

Supporting Information

Green Synthesis of Pt/CeO₂/Graphene Hybrid Nanomaterials with Remarkably Enhanced Electrocatalytic Properties

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Experimental Section

Synthesis of GO: GO was synthesized from natural graphite powder according to a modified Hummers method.^{1,2} Briefly, 0.9 g of graphite powder was added into a mixture of 7.2 mL of 98% H₂SO₄, 1.5 g of K₂S₂O₈, and 1.5 g of P₂O₅. The solution was kept at 80 °C for 4.5 h, followed by thorough washing with water. Thereafter, the as-treated graphite was put into a 250 mL beaker, to which 0.5 g of NaNO₃ and 23 mL of H₂SO₄ (98%) were then added while keeping the beaker in the ice bath. Subsequently, 3 g of KMnO₄ was added slowly. After 5 min, the ice bath was removed and the solution was heated up to and kept at 35 °C under vigorous stirring for 2 h, followed by the slow addition of 46 mL of water. Finally, 40 mL of water and 5 mL of H₂O₂ was added, followed by water washing and filtration. The exfoliation of graphene oxide was then dispersed in deionized water (1 mg mL⁻¹) under ultrasonication for 5 h to yield a homogeneous suspension.

Synthesis of CeO₂/graphene composite: In a typical experiment, 0.40 g Ce(NO₃)₃·6H₂O was added into 15 mL of aqueous solution, then 40 μL of NaOH (2 M) solution was added into the as-prepared GO dispersions while stirring, the mixture was then sealed in a Teflon-lined stainless steel autoclave and maintained at 100 °C for 24 h and was cooled to room temperature. Finally, the resulting stable black dispersion was centrifuged and washed with water. Then, the obtained CeO₂/graphene was redispersed in water before further use.

Synthesis of Pt/CeO₂/graphene composite: 1 mmol of lysine was added into the above CeO₂/graphene solution, followed by sonicating 10 min, then the solution was centrifuged and redispersed into 1 mmol of lysine solution to repeated the procedure

twice, and then the solution was centrifuged and redispersed in ~~the~~ 10 mL deionized water, 2 mL of K_2PtCl_6 aqueous solution (0.015 M) was successively added into the as-obtained lysine-stabilized CeO_2 /graphene solution while stirring, and then 8 mg of NaBH_4 dissolved in the 0.1 mL of deionized water was added in the solution. The mixture was stirred for 2 h at room temperature, and then the as-obtained products was centrifuged and washed with water and used for further characterizations.

Characterization and electrochemical measurements: The X-ray diffraction pattern of the products was collected on a Rigaku-D/max 2500 V X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), with an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. Topological images were obtained on a multimode 8 AFM system (Veeco, U.S.A.) operated in tapping mode. XPS measurement was performed on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) with $\text{Al K}\alpha$ X-ray radiation as the X-ray source for excitation. Raman spectra were obtained on a J-Y T64000 Raman spectrometer using an Olympus microscope and a $50\times$ long working distance objective to focus the laser beam onto a spot of about $1 \mu\text{m}^2$. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. Electrochemical experiments were performed with a CHI 832 electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as counter-electrode and modified glassy carbon as working electrode.

Electrochemical measurements:

Prior to the surface coating, the glassy carbon electrode was polished carefully with 1.0, 0.3, and $0.05 \mu\text{m}$ alumina powder, respectively, and rinsed with deionized water, followed by sonication in acetone and doubly distilled water successively. Then, the electrode was allowed to dry under nitrogen. For cyclic voltammetry (CV) and chronamperometric curves, $5 \mu\text{L}$ of Pt/CeO_2 /graphene composite (1 mg mL^{-1}) or

Pt/graphene composite (1 mg mL^{-1}) was mixed with Nafion (0.5%) and then dropped on the surface of glassy carbon electrode and dried with an infrared lamp. Electrochemically active surface area (ECSA) of Pt nanoparticles was calculated from hydrogen electrosorption curve, which was recorded between -0.2 and $+1.2$ V in 0.5 M H_2SO_4 solution. The ECSA calculations of Pt/CeO₂/graphene, Pt/graphene and commercial Pt/C catalysts are 75.6 , 73.7 , and 27.1 $\text{m}^2 \text{ g}^{-1}$, respectively. To measure methanol electrooxidation reaction activity, CV was performed between 0 and $+1.0$ V in a mixing solution containing 1 M CH_3OH and 0.5 M H_2SO_4 . The scan rate was set at 100 mV s^{-1} . Chronoamperometry data were collected for 1 h at 0.742 V versus Ag/AgCl for the catalysts in a mixture of 0.5 M H_2SO_4 and 1.0 M methanol solution at room temperature.

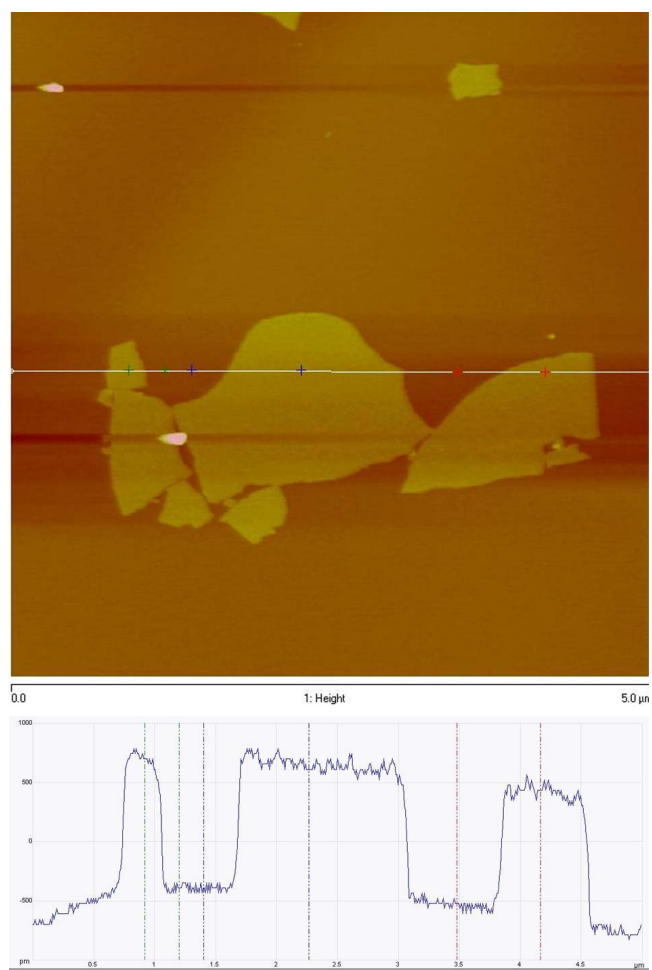


Fig. S1 AFM image of GO.

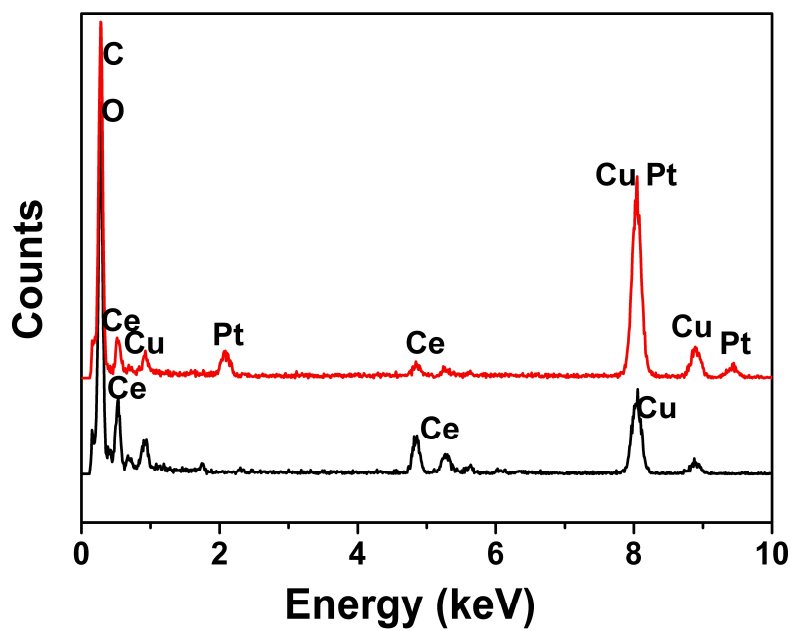


Fig. S2 EDX spectrum of CeO₂/graphene (black line) and Pt/CeO₂/graphene composites (red line).

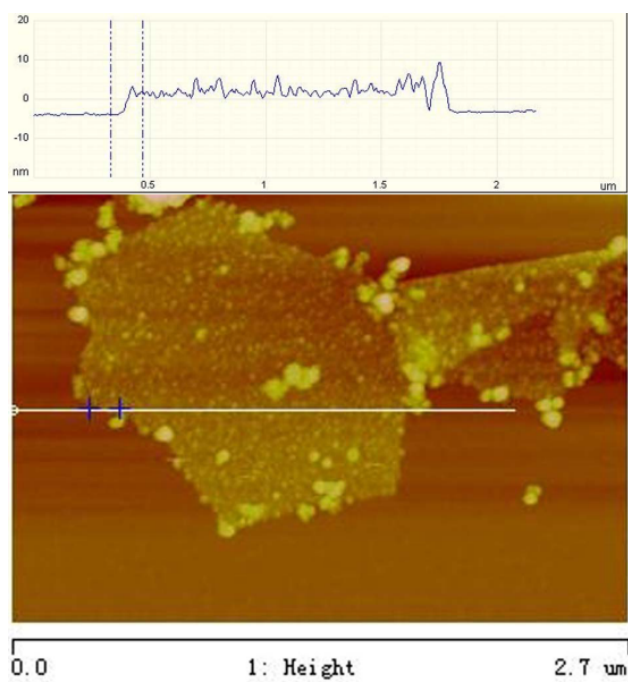


Fig. S3 AFM image of CeO₂/graphene composites.

