

## Supporting Information

### **Graphene supported platinum/nickel phosphide electrocatalyst with improved activity and stability for methanol oxidation**

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### Preparation of Ni<sub>2</sub>P nanoparticles

The 0.3 g NiS<sub>2</sub> was mixed in 20 mL distilled water and subjected to ultrasonic vibration to form a homogeneous suspension. Then 1.03 g NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O was dispersed in 20 mL distilled water and mixed with the above suspension. Then the mixture was calcined at 500 °C for 1 h and cooled to room temperature. The solid obtained was washed thoroughly with distilled water and absolute ethyl alcohol to remove the by-products. After that, the wet products were dried at 80 °C for 12 h in a vacuum oven.

### Preparation of the Ni<sub>2</sub>P working electrode

The Ni<sub>2</sub>P slurry was prepared by ultrasonically dispersing 4 mg Ni<sub>2</sub>P nanoparticles in the solution of 0.2 mL ethanol, 0.8 mL ultrapure water and 20 μL Nafion (5 wt. % solution in a mixture of lower aliphatic alcohols and DuPont water) for 30 min. A glassy carbon electrode (GCE) with the diameter of 4 mm was polished with alumina suspensions and served as the underlying substrate of the working electrode. A quantity of 5 μL of the dispersion was extracted out on the top of the GC followed by drying at room temperature for 4 h.

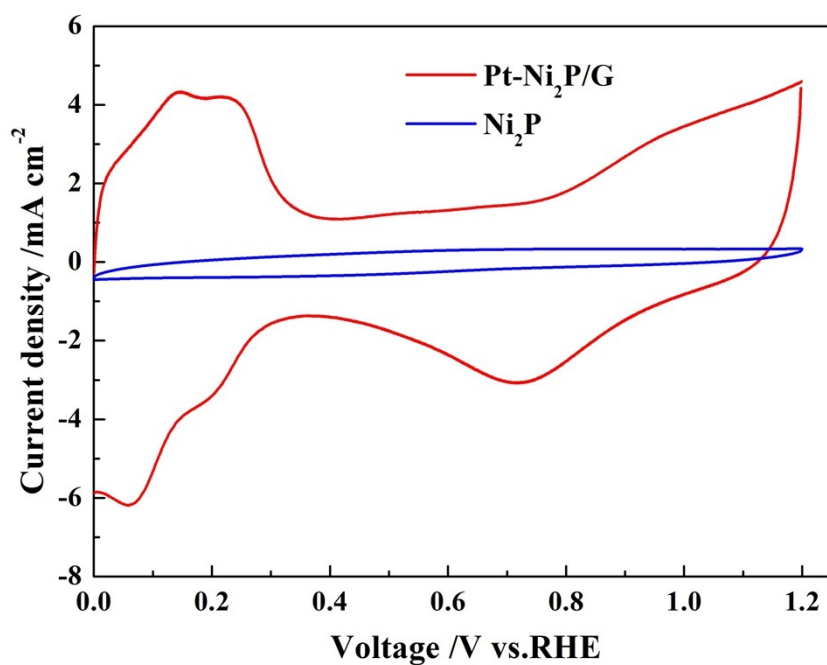


Fig. S1 Cyclic voltammetric curves with a scan rate of 50 mV s<sup>-1</sup> for Pt-Ni<sub>2</sub>P/Graphene and Pt-Ni<sub>2</sub>P catalysts in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>

