

## Supporting Information Available

### Stabilization of Platinum Nanoparticles Dispersed on Carbon

#### Nanotubes by Ionic Liquid Polymer

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#### 1. Experimental Details

Multi-walled CNTs (diameter 20 - 60 nm, length 5 - 15  $\mu\text{m}$ ) prepared by chemical vapor deposition were purchased from Shenzhen Nanotech Port Co. Ltd., China, and used without any purification. 1-AP and 1-vinylimidazole were purchased from Alfa Aesar. All other chemicals were of analytical grade and used as received.

The procedure for the noncovalent functionalization of CNTs using 1-AP was referred to the literature.<sup>S1</sup> The details were as follows: 100 mg of pristine CNTs was sonicated in 50 mL of ethanol containing 10 mg of 1-AP for 1 h and stored at room temperature overnight. Then the solution was filtered through a nylon filter membrane and washed with double-distilled water several times. The functionalized CNTs were dried in a vacuum oven at 343 K for 10 h and collected.

Deposition of PtNPs on 1-AP-functionalized CNTs (AP-CