

Electronic supplementary information

Formation of Pt-TiO₂-rGO 3-phase junctions with significantly enhanced electro-activity for methanol oxidation

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1. Experimental section

1.1 Preparation of graphene oxide (GO)

GO was made by a modified Hummer method.^{1,2} The graphite powder (1g) was mixed with 23 mL of concentrated sulfuric acid in a 250 mL round bottom flask and stirred at room temperature for 24 hours. The flask was placed in an oil bath at 40 °C and 300 mg of NaNO₃ was added into the suspension and allowed to dissolve for 5 minutes. Then 3g of KMnO₄ was added slowly into the mixed solution, keeping the temperature below 45 °C. The solution was stirred for another 30 minutes. Afterwards, 3 mL of water was added to the flask, followed by another 3 mL after 5 minutes. In another 5 minutes, 40 mL of water was added. After 15 minutes, the solution was removed from the oil bath and 140 mL of water and 10 mL of 30% H₂O₂ were added to end the reaction. The suspension was stirred at room temperature for 30 minutes and then repeatedly centrifuged and washed twice with a 5% HCl solution, then repeatedly washed with water. The collected precipitate was dispersed in water and ultrasonicated for 30 minutes. After the centrifugation for 5 minutes, the brown homogeneous supernatant was obtained. The obtained GO was dried at 80 °C for 24 hours for the later studies.

1.2 Synthesis of hybrid TiO₂ NPs@GO.

In a typical preparation of TiO₂@GO, 6 mg of GO was dispersed into 30 mL of water

by ultrasonication for 30 minutes, and then 30 μL of TiCl_4 was added into the as-prepared GO suspension. The mixture was then transferred into a Teflon-lined autoclave with a stainless steel shell and heated to 100 $^\circ\text{C}$ in an oven. The sample was kept at 100 $^\circ\text{C}$ for 12 hours in the oven and then cooled to room temperature. Finally, the resultant stable black dispersion was washed with water for several times and collected by centrifugation. The precipitates were dried at 80 $^\circ\text{C}$ in a vacuum oven overnight for the textural analysis. For comparison, 9 μL and 24 μL of TiCl_4 were added, and the obtained $\text{TiO}_2@\text{GO}$ samples under the same condition were denoted $\text{TiO}_2@\text{GO-I}$ and $\text{TiO}_2@\text{GO-II}$, respectively.

1.3 Preparation of Pt electrocatalysts.

The $\text{Pt}/\text{TiO}_2@\text{rGO}$ electrocatalyst was prepared using the polyol process. Firstly, the $\text{TiO}_2@\text{GO}$ powder was dispersed into ethylene glycol (EG) by ultrasonication. Then, a predetermined amount of a Pt precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) dissolved in EG was added slowly. The mixed solution was heated at a desired temperature of around 140 $^\circ\text{C}$ for 3 hours under continuous magnetic stirring. After cooling to room temperature, the material was then filtered, dried at 80 $^\circ\text{C}$ for 24 h and stored for further studies. The Pt loading on the $\text{TiO}_2@\text{GO}$ was controlled to be 20 wt%. For comparison, Pt nanoparticles deposited on carbon black (CB), GO, $\text{TiO}_2@\text{GO-I}$ and $\text{TiO}_2@\text{GO-II}$ under the same condition were denoted as Pt/CB , Pt/rGO , $\text{Pt}/\text{TiO}_2@\text{rGO-I}$ and $\text{Pt}/\text{TiO}_2@\text{rGO-II}$, respectively.

1.4 Electrochemical Measurements.

The electrochemical activities of Pt nanocatalysts were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The experiments were performed using a three-electrode cell with a CHI660 electrochemical workstation at ambient temperature. The working electrode is a glassy carbon (GC) cylinder with a diameter of 5 mm, and the Pt loading on the GC electrode was controlled to be 0.2 mg cm^{-2} . A saturated calomel electrode (SCE) and a large-area Pt plate were used as the reference electrode and the counter electrode, respectively. The CV profiles were recorded at a scan rate of 20 mV s^{-1} within the potential range from -0.241 to 1V vs. SCE in a 0.5 M H_2SO_4 solution. Methanol oxidation experiments were carried out in 1

M CH₃OH +0.5 M H₂SO₄ electrolyte at a scan rate of 20 mV s⁻¹ from the potential of -0.241 to 1V vs. SCE. CA curves were recorded at 0.75 V in 1 M CH₃OH +0.5 M H₂SO₄ for 600 s to investigate the durability of the electrocatalysts.

1.5 Materials Characterization.

The product morphology and microstructure were studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) and high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, 200 kV). Selected area electron diffraction (SAED) was performed to study the crystalline and structure of the Pt nanoparticles. The elemental mapping was carried out to analyze the elemental mapping of the sample. Powder X-ray diffraction (XRD) experiments were performed to study the crystallographic information of the samples. XRD patterns were recorded using a Bruker diffractometer with Cu K α radiation (D8 Advance X-ray diffractometer, Cu K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV and 40 mA). Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 10 °C min⁻¹ from room temperature to 800 °C.

