

## Supporting information

### **Nitrogen-doped carbon/graphene composites enhance the electrocatalytic performance of the supported Pt catalysts for methanol oxidation**

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### **Experimental**

#### **Materials**

The as-received pyrrole was purified by a process of reduced pressure distillation and preserved in an ampoule bottle. 5 wt% Nafion ionomer was obtained from Aldrich. Commercial state-of-the-art 20 wt% Pt/C (Johnson Matthey Company, HiSPEC™ 3000) was used as the benchmark for comparison and was denoted as Pt/C-JM. Ethylene glycol, H<sub>2</sub>SO<sub>4</sub>, and NaOH were purchased from the Shanghai Chemical Factory (Shanghai, China) and were used as received without further purification. Ultrapure water (Millipore, 18.2 MΩ cm) was used throughout all experiments.

#### **Synthesis of GO**

Graphene Oxidation (GO) was synthesized from natural graphite by a modified Hummers' method.<sup>4,9</sup> In a typical synthesis, 5.0g graphite powder was added into an 80°C solution of concentrated H<sub>2</sub>SO<sub>4</sub> (7.5ml), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>(2.5g), P<sub>2</sub>O<sub>5</sub>(2.5g) and allowed to proceed for 3 hours under vigorous stirring. The obtained dark mixture was then cooled to room temperature over a period of 6 hours and carefully diluted with distilled water, filtered, and washed until the rinse water became neutral. The black

product was finally dried in vacuum at room temperature over 48 hours to obtain the preoxidized graphite. Then 1.0g preoxidized graphite, 23ml concentrated  $\text{H}_2\text{SO}_4$  were stirred together in an ice bath. Next, 3g  $\text{KMnO}_4$  was slowly added into the above solution under stirring. Once mixed, the solution was raised to  $35^\circ\text{C}$  oil bath and stirred for about 2 hours, forming a thick paste. Next, 27.6ml distilled water was added to obtain an olive solution, followed by addition of 84ml distilled water and slow addition of 1.5ml of  $\text{H}_2\text{O}_2$  (30%), turning the color of the solution from dark brown to yellow. Finally, the solution was cooled to room temperature and then filtered with 150 ml  $\text{HCl}(1:10)$ . The yellow cake-like product was dried in vacuum and then dispersed in distilled water by mechanical agitation, dialyzed for 4 days, dried in vacuum at room temperature for further use.

### **Synthesis of GP-X-T supports**

Graphene Oxidation/Polypyrrole(GO/PPy) composites were synthesized by the in suit polymerization of pyrrole on the graphene oxidation sheets in ethanol/water system. Briefly, 2 g pyrrole and 100 mg GO were added into a water/ethanol solution (v/v=1). After ultrasonic dispersion, 2 g APS pre-cooled ammonium persulfate (APS) solution (in 5 ml  $\text{H}_2\text{O}$ ) was added into the pyrrole/GO suspension. Subsequently, the mixture solution was kept at room temperature for 24 h following with filtration and rinsed with large amount of deionized water. The products were marked as GP-X (X is the proportion of pyrrole/GO). thermal annealing of the GP composites to gain the catalysts support Briefly, the obtained solid GP-X samples were ground into powders, put in a quartz boat, and annealed for one hours in a tube furnace at target

temperatures of 700 and 800 900 and 1000°C, yielding products denoted as GP-X-T (marked as GP-X-700, GP-X-800, GP-X-900, and GP-X-1000, respectively). The heating rate during ramp-up was 5 °C min<sup>-1</sup> and the N<sub>2</sub> flow rate was 80 mL min<sup>-1</sup>.

### **Synthesis of Pt/GP-X-T catalysts**

Pt/GP-X-T catalysts with the Pt loading of 20% were prepared via the microwave-assisted polyol method in ethylene glycol solution. A typical synthesis procedure is as follows: GP-X-T (50 mg) was suspended separately in 40 ml ethylene glycol then ultrasonic dispersion for 1 h, then 893 μL of chloroplatinic acid (14 mg mL<sup>-1</sup>) in 10 ml ethylene glycol was added dropwise and the PH of the suspension was adjust to 10 with 0.1 M NaOH aqueous solution. The mixture solution was then suspended in the microwave reactor over 90 s. After microwave radiation the solution was stirring for another 8 h, then the product was filtrated, washed by alcohol and distilled water and dried at 80 °C in a vacuum oven for 8 h. Thus obtain Pt/GP-X-T catalysts.

