Supplementary Information

Platinum nanoparticles on porphyrin functionalized graphene nanosheets as superior catalyst for methanol electrooxidation

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1. TEM characterization of 20% commercial Pt/C catalyst

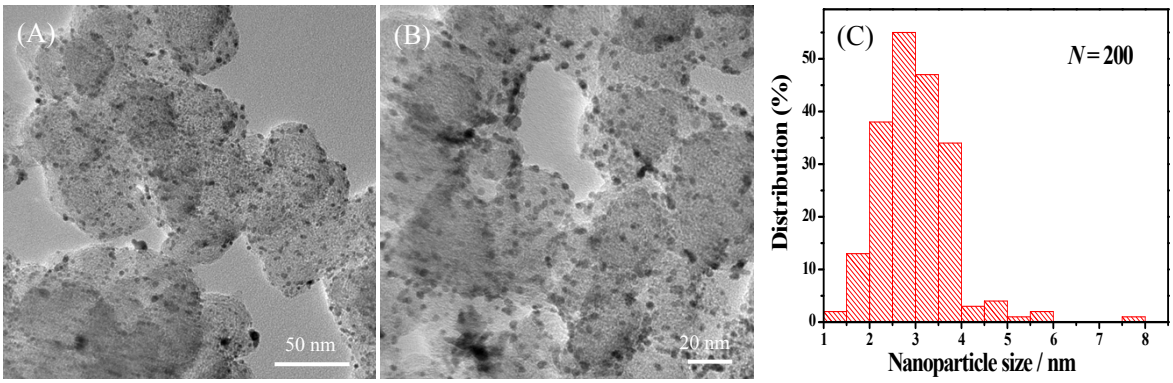

Fig. S1 TEM images (A and B) and the size distribution histogram (C) of commercial Pt/C catalyst (20% Pt loading).

Fig. S1 shows the TEM images (A and B) and the size distribution histogram (C) of commercial Pt/C catalyst (20% Pt loading). From A and B, we can see that most of Pt nanoparticles are uniformly dispersed on the carbon support with a little aggregation. The average particle size of Pt revealed by the size distribution histogram is approximately 3.0 nm.

2. High-resolution XPS characterization of TMPyP-graphene composite

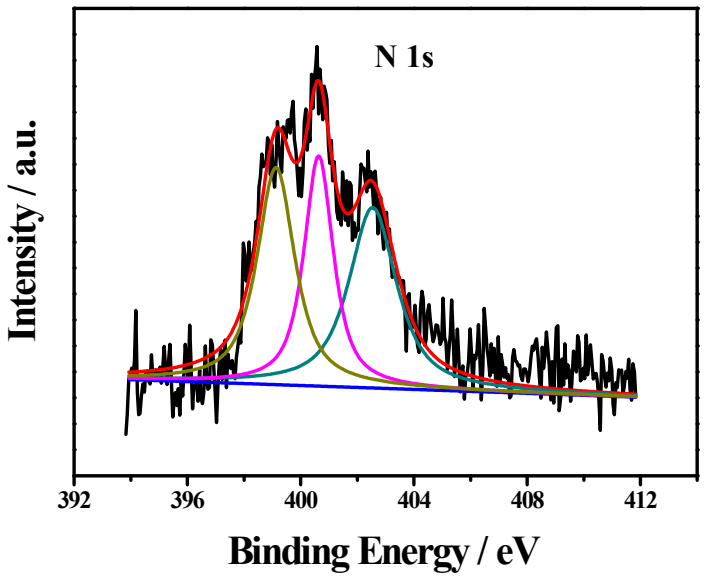

Fig. S2 N 1s spectrum of TMPyP-graphene composite.

Fig. S2 shows the N 1s spectrum of TMPyP-graphene composite. We can see that the N 1s line of TMPyP-graphene is deconvoluted into three peaks at 399.1, 400.6 and 402.5 eV, which can be assigned to the pyridinic-N, pyrrolic-N and graphitic-N, respectively.[S1,S2]