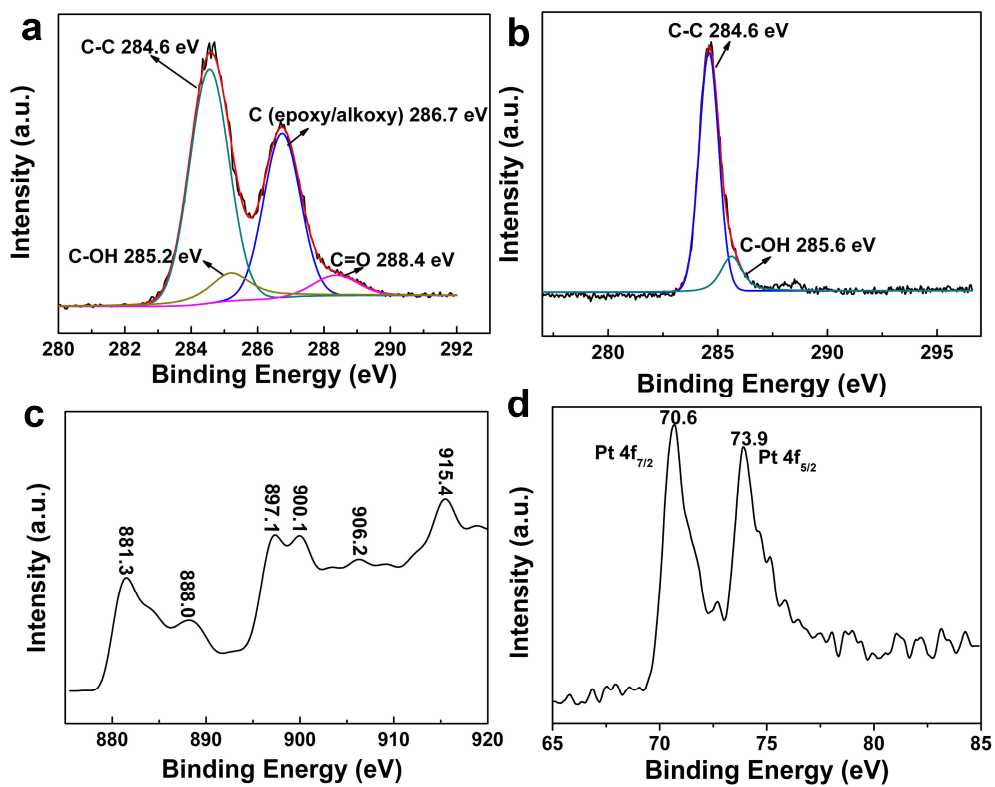


Fig. S4 XPS analysis of CeO₂/graphene (a, c) and Pt/CeO₂/graphene composites (b, d).

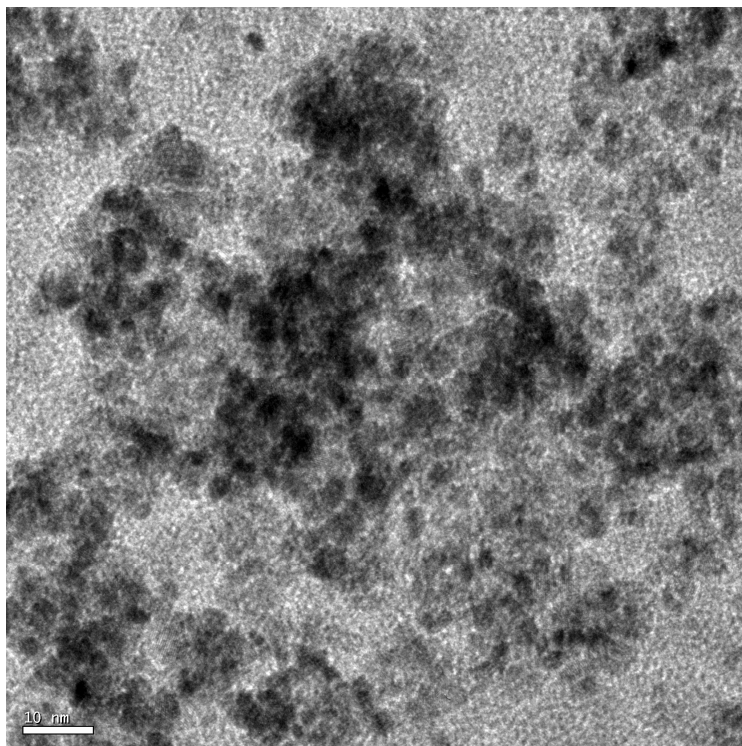
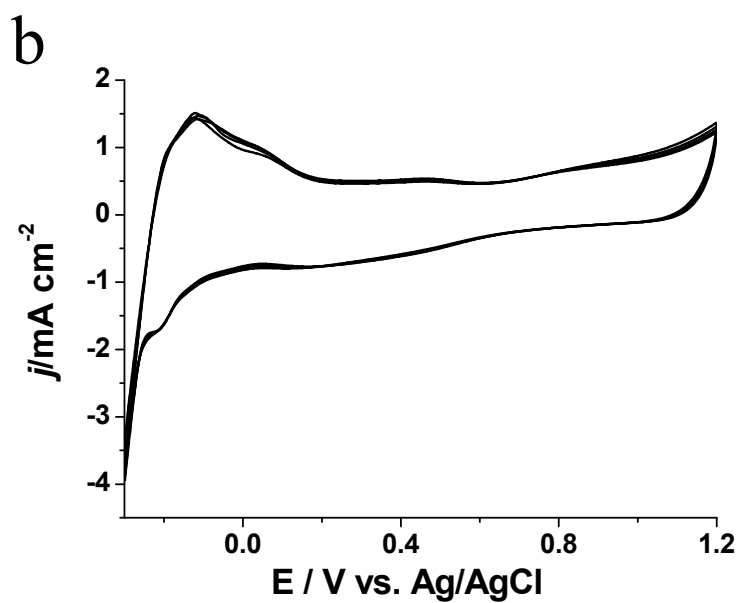
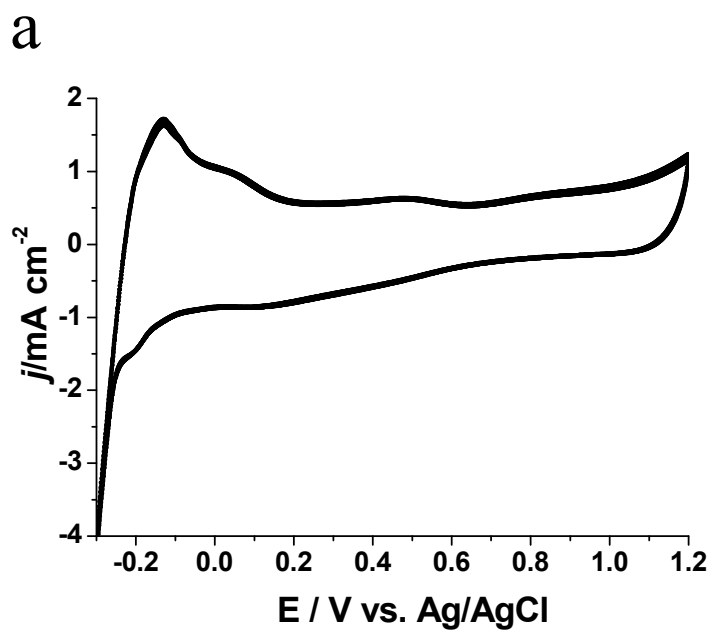