### **Physical characterizations**

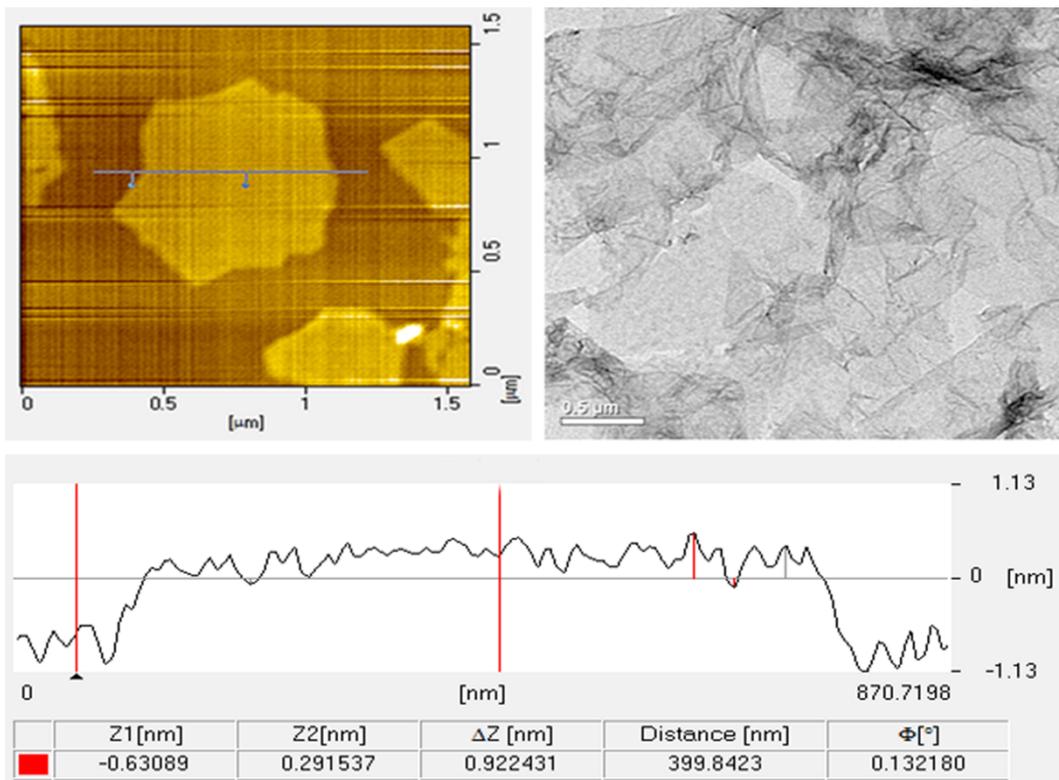
The Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex 70 RTIR spectrometer. Raman spectra were collected on a J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. Scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and element mapping analysis were conducted on a XL30 ESEM FEG field emission scanning electron microscope operating at 20 kV. Transmission electron microscopy (TEM) was used to analyze the size and morphology of catalysts on a Philips TECNAI G2 operating at

200KV. The X-ray diffraction (XRD) patterns of the catalysts were obtained using a PW1700 diffractometer (Philips Co.) with a Cu K $\alpha$  ( $\lambda = 0.15405$  nm) radiation source operating at 40 kV and 30 Ma. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg Ka radiation source.

### **Electrochemical measurements**

All electrochemical measurements were carried out with an EG&G mode 273 potentiostat/Galvanostat and a conventional three-electrode test cell at the ambient temperature. A glassy carbon disk coated with catalyst was used as the working electrode. The counter-electrode and reference-electrode were a Pt foil and a saturated calomel electrode (SCE) respectively. The glassy carbon disk was polished with 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$  alumina powder respectively, sonication and rinsed with deionized water before used. The homogeneous catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalyst, 950  $\mu\text{L}$  ethanol, and 50  $\mu\text{L}$  Nafion alcohol solution (Aldrich, 5 wt% Nafion) for approximately 30 min. Next, 5 $\mu\text{L}$  catalyst ink was pipetted and spread on a 3 mm-diameter pre-cleaned glassy carbon disk as the working electrode. All electrolyte solutions were deaerated by high-purity nitrogen for at least 15 min prior to any measurement. To evaluate the catalytic activity for methanol, the cyclic voltammetry experiments were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> +1 M CH<sub>3</sub>OH solution with a scan rate of 50 mVs<sup>-1</sup>. The chronoamperometry experiments were performed in the same solution at the potential of 0.5V (vs.SCE) for 3600 s.