3. Cyclic voltammogram of methanol oxidation on 10% commercial Pt/C catalyst

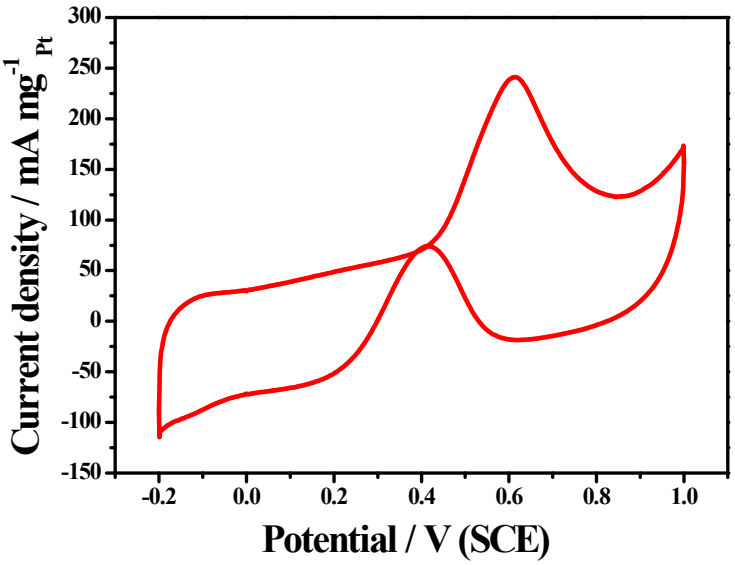

Fig. S3 Cyclic voltammogram of commercial Pt/C catalyst (10% Pt loading) in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution with a scan rate of 50 mV s^{-1}.

Fig. S3 shows the cyclic voltammogram of commercial Pt/C catalyst (Alfa Aesar, 10% Pt loading) in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution. We can see that the peak current densities of methanol oxidation on the 10% commercial Pt/C catalyst in the forward potential scan and in the backward potential scan are 241.2 and 74.1 mA mg_{Pt}^{-1}, respectively, much lower than those on the Pt/TMPyP-graphene (731.8 and 677.9 mA mg_{Pt}^{-1}) and Pt/graphene (346.6 and 324.6 mA mg_{Pt}^{-1}) catalysts.

4. The specific activity evaluation of as-prepared catalysts for methanol oxidation

Fig. S4 shows the cyclic voltammograms of methanol oxidation on Pt/TMPyP-graphene, Pt/graphene and 20% commercial Pt/C catalysts in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution. The oxidation current has been normalized to the electroactive surface area of Pt catalysts which was calculated by the electronic charge of hydrogen

adsorption/desorption.[S3] It can be seen that the peak current densities of methanol oxidation on the Pt/TMPyP-graphene catalyst (curve a) in the forward potential scan and in the backward potential scan are 0.58 and 0.54 mA cm^{-2}, respectively, higher than those on the Pt/graphene (curve b, 0.44 and 0.41 mA cm^{-2}) and commercial Pt/C (curve c, 0.42 and 0.46 mA cm^{-2}) catalysts. The results demonstrate that the presence of TMPyP in the Pt/TMPyP-graphene brings better electrocatalytic activity as compared to the Pt/graphene and commercial Pt/C catalysts.

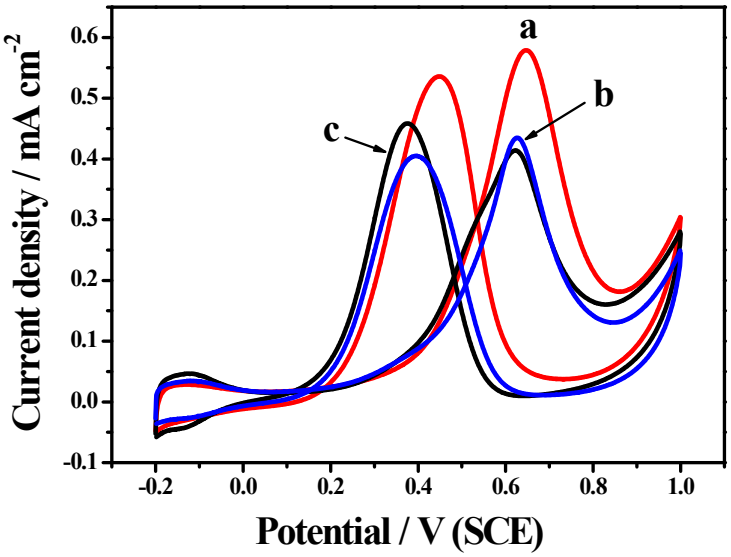

Fig. S4 Cyclic voltammograms of Pt/TMPyP-graphene (a), Pt/graphene (b) and 20% commercial Pt/C (c) catalysts in 0.5 M CH_3OH + 0.5 M H_2SO_4 solution with a scan rate of 50 mV s^{-1}.

[S1] L. Ding, J.L. Qiao, X.F. Dai, J. Zhang, J.J. Zhang, B.L. Tian, Int. J. Hydrogen Energy 37 (2012) 14103–14113.

[S2] K.C. Lee, L. Zhang, H.S. Liu, R. Hui, Z. Shi, J.J. Zhang, Electrochim. Acta 54 (2009) 4704–4711.

[S3] N. Tian Z.Y. Zhou, S.G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732–735.