References

1. W. S. Hummers and R. E. Offeman, *J Am Chem Soc*, 1958, **80**, 1339-1339.
2. H. J. Dai, H. L. Wang, J. T. Robinson and X. L. Li, *J Am Chem Soc*, 2009, **131**, 9910-9911.

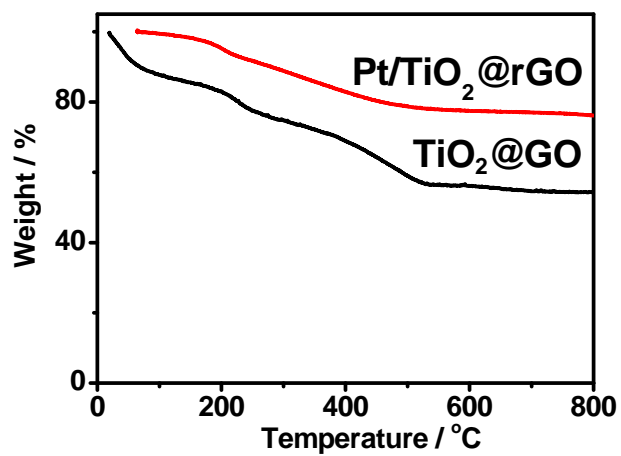


Figure S1. TGA curves of TiO₂@GO and the corresponding Pt/TiO₂@rGO electrocatalyst. The results show the Pt content of ~ 30 wt% and C content of ~ 21.5 wt%.

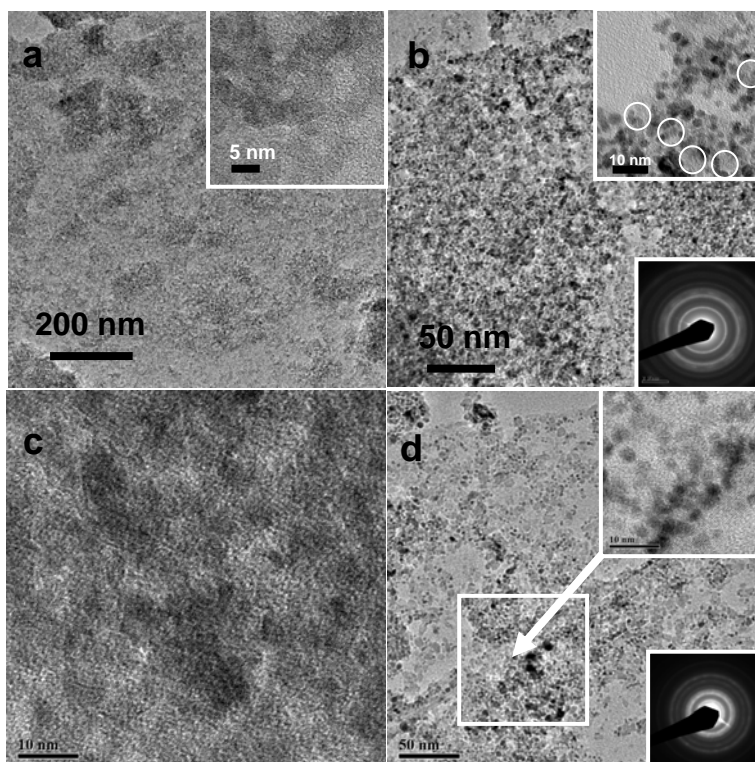


Figure S2. TEM images of $\text{TiO}_2@\text{GO-I}$ (a) and the corresponding $\text{Pt}/\text{TiO}_2@\text{rGO-I}$ (b). The insets of Figure S2b show the corresponding SAED pattern and high magnification TEM image. TEM images of $\text{TiO}_2@\text{GO-II}$ (c) and the corresponding $\text{Pt}/\text{TiO}_2@\text{rGO-II}$ (d). The high magnification TEM and SAED pattern are shown in the insets of Figure S2d.