**Fig S1** The AFM (a, c) and TEM (b) image of the synthesized GO

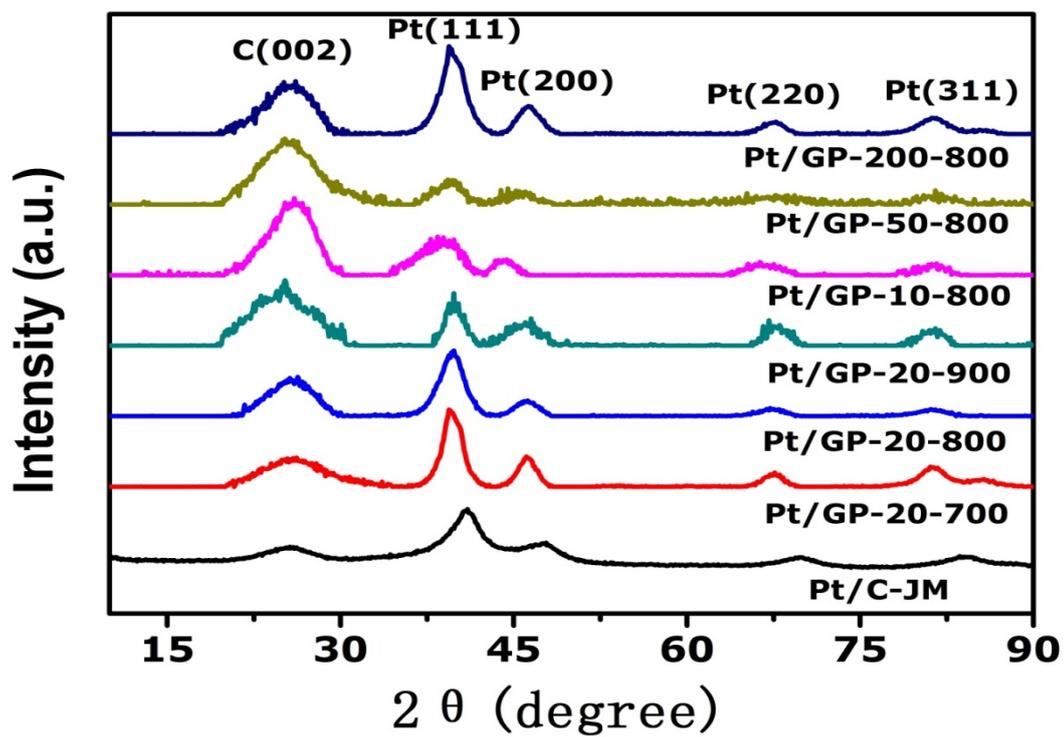
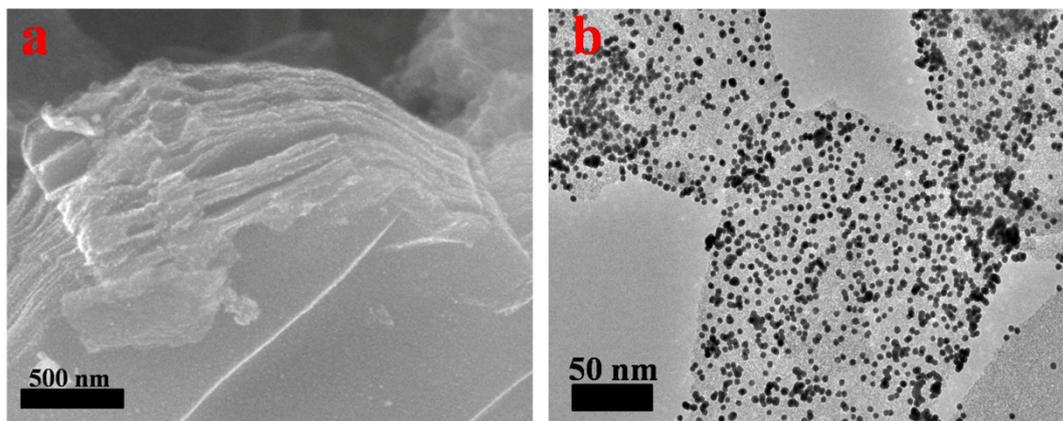
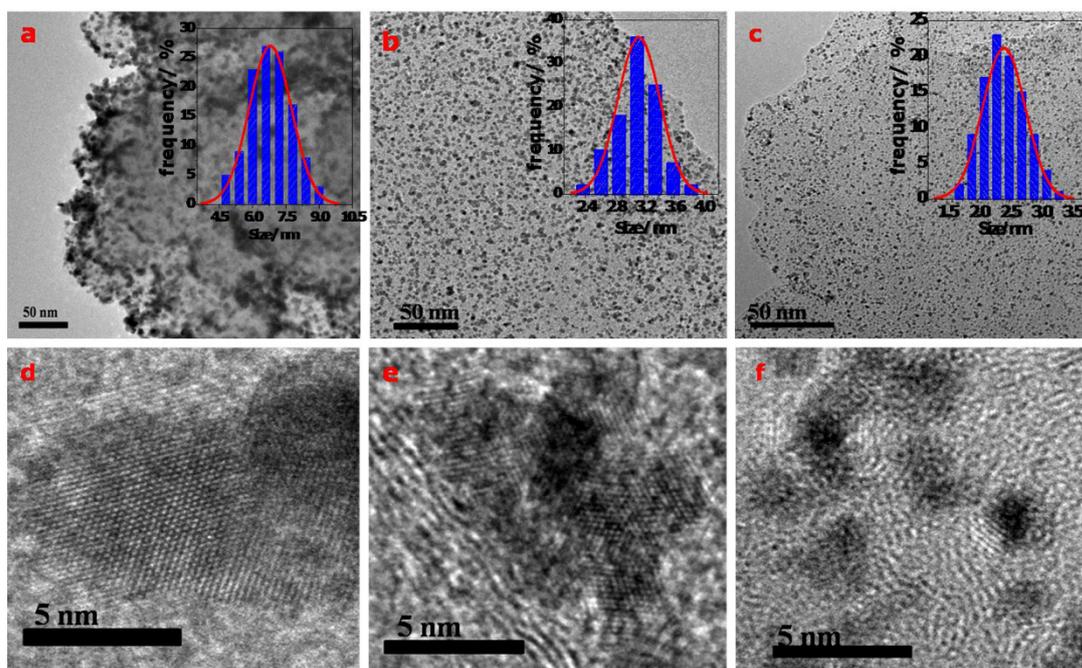


