Electronic Supplementary Information (ESI)

A facile strategy to three-dimensional Pd@Pt core-shell nanoflowers supported on graphene nanosheets as an enhanced nanoelectrocatalyst for methanol oxidation

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1. Experimental section:

1.1 Chemicals

Natural graphite powders used for preparing GO were available from Duratight Sealing Product Co., Ltd. Qingdao, China. 5 wt% Nafion and Pt/C power were purchased from Alfa Aesar. $PdCl_2$, $H_2PtCl_4 \cdot 6H_2O$, methanol, NaOH, L-ascorbic acid and N-methyl-2-pyrrolidone (NMP) were obtained from Sinopharm Chemical Reagent Co. Unless otherwise stated, all reagents were analytical grade and used as received without further purification. The deionized pure water used in the experiments was freshly prepared from a Kertone Ultrapure Water System P60-CY (Kertone Water Treatment Co. Ltd, resistivity = 18.25 MΩ·cm).

1.2 Synthetic procedure

1.2.1 Preparation of GO

GO was prepared from Natural graphite by a modified Staudenmaier's method according to our previous report.[1] The detailed procedure is as follows: Sulfuric acid (72 mL) and nitric acid (36 mL) were first poured into a flask. The flask was then immersed in an ice bath and Natural graphite (4 g) was added into it under vigorous stirring to avoid agglomeration. After that the potassium chlorate (44 g) was slowly added for 1 hour to avoid the rapid increase of temperature. The flask was then allowed to stir for 96 h at room temperature. In order to avoid environment pollution, sodium hydroxide solution was employed to absorb the generated chlorine. After that the mixture was slowly poured into a beaker and then filtered. The products were then dissolved in deionized water and washed by 5% HCl solution twice in order to remove sulfate ions. After that the resulting graphite oxide was re-dissolved in water and ultrasonicated for 30 min to further exfoliate the graphene oxide sheets, and then centrifuged at 8000 r/min for 10 min in order to remove the unexfoliated graphite. The collected supernatant was brown-yellow GO solution with homogeneous dispersion. 20 mL of NaOH (5 mol L^{-1}) was then added into the GO solution (1000 mL) with stirring. After standing for 1 h, GO was coagulated from the GO solution. Solid GO was filtered and washed with ethanol until neutral in order to remove excessive NaOH. The GO solids were obtained after dried under vacuum at 40 °C.

1.2.2 Preparation of Pd@Pt nanoflowers on graphene, PdPt/graphene and Pt/graphene

Pd@Pt nanoflowers on graphene was synthesized using a seed-mediated growth strategy. The detailed procedure is as follows: 10 mg of the as-prepared GO powder was first ultrasonically dispersed in 100 ml water for about 1 hour to get a visually homogeneous solution. After that, 600 μl of $PdCl_2$ aqueous solution (0.015 M) was added dropwise. The mixture was then continuously stirred for 15 min. Afterwards, 250 mg of L-ascorbic acid was added to the mixture. Subsequently, the mixture was continuously stirred for 1 hour to obtain graphene/Pd seeds. After that, the mixture was transferred into a MAS-I microwave oven (Sineo Microwave Chemistry Technology (China) Co., Ltd.) with a refluxing system outside. Subsequently, 400μl of $H_2PtCl_4{\cdot}6H_2O$ aqueous solution (0.015M) was added into the mixture and then the reaction flask was irradiated by microwave (400W) at 80 °C for 5 min. After cooled to ambient temperature, the suspension was filtered and repeatedly washed with deionized water and ethanol to remove impurities and finally dried via the freeze-drying method to yield Pd@Pt nanoflowers on graphene. For comparison, PdPt/graphene and Pt/graphene were prepared by the same procedure except that Pd and Pt precursors were added simultaneously or Pt precursor was added solely.

1.3 Structure characterizations

Power XRD was conducted on a D8-Advance diffractometer (Bruker, Germany) with a Cu Kα radiation source (λ =0.15418 nm). The microstructure and morphology of the samples were observed from TEM (FEI TECNAI20, USA) and FE-SEM (ZEISS, Germany). The EDX analysis of the chemical composition was obtained from the analyzer coupled to SEM. Thermo gravimetric analysis (TGA) was performed on a thermo gravimetric analyzer (Perkin-Elmer TGA-7, USA).

1.4 Electrochemical measurements

Prior to the surface modification, the glass carbon electrode (GCE) (3 mm in diameter) was polished with 0.05 mm alumina powder and rinsed thoroughly with doubly distilled water. The electrode was then cleaned successively with anhydrous ethanol and doubly distilled water in an ultrasonic bath and dried under nitrogen. To prepare the catalyst inks, each sample was ultrasonically dispersed in 500 μl of NMP for at least 60 min to get a homogeneous ink of 2 mg/ml. For CV, 3 ul of the resulting suspension was pipetted onto the GCE surface and dried at room temperature. Prior to each measurement, the electrolyte containing 1 M KOH and 1 M CH_3OH was bubbled with N_2 for at least 30 min.

The electrochemical measurements were carried out on an IM6 electrochemical workstation (Zahner-Electrik, Germany) with a standard three-electrode system at room temperature. A modified GCE served as a working electrode; a platinum electrode and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively.

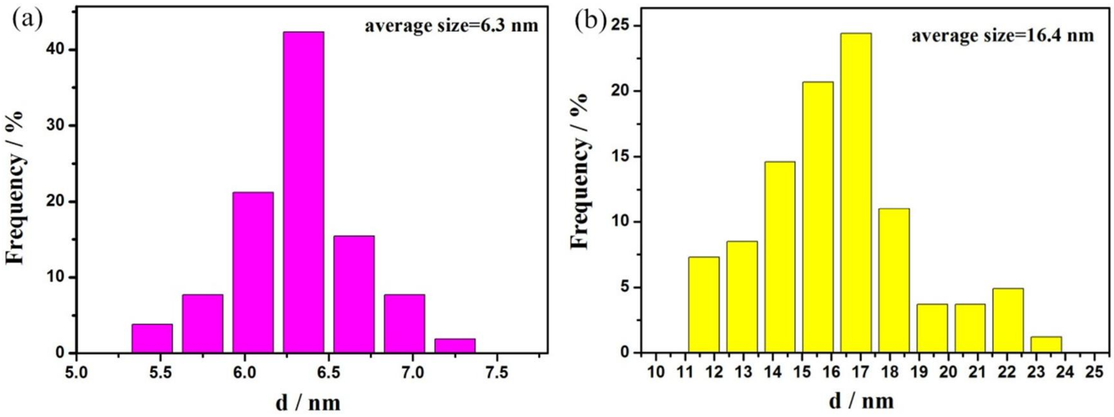


Fig. S1 Size distribution of Pd nanoparticles (a) and Pd@Pt nanoflowers (b) on graphene.