Fig. S5 TEM image of Pt/CeO₂/graphene composites prepared without L-lysine.



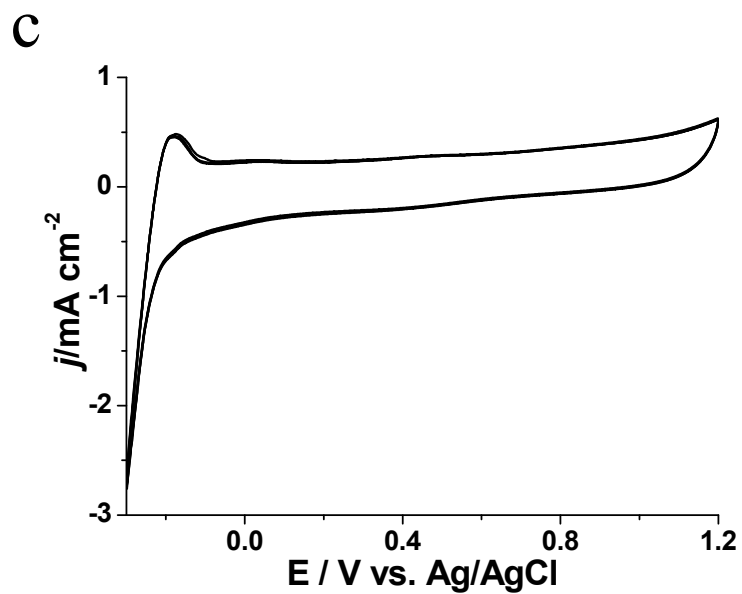


Fig. S6 CV curves of the Pt/CeO₂/graphene (a), Pt/graphene (b) and Pt/C catalysts (c) in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 100 mV s⁻¹.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
2. C. Hontoria-Lucas, A. J. Lopez-Peinado, J. de D. Lopez-Gonzalez, M. L. Rojas-Cervantes and R. M. Martin-Aranda, *Carbon*, 1995, **33**, 1585.