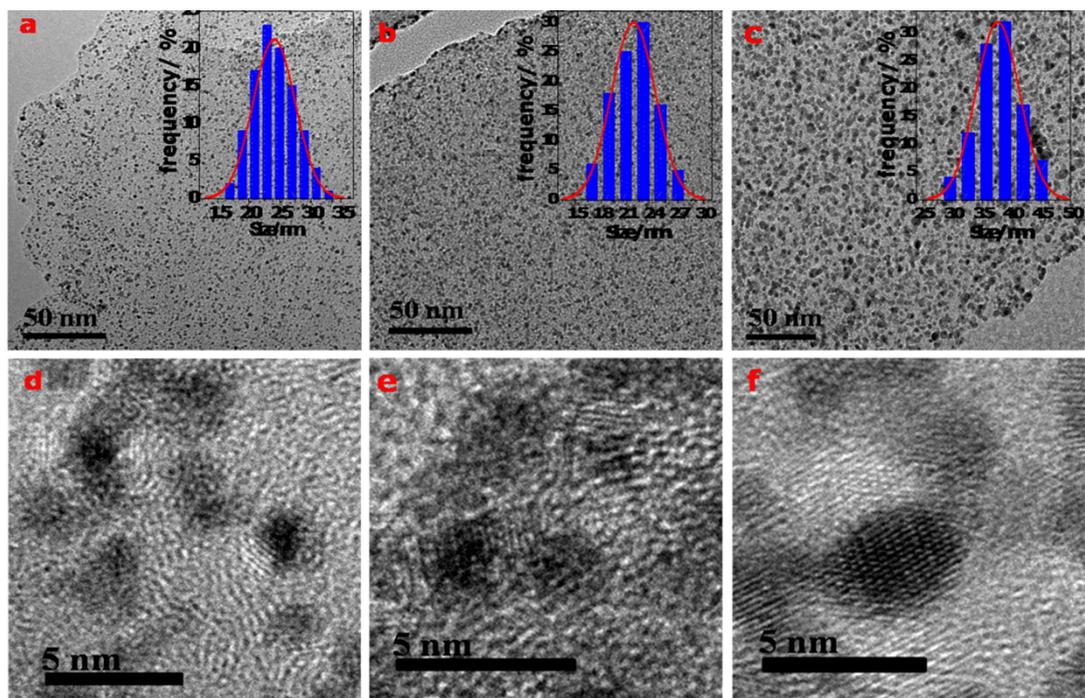
Fig S2 XRD patterns of the Pt/GP-X-T and Pt/C-JM catalysts



