

Supplementary Information

The role of reducing agent in Perylene tetracarboxylic acid coating on graphene sheets enhances Pd nanoparticles-electrocatalytic ethanol oxidation

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Inductive coupled plasma atomic emission spectrometer (ICP-AES) analyses were conducted with Perkin Elmer (Optima-4300DV).

Table S1 Pd loadings measured by ICP.

Catalysts	Pd (wt%)
Pd/PTCA-GS(NaBH ₄)	14.12
Pd/PTCA-GS(EG)	12.50
Pd/PTCA-GS(H ₂)	13.92
Pd/GS(NaBH ₄)	13.55
Pd/GS(EG)	10.40
Pd/GS(H ₂)	13.32
Pd/ rGO(NaBH ₄)	13.24
Pd/C	10.00

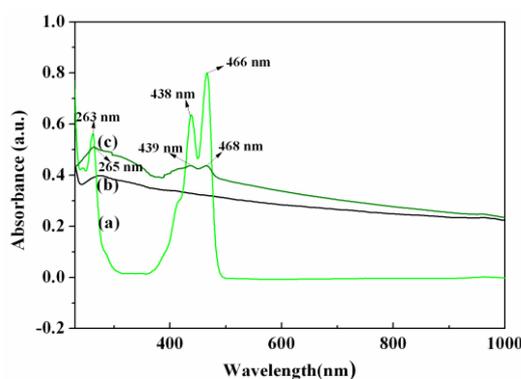


Fig. S1 UV-vis absorption spectra of (a) PTCA (0.01 mg mL⁻¹), (b) GS (0.02 mg mL⁻¹) and (c) PTCA-GS (0.02 mg mL⁻¹).

To further investigate the PTCA functionalized on the surface of GS, the UV-vis spectra of PTCA, GS and PTCA-GS in water were measured and were displayed in Fig.S1. UV-Vis absorption spectra were recorded using a T6 UV-vis spectrometer. Three characteristic peaks around 263 nm, 438 nm and 466 nm were clearly observed in the spectra of PTCA, which were attributed to the PTCA molecules.^{1, 2} The characteristic absorption of GS appeared at 276 nm corresponding to the restored π -conjugation network.³ Compared with GS, the PTCA-GS revealed obvious absorption peaks at 265 nm, 439 nm and 468 nm. In particular, there was a slight red shift of 2 nm compared with the PTCA, which were generated by the π - π stacking interaction between PTCA unit and GS.⁴ The results of UV-Vis spectra implied that the PTCA has been successfully immobilized on the surface of GS by the π - π stacking.

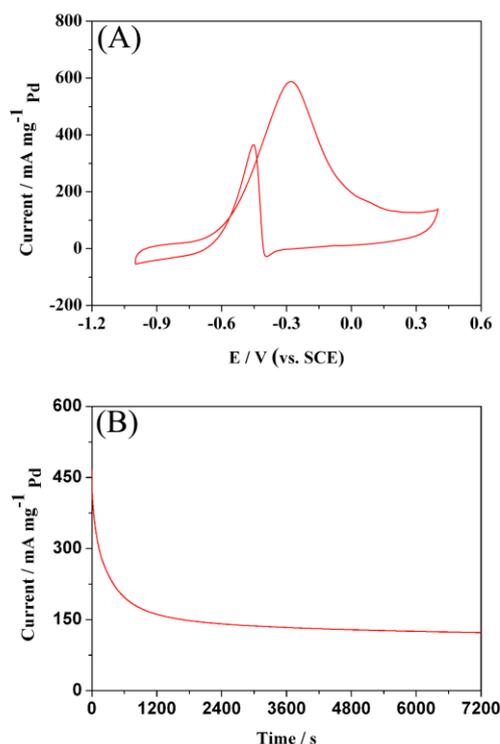


Fig. S2 (A) CVs of Pd/rGO(NaBH₄) at a scan rate of 50 mV s⁻¹ and (B) Chronoamperometric curves of Pd/rGO(NaBH₄) for ethanol electrooxidation in nitrogen-saturated 1 M KOH + 1 M CH₃CH₂OH solution

As a comparison, the Pd NPs loading on the chemical reduced graphene (Pd/rGO(NaBH₄)) was prepared and the performance of Pd/rGO(NaBH₄) has been carried out (Fig. S2). The preparation process of Pd/rGO(NaBH₄) was as following. The GO which was synthesized by Hummer's method⁵ (20 mg) was dissolved in H₂O (20 mL) with ultrasonic treatment to form a uniform suspension. Then, PdCl₂ solution (0.01 M, 3.4 mL) was added into the suspension under stirring and the mixture was stirred for 30 min in room temperature. Subsequently, the NaBH₄ solution (5.0 mL 0.1 M) was delivered by drops into the above suspension under continuous stirring. After reacting for 4 h at room temperature, the black solid material was separated by centrifugation, washed repeatedly with water and ethanol several times, and dried in a vacuum at 60 °C for 12 h. As shown in Fig.S2, the I_f and I_s (588.0 mA mg⁻¹ and 123.3 mA mg⁻¹) for Pd/rGO(NaBH₄) were lower than that of Pd/GS(NaBH₄). It was due to the structural damage of graphene which adversely affects the electrical, mechanical, and stable properties of the material because of the transformation of carbon atoms from a planar sp²-hybridized geometry to a distorted sp³-hybridized geometry.⁶ In addition, the oxygen existing in the GO also could reduce the conductivity for

graphene. However, the E_S (-0.692 V) for the Pd/rGO(NaBH₄) was more negative than those on the Pd/PTCA-GS(NaBH₄) owing to the oxygen-contained groups improve the kinetics of the ethanol oxidation. All the results indicated the Pd/PTCA-GS(NaBH₄, EG and H₂) displayed better kinetics, higher electrocatalytic activity, better tolerance and electrochemical stability than the Pd/rGO(NaBH₄).

References

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