\mu$ L of Nafion (0.05 %) to seal the samples in place. In each case, the specific loading of the catalyst is 0.06 mg without a dramatic difference. Current densities were normalized in reference to the geometric area of the GCE.

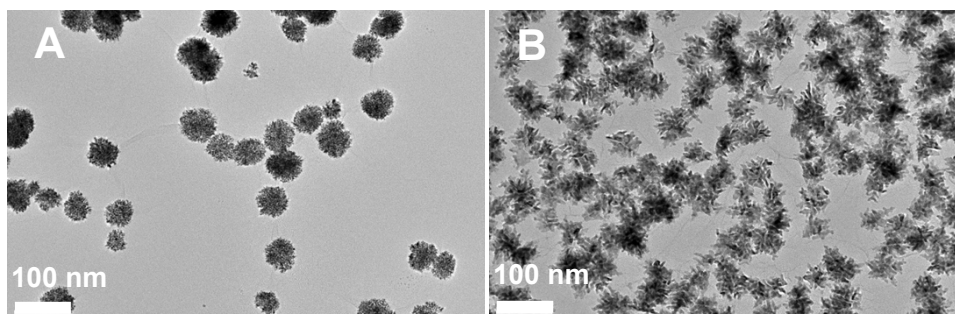
CO-stripping voltammetry experiments were conducted by oxidizing preadsorbed CO in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of 50  $\text{mV s}^{-1}$ . Methanol and ethanol oxidation reaction measurements were carried out in 1.0 M KOH containing 1.0 M methanol and 1.0 M ethanol at a scan rate of 50  $\text{mV s}^{-1}$ , respectively. The electrochemically active surface area (EASA) of the catalysts was estimated by the CO-stripping measurements, assuming a value of 420  $\mu\text{C cm}^{-2}$  for the process. Then, the specific EASA was calculated according to the following equation (1):<sup>3-5</sup>

$$EASA = \frac{Q}{m \times 420} \quad (1)$$

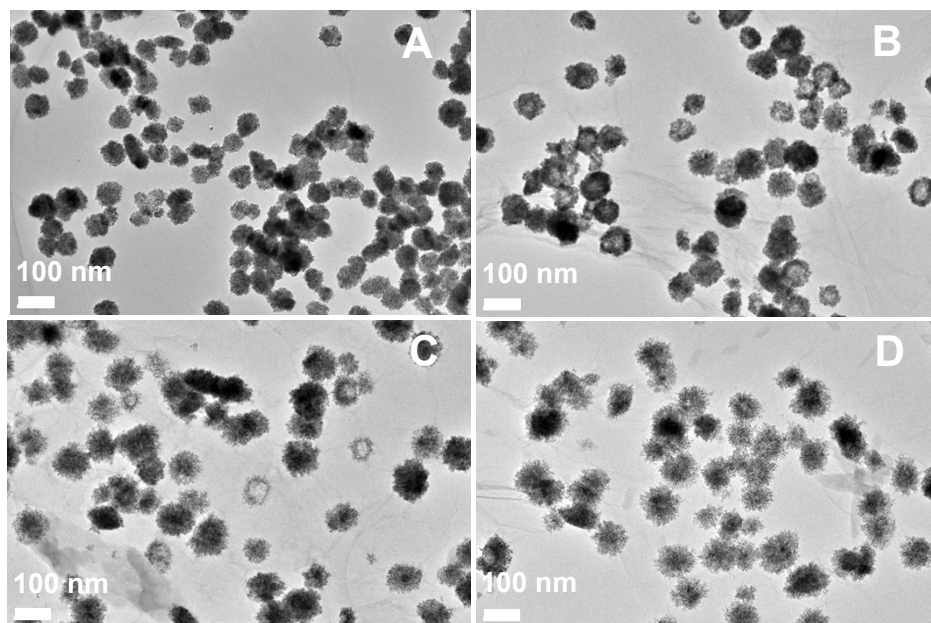
where  $Q$  is the charge of oxidation of the adsorbed CO ( $\mu\text{C}$ ),  $m$  represents the total amount of metal ( $\mu\text{g}$ ) on the electrode.



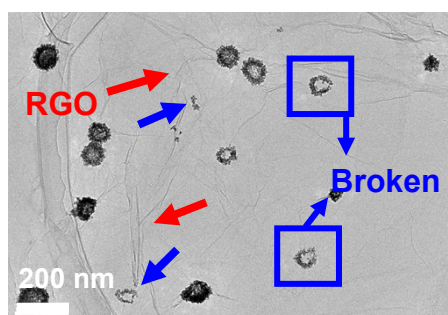
**Fig. S1** Low-angle XRD spectrum of the garland-like PtPd/RGO.