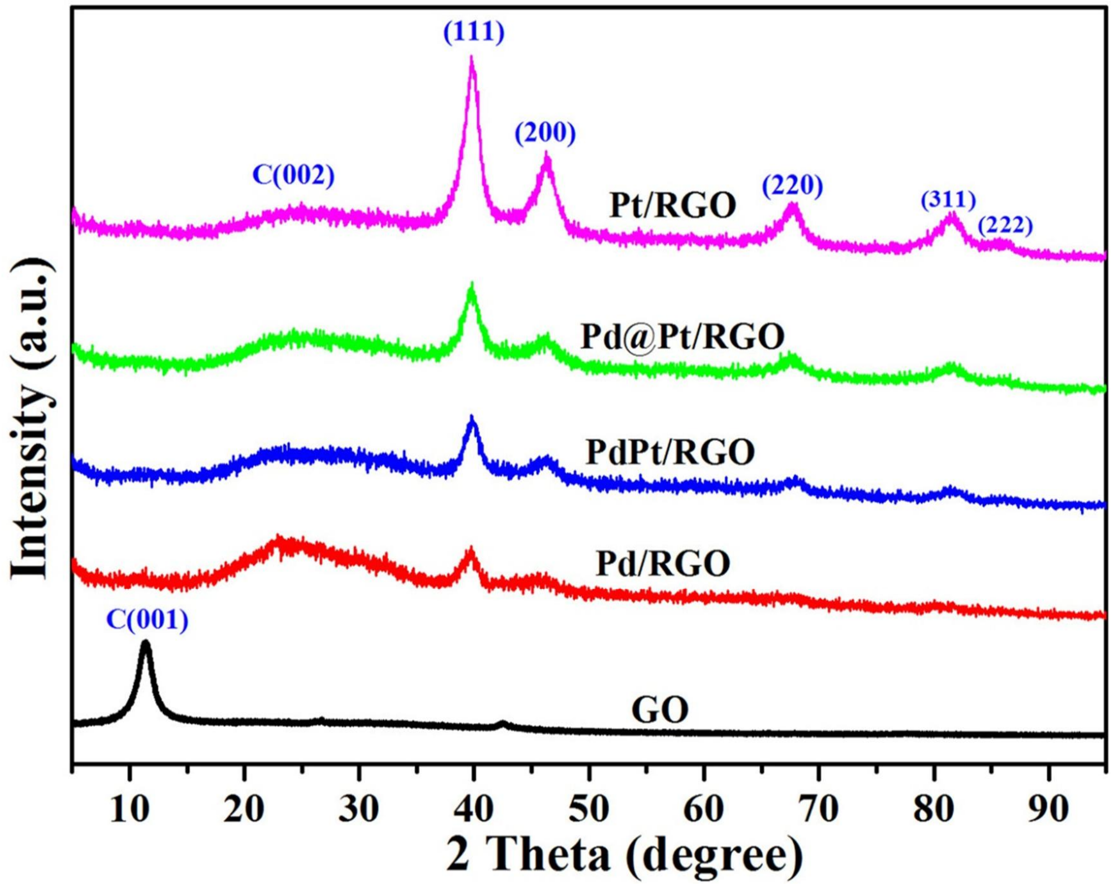
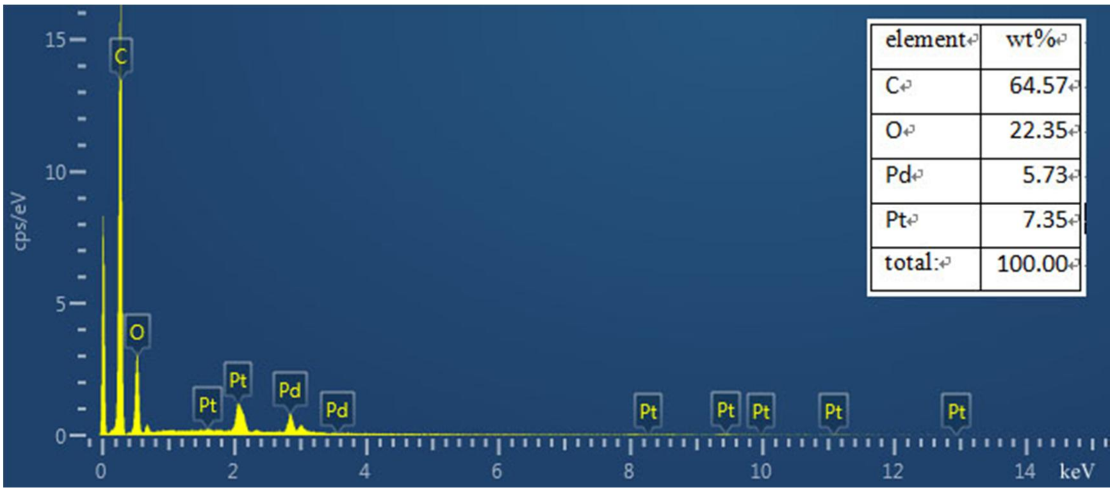


Fig. S2 XRD pattern of GO, Pd/RGO, Pt/RGO, PdPt/RGO and Pd@Pt/RGO.



element	wt%
C	64.57
O	22.35
Pd	5.73
Pt	7.35
total:	100.00

Fig. S3 EDX spectrum of Pd@Pt/graphene.