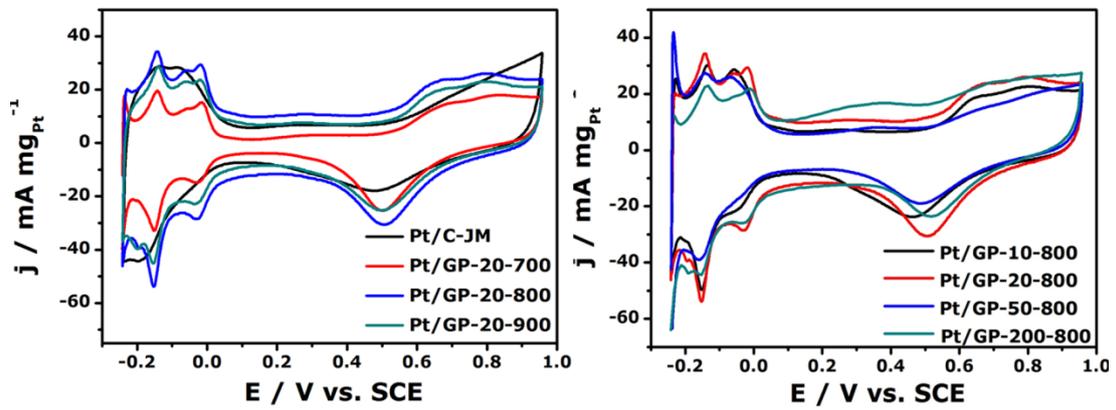
**Fig S3** SEM (a) and TEM (b) image of Pt/Graphene-800 catalyst.



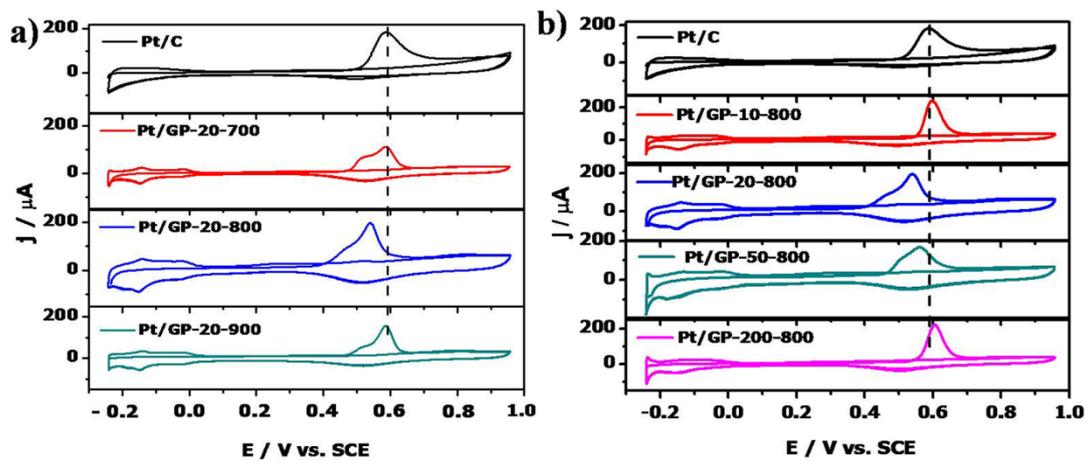
**Fig S4** TEM and HRTEM images of Pt/GP-20-*T* catalysts; (a,d) Pt/GP-20-700; (b,e) Pt/GP-20-800; (c,f) Pt/GP-20-900.