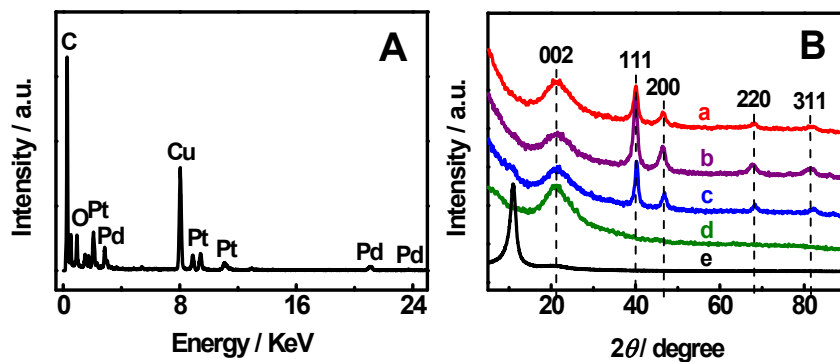
**Fig. S2** TEM images of the Pt/RGO (A) and Pd/RGO (B).



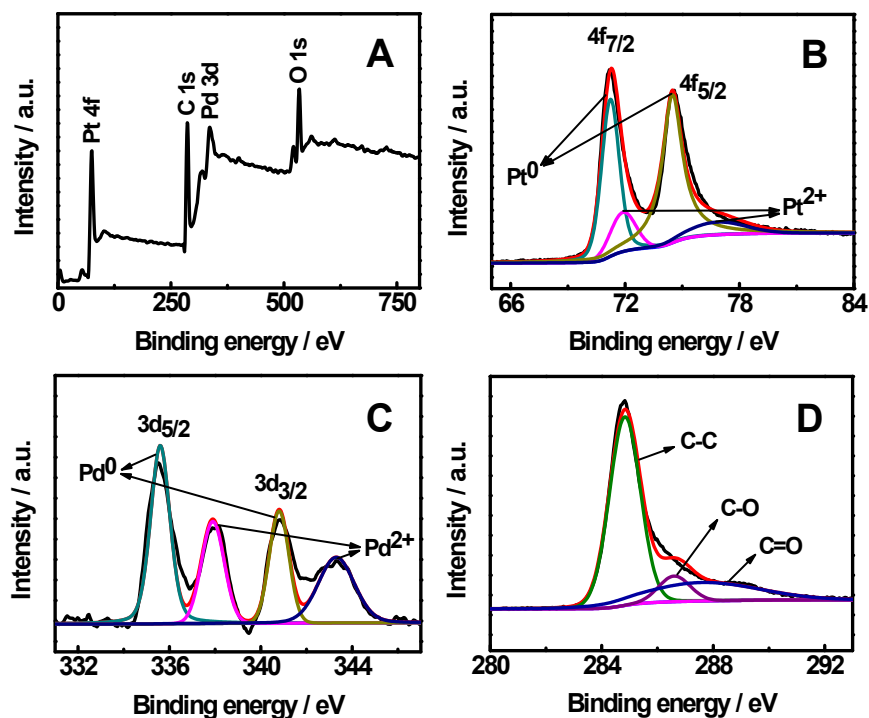
**Fig. S3** TEM images of the PtPd/RGO obtained without (A), and with 0.1 mg (B), 0.5 mg (C), and 1.0 mg (D) NP-40.



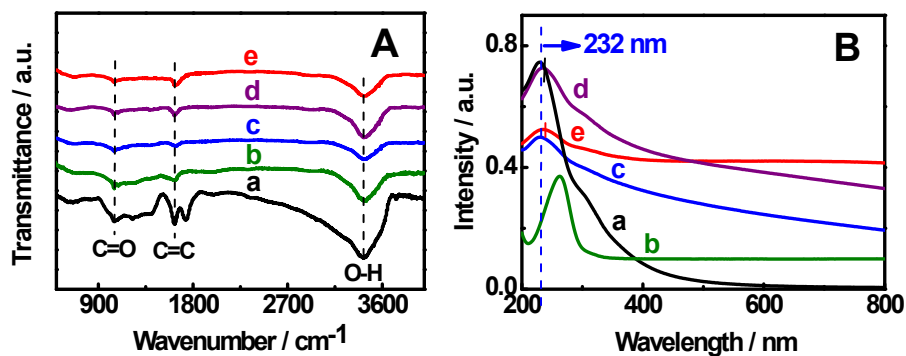
**Fig. S4** TEM images of the PtPd/RGO obtained with the reaction time of 36 h. Red arrows indicate the wrinkles of the RGO.