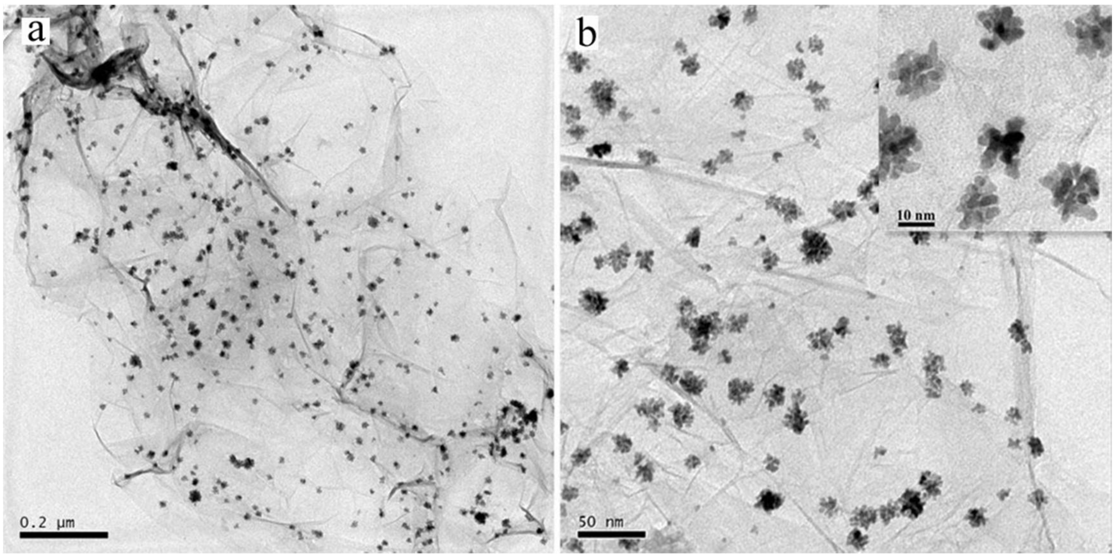
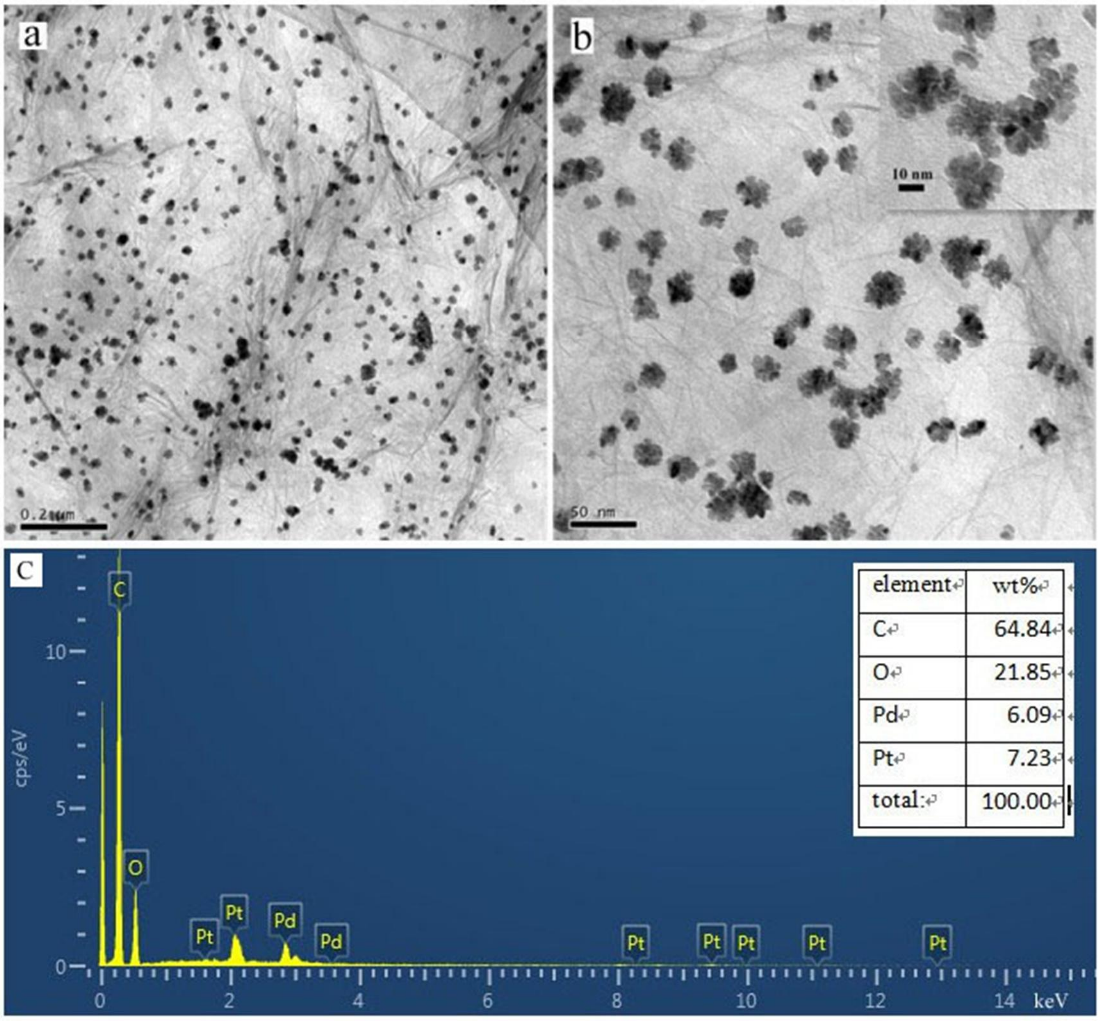