**Fig S5** TEM and HRTEM images of Pt/GP-X-800 catalysts; (a,d) Pt/GP-10-800; (b,e) Pt/GP-50-800; (c,f) Pt/GP-200-800.



**Fig S6** CV of the Pt/GP-X-T and Pt/C-JM catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mVs<sup>-1</sup>



**Fig S7** CO-stripping voltammograms of the Pt/GP-X-T and Pt/C-JM catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 20 mV s<sup>-1</sup>

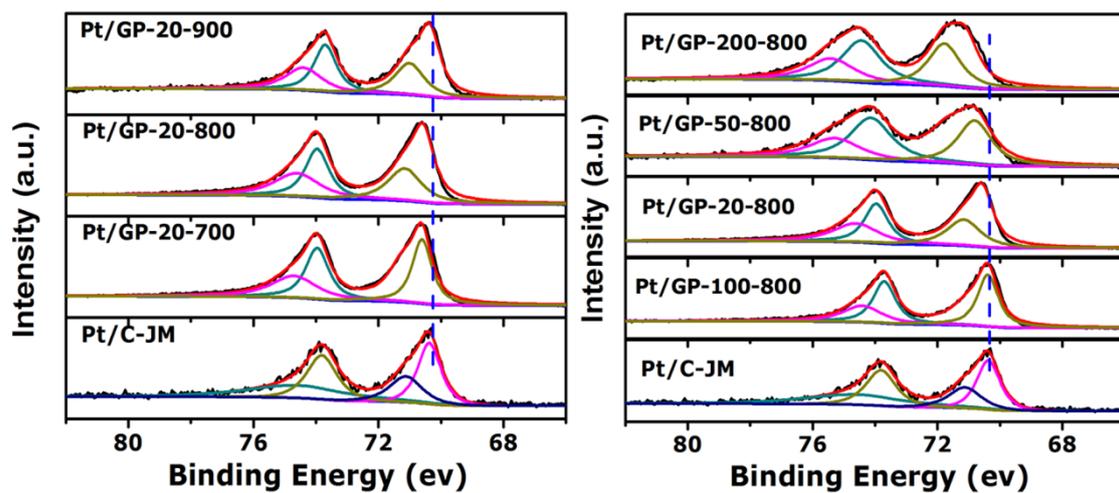


Fig S8 Deconvoluted and comparison of the Pt 4f binding energy between Pt/GP-X-T and Pt/C-JM catalysts