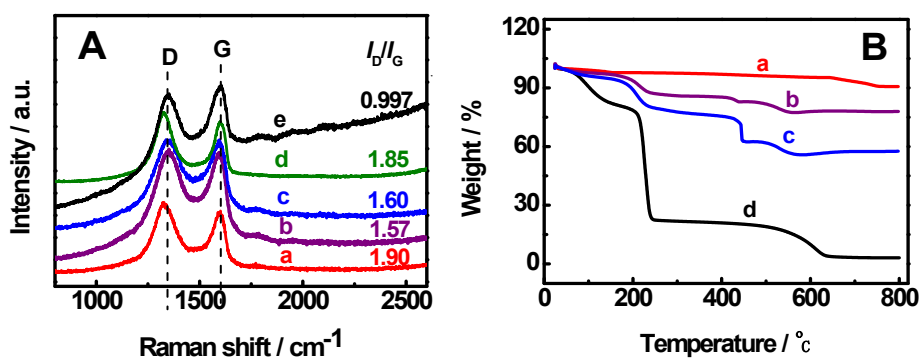
**Fig. S5** EDS pattern (A) of the garland-like PtPd/RGO. Wide-angle XRD patterns (B) of the PtPd/RGO (curve a), Pt/RGO (curve b), Pd/RGO (curve c), RGO (curve d), and GO (curve e), respectively.



**Fig. S6** Survey (A), and high-resolution XPS spectra of Pt 4f (B), Pd 3d (C), and C 1s (D) of the garland-like PtPd/RGO.

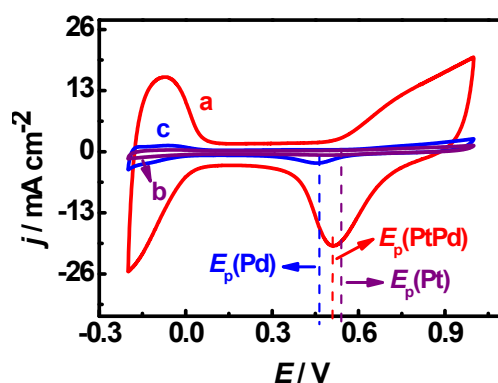


**Fig. S7** FT-IR (A) and UV-vis absorption (B) spectra of the GO (curve a), RGO (curve b), Pd/RGO (curve c), Pt/RGO (curve d), and PtPd/GO (curve e), respectively.

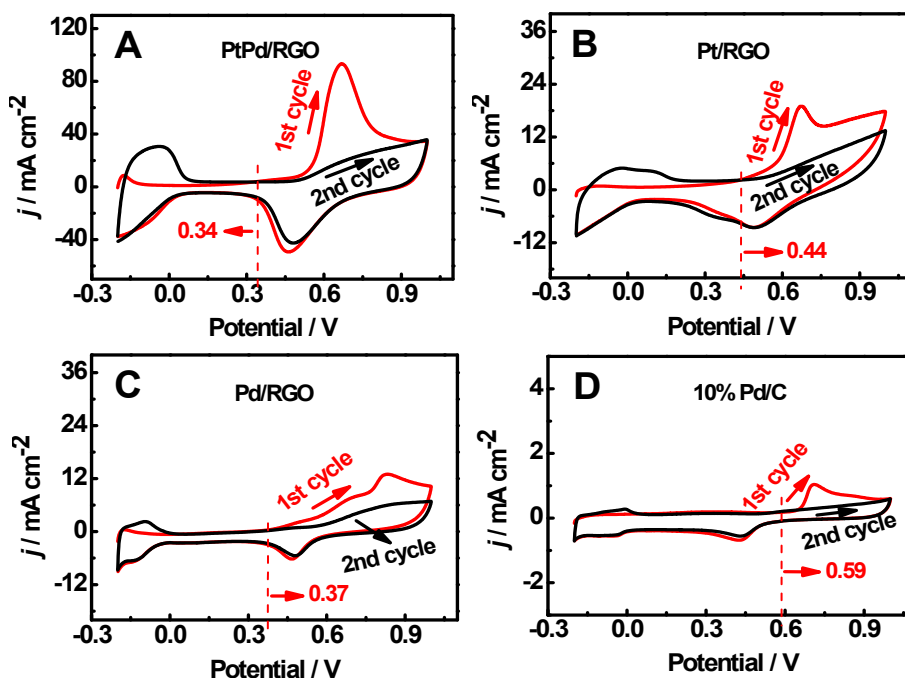


**Fig. S8** (A) Raman spectra of the PtPd/RGO (curve a), Pt/RGO (curve b), Pd/RGO (curve c), RGO (curve d), and GO (curve e), respectively. (B) TGA curves of the PtPd/RGO (curve a), Pt/RGO (curve b), Pd/RGO (curve c), and GO (curve d), respectively.