Fig. S4 TEM images of branched Pt nanoparticles on graphene at different magnifications.



element	wt%
C	64.84
O	21.85
Pd	6.09
Pt	7.23
total:	100.00

Fig S5 TEM images (a, b) and EDX spectrum (c) of PdPt alloy nanofoams on graphene.

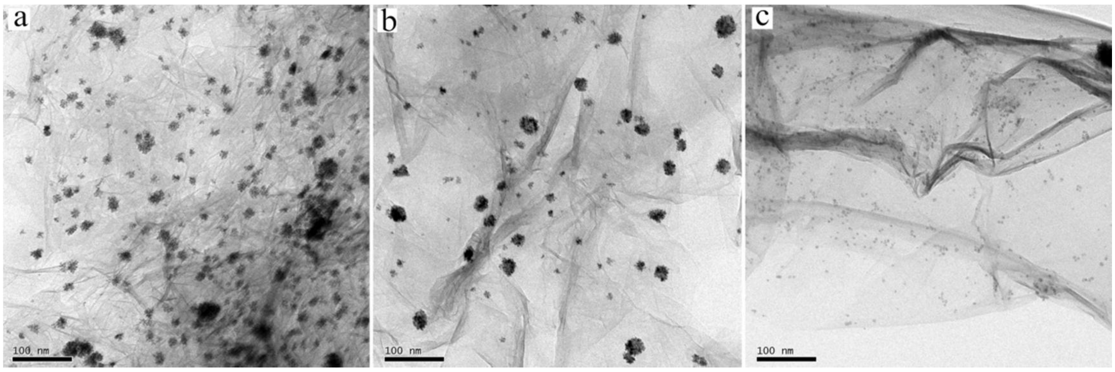


Fig S6 TEM images of graphene-supported Pd@Pt products synthesized at different Pt/Pd molar ratios: 4 : 1 (a), 3 : 2 (b), and 1:4 (c).

