Supplementary Material (ESI) for Chemical Communications

Supporting Information

A facile approach to the synthesis of highly electroactive Pt nanoparticles on graphene as anode catalyst for direct methanol fuel cells

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Experimental Section

Materials and Methods:

Graphite oxide (GO) was synthesized from analytical grade graphite (Shanghai Carbon Co., Ltd.) by the modified Hummer′s method that was originally presented by Kovtyukhova and colleagues[1]. The synthesized GO was suspended in water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Then, the GO suspension was dried under 60 ^{o}C for 3 h. The exfoliated GO was obtained by ultrasonic of 0.5 wt% GO dispersion, using a Sonifier (KQ 100E, 100W, Kunshan, China). A 6 μL portion of the resulted GO dispersion was spread on a pretreated bare glassy carbon electrode (GCE) and dried under room temperature to get GO modified GCE (GO/GCE). A Vulcan (0.5 wt%) modified GCE (Vulcan/GCE) was fabricated in the same way. All electrochemical experiments were performed on a CHI 1140 electrochemical workstation (CH Instrument Co., USA). A conventional

three-electrode system was employed, involving a modified GCE as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) or a reversible hydrogen electrode (RHE) as the reference. The one-step electrochemical reduction experiment was carried out at a constant potential of –1.5 V (vs SCE) in 10 mM KH_2PO_4 containing 5 mM H_2PtCl_6 for 500 s to obtain Pt NPs@G/GCE and Pt NPs@Vulcan/GCE.

Characterization:

Pt NPs@G/GCE and Pt NPs@Vulcan/GCE were characterized on a Hitachi S4800 (Hitachi Japan) field emission scanning electron microscope (FESEM) equipped with an X-ray energy dispersive spectroscopy analyzer. Raman scattering was performed on a JY-HR800 Raman spectrometer using a 488-nm laser source. X-ray diffraction (XRD) was performed with an XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Cu Kα radiation. Pt loadings on the graphene and Vulcan were measured on a J-A1100 inductively coupled plasma spectrum instrument (ICP) (Jarrell-Ash, America). All electrochemical experiments were performed on a CHI 1140 electrochemical workstation (CH Instrument Co., USA). The three-electrode system was consisted of modified GC electrodes as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) or a reversible hydrogen electrode (RHE) as the reference.

Experiment details regarding FESEM

After the GO was successfully reduced to graphene, we tried several approaches to obtain graphene/Pt NPs by electrochemical reduction. In the first approach, GO was reduced at a potential of -1.5 V (vs SCE) in 10 mM KH_2PO_4 for 500 s, followed by a reduction of 5 mM H_2PtCl_6 at a potential of -0.25 V (vs SCE) in 10 mM KH_2PO_4 for 200 s. The FESEM characterization of the as-resulted graphene/Pt NPs is shown in Figure S1. We can see that almost all the Pt NPs were deposited on both sides of graphene resulting that only one side of graphene could be utilized. Besides, the average sizes of the NPs are 200-300 nm that are too large to obtain good catalytic

performance.

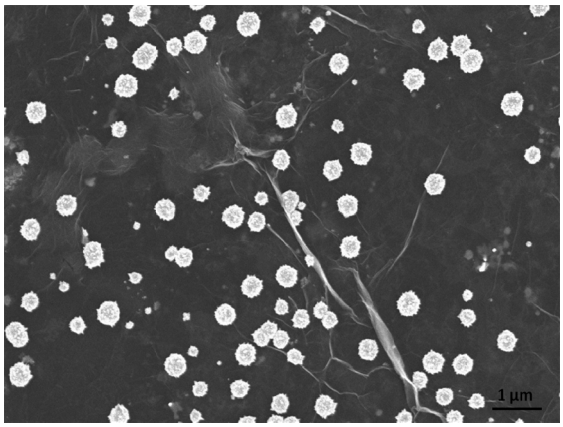

Figure S1. FESEM image of graphene/Pt NPs obtained by using the two-step electrochemical reduction method (reduce GO first, then reduce H_2PtCl_6).

In the second approach, we first reduced 5 mM H_2PtCl_6 at a potential of -0.25 V (vs SCE) in 10 mM KH_2PO_4 for 200 s, and then reduced GO at a potential of -1.5 V (vs SCE) in 10 mM KH_2PO_4 for 500 s. It was found from the FESEM image shown in Figure S2a that the Pt NPs were deposited onto both sides of graphene (bright particles on the forth side and dark particles on the back side). Figure S2b clearly demonstrated that the Pt NPs were deposited onto the back side of the graphene. However, the sizes of Pt NPs are uneven. The ones on the forth side are much larger.

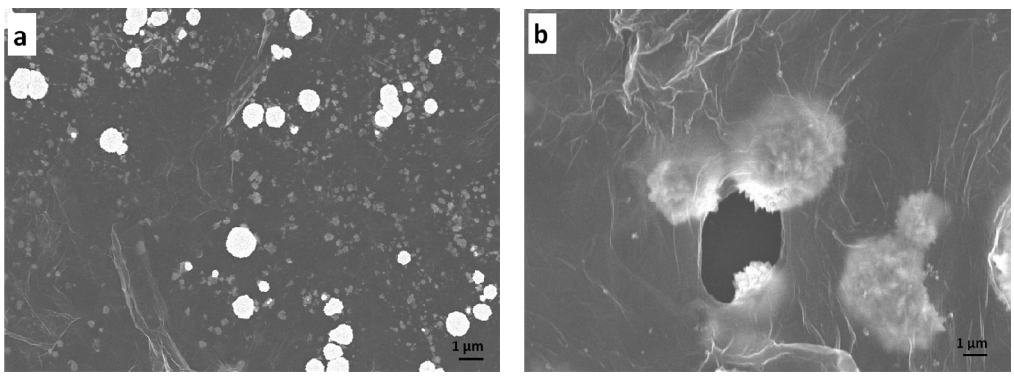

Figure S2. FESEM photos of the graphene/Pt NPs hybrids obtained by two-step electrochemical reduction method (reduce H_2PtCl_6 first, then reduce GO).

Finally, the one-step electrochemical reduction of GO and H_2PtCl_6 was taken. The FESEM illustrated that the Pt NPs were evenly spread over both sides of the graphene with the even size of about 10-20 nm. Thus both size of the graphene could be utilized for supporting Pt NPs and the Pt NPs with much smaller sizes could exert their higher catalytic ability. Therefore we selected the simultaneous electrochemical reduction by the above comparisons for the synthesis of graphene/Pt NPs composites for the further experiments.

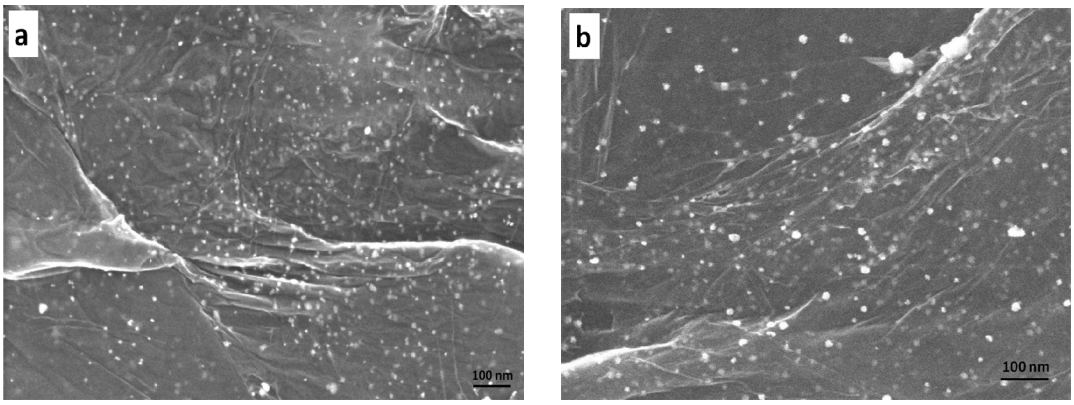

Figure. S3. FESEM photos of the graphene/Pt NPs by one-step electrochemical reduction of GO and H_2PtCl_6.

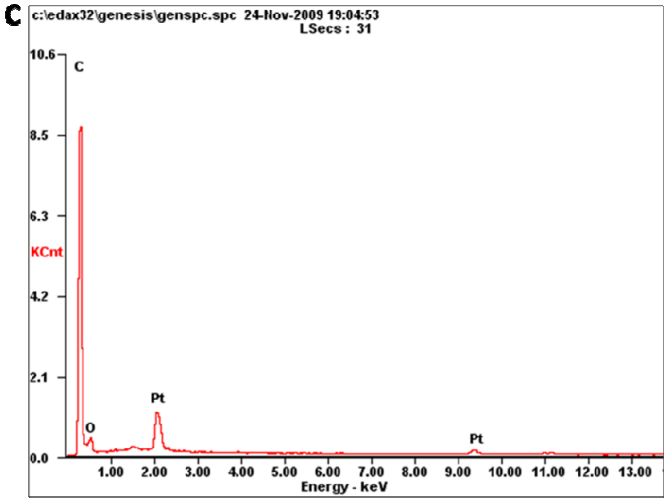

Figure S4. EDS spectrum of the Pt NPs@G/GCE.

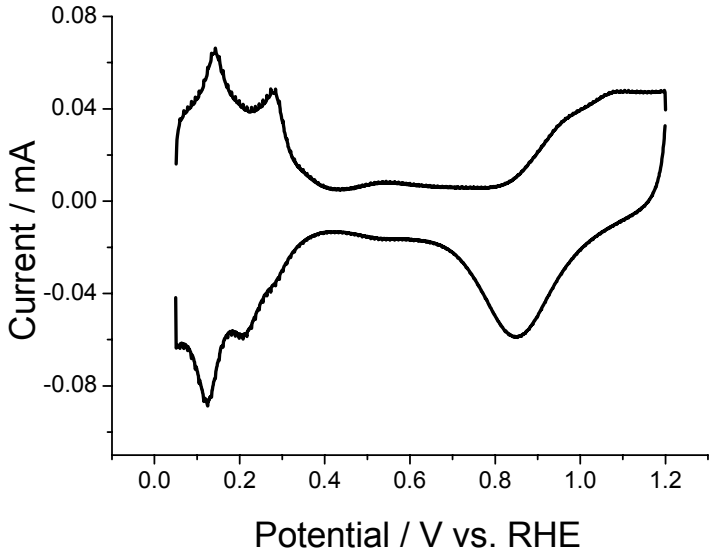

Figure S5. Cyclic voltammetry (CV) of Pt NPs@G/GCE in a N_2 saturated aqueous solution of 0.5M H_2SO_4 at a scan rate of 10 mV/s.

References for Supporting Information

1. (a) N. Kovtyukhova, P. Ollivier, B. Martin, T. Mallouk, S. Chizhik, E. Buzaneva, A. Gorchinskiy, *Chem. Mater.* 1999, **11**, 771;

(b) W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.