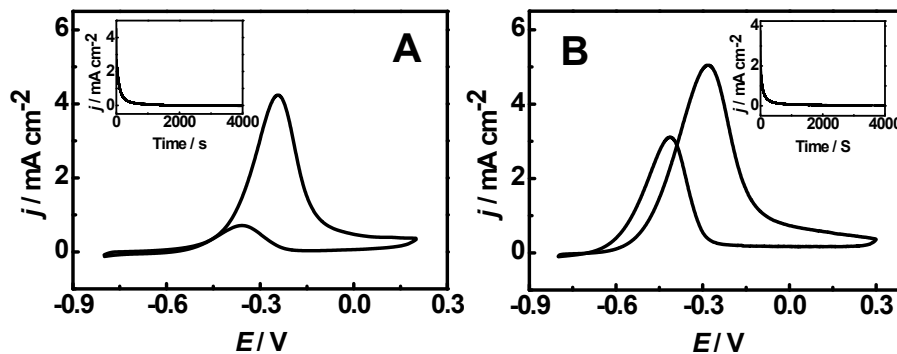




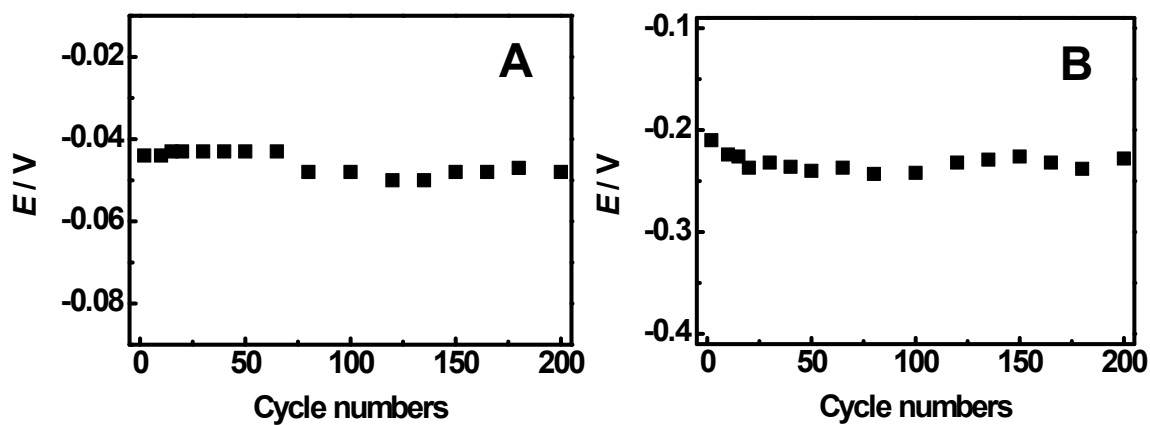
**Fig. S9** Cyclic voltammograms of the PtPd/RGO (curve a), Pt/RGO (curve b), and Pd/RGO (curve c) catalysts modified electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S10** CO-stripping voltammograms of the PtPd/RGO (A), Pt/RGO (B), Pd/RGO (C), and commercial 10% Pd/C (D) catalysts modified electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $50 \text{ mV s}^{-1}$ .



**Fig. S11** Cyclic voltammograms of the common PtPd nanoparticles/RGO modified electrode in 1.0 M KOH containing 1.0 M methanol (A) and 1.0 M ethanol (B). Insets show the corresponding chronoamperometry curves.



**Fig. S12** The  $E_p$  changes of the PtPd/RGO modified electrode for methanol (A) and ethanol (B) oxidation in the ADT measurements.

**Table S1** XPS surface atomic concentration of the PtPd/RGO.

Sample	C (%)	O (%)	Pt (%)	Pd (%)
PtPd/RGO	77.108	15.964	4.565	2.363

**Table S2** Comparison of the electrochemical performance of the five catalysts for methanol and ethanol oxidation.

Catalysts	$E_{\text{on}} / \text{V}$ (methanol)	$j_{\text{F}} / \text{mA cm}^{-2}$ (methanol)	$E_{\text{on}} / \text{V}$ (ethanol)	$j_{\text{F}} / \text{mA cm}^{-2}$ (ethanol)
PtPd/RGO	-0.67	252	-0.69	228
Pt/RGO	-0.66	23	-0.65	12
Pd/RGO	-0.55	22	-0.66	23
10% Pt/C	-0.6	10	-0.62	6.4
10% Pd/C	-0.58	8.1	-0.65	4.6

## References

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