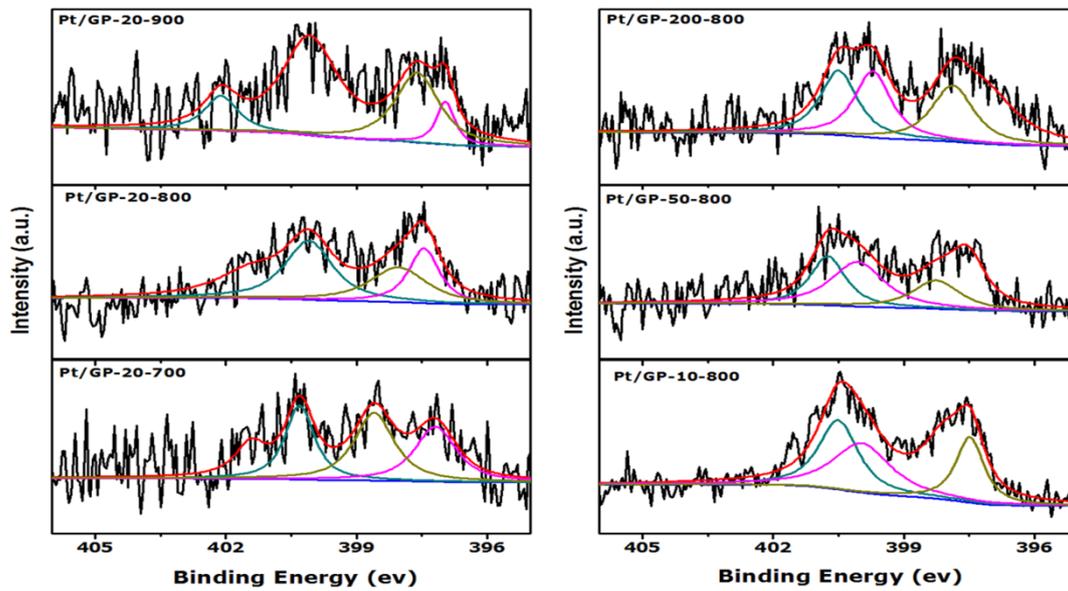


Fig S9 Deconvoluted N 1s spectra of the Pt/GP-X-T catalysts

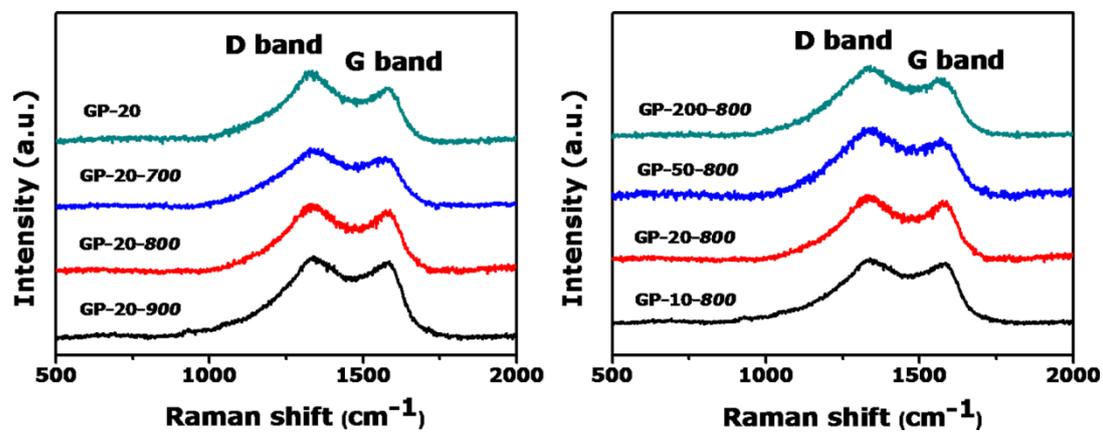


Fig S10 Raman spectra of GP-X-T supports

**Table S1 Sum of CO-stripping and the corresponding ECSA  
of the Pt/GP-X-T and Pt/C-JM catalysts**

	<b>E<sub>onset</sub> / V</b>	<b>E<sub>peak</sub> / V</b>	<b>ECSA/m<sup>2</sup>g<sup>-1</sup></b>
<b>Pt/GP-20-700</b>	<b>0.478</b>	<b>0.586</b>	<b>32.15</b>
<b>Pt/GP-20-800</b>	<b>0.408</b>	<b>0.538</b>	<b>54.35</b>
<b>Pt/GP-20-900</b>	<b>0.480</b>	<b>0.585</b>	<b>33.12</b>
<b>Pt/GP-10-800</b>	<b>0.551</b>	<b>0.595</b>	<b>36.69</b>
<b>Pt/GP-50-800</b>	<b>0.468</b>	<b>0.560</b>	<b>51.85</b>
<b>Pt/GP-200-800</b>	<b>0.546</b>	<b>0.605</b>	<b>37.48</b>
<b>Pt/C-JM</b>	<b>0.493</b>	<b>0.591</b>	<b>49.63</b>

**Table S2 N1s composition from XPS**

	<b>Total N</b>	<b>pyridinic N</b>	<b>pyrrolic N</b>	<b>quaternary N</b>	<b>oxidized N</b>
	<b>atom%</b>				
<b>Pt/GP-20-700</b>	<b>4.16</b>	<b>1.17</b>	<b>1.39</b>	<b>1.11</b>	<b>0.49</b>
<b>Pt/GP-20-800</b>	<b>3.49</b>	<b>0.74</b>	<b>0.87</b>	<b>1.22</b>	<b>0.66</b>
<b>Pt/GP-20-900</b>	<b>2.32</b>	<b>0.18</b>	<b>0.68</b>	<b>1.20</b>	<b>0.26</b>
<b>Pt/GP-10-800</b>	<b>3.87</b>	<b>0.75</b>	<b>0.88</b>	<b>1.14</b>	<b>1.10</b>
<b>Pt/GP-50-800</b>	<b>3.62</b>	<b>0.86</b>	<b>0.68</b>	<b>1.20</b>	<b>0.88</b>
<b>Pt/GP-200-800</b>	<b>3.84</b>	<b>1.00</b>	<b>0.93</b>	<b>0.96</b>	<b>0.95</b>

Table S3 The calculated value of  $I_d/I_g$  from Raman spectra

	$I_d/I_g$
<b>GP-20</b>	3.68
<b>GP-20-700</b>	2.61
<b>GP-20-800</b>	2.21
<b>GP-20-900</b>	1.91
<b>GP-10-800</b>	2.08
<b>GP-50-800</b>	2.60
<b>GP-200-800</b>	2.91