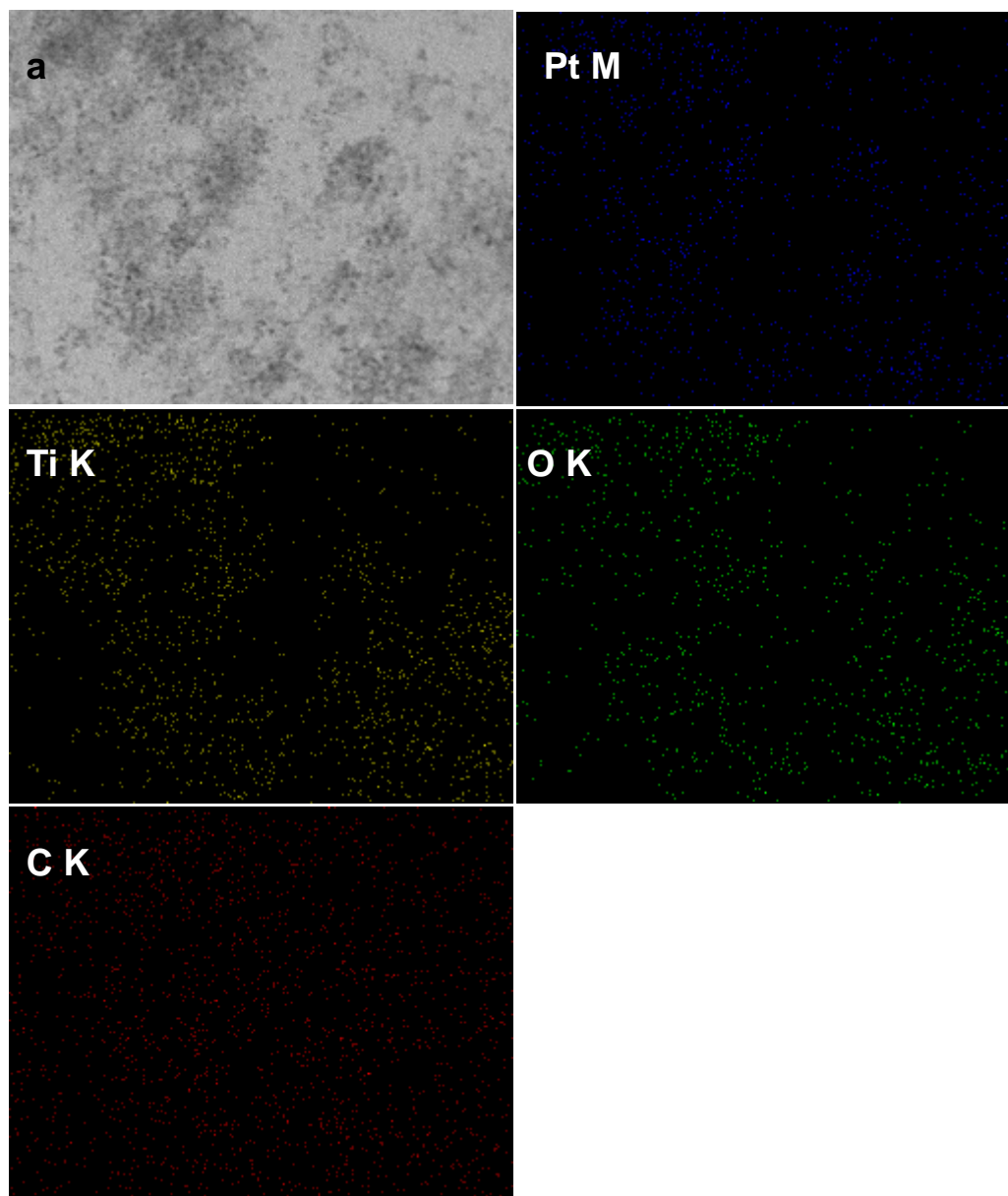


Figure S3. TEM image of the Pt/TiO₂@rGO electrocatalyst and the corresponding elemental mapping images for: Pt, Ti, O and C.

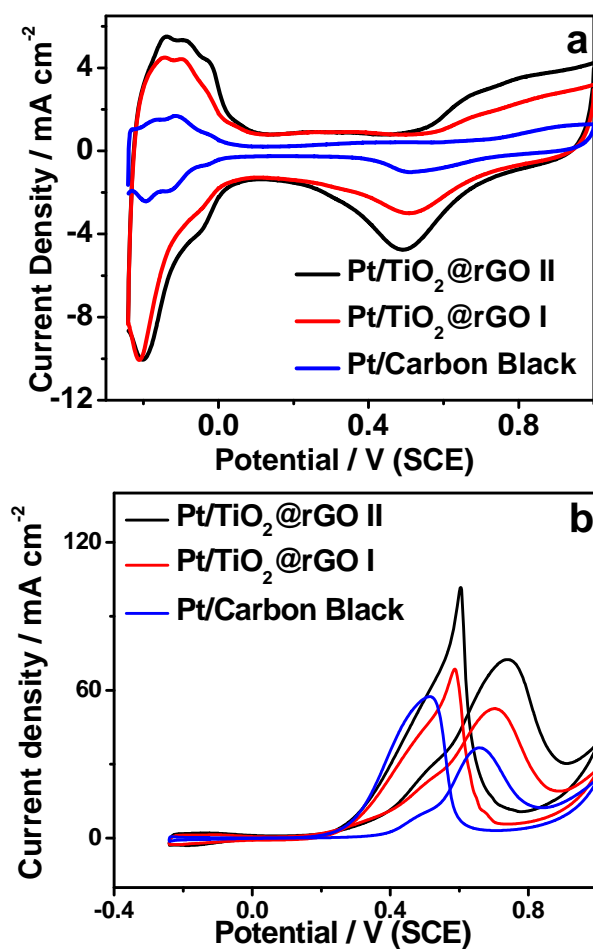


Figure S4. a) Cyclic voltammograms (CVs) of the different Pt electrocatalysts in a 0.5 M H₂SO₄ solution, b) CVs of methanol oxidation on the Pt catalyst in 0.5 M H₂SO₄ + 1 M CH₃OH solution. The Pt loading on the electrode is 0.2 mg cm⁻² and the sweep rate is 20 mV s⁻¹