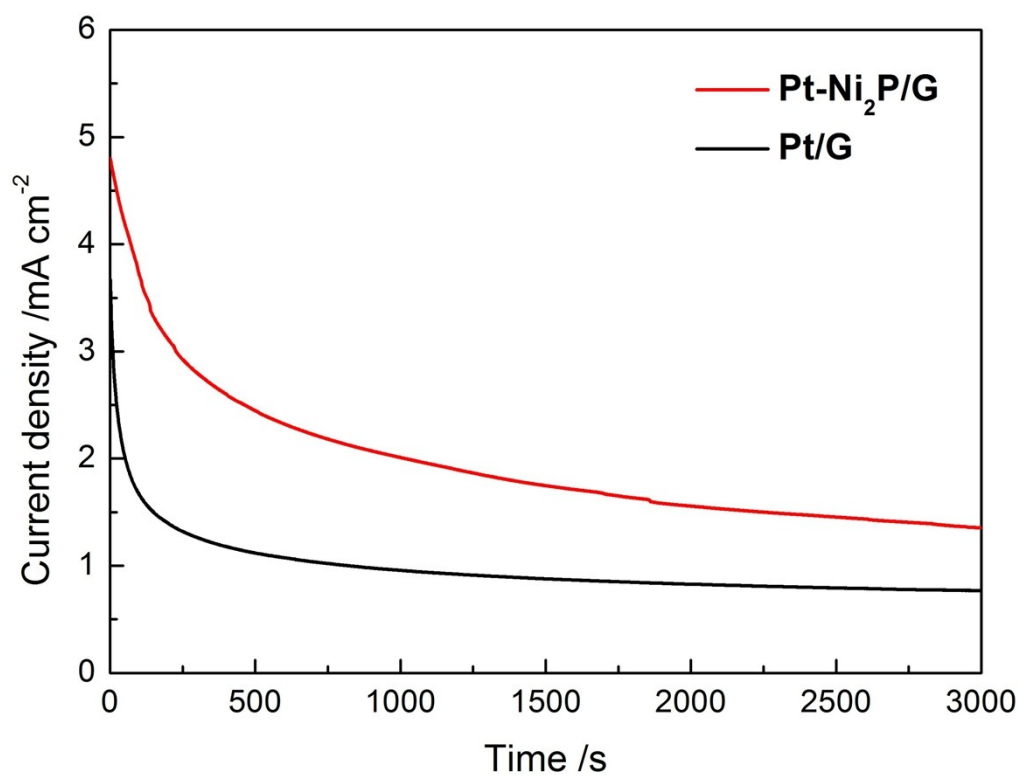


Fig. S2 Chronoamperometric curves in N<sub>2</sub> saturated 0.5 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a step potential of 0.6 V vs. RHE

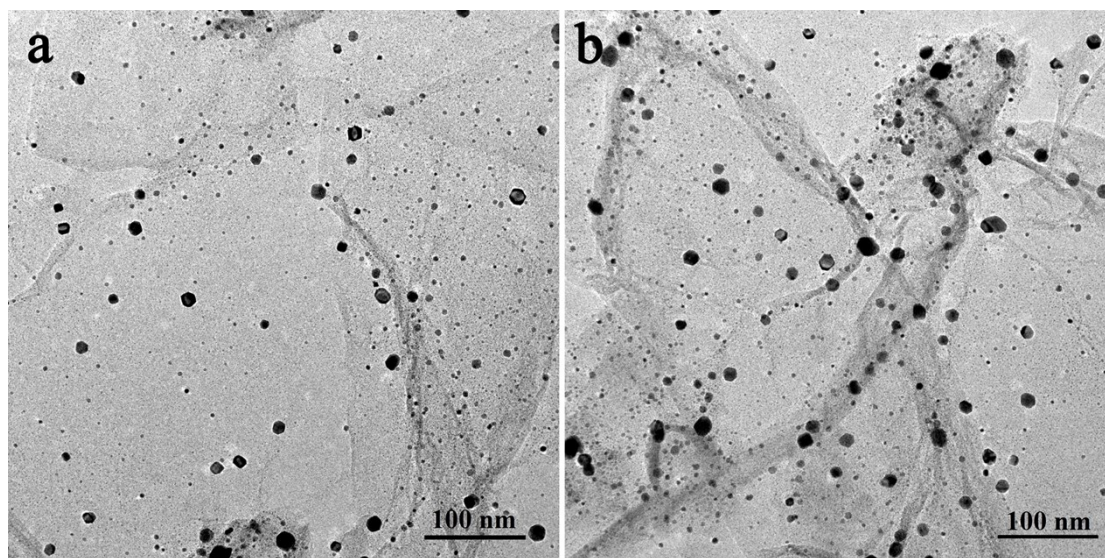


Fig. S3 The TEM images of Pt-Ni<sub>2</sub>P/Graphene catalyst before (a) and after (b) current density-time responses measurement.

After a typical current density-time responses measurement, the catalyst has a slight stacking phenomenon, which may be caused by the addition of Nafion during the preparation of the working electrode.