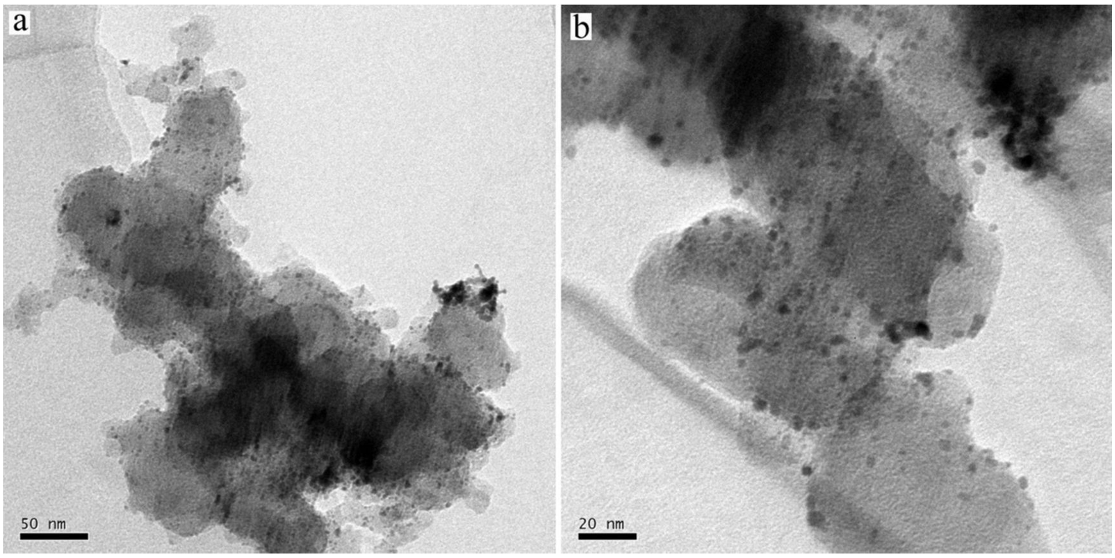


Fig S7 TEM images of commercial Pt/C (Alfa Aesar) at different magnifications.

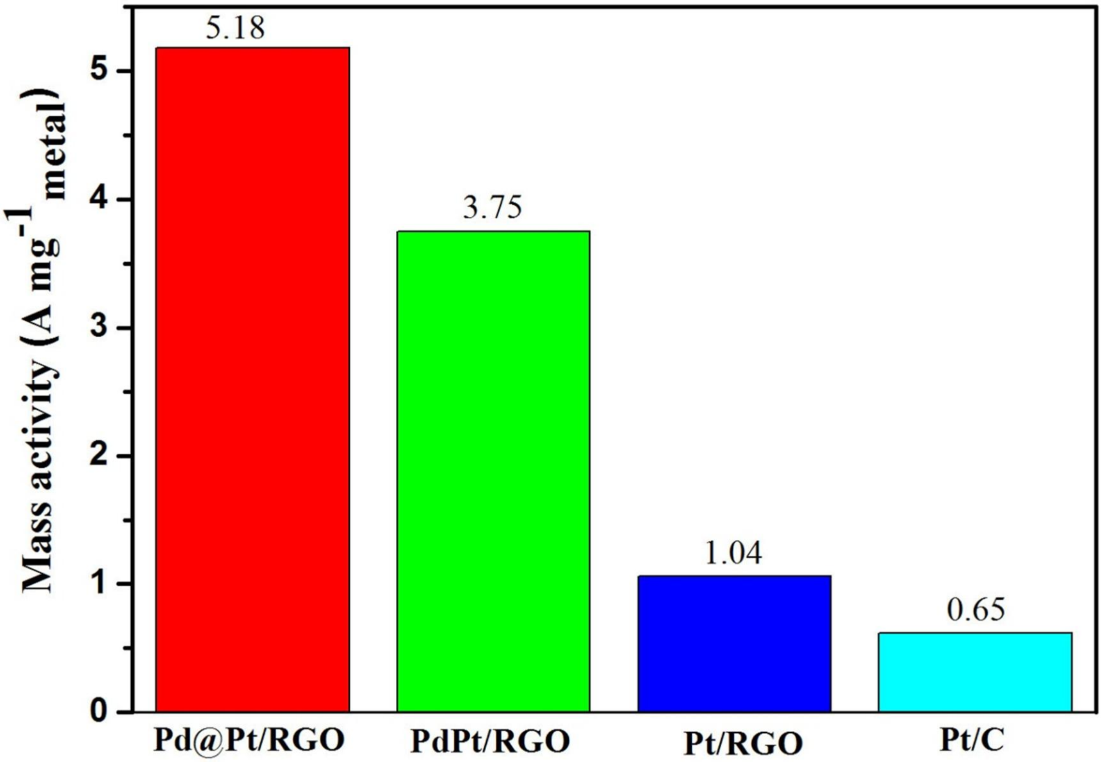


Fig. S8 Mass-normalized peak current density of Pd@Pt/RGO, PdPt/RGO, Pt/RGO and Pt/C. The currents were normalized by the total amount of Pd and Pt.

1. Y. Chen, J. Li, T. Mei, X. G. Hu, D. W. Liu, J. C. Wang, M. Hao, J. H. Li, J. Y. Wang and X. B. Wang, *J. Mater. Chem. A*, 2014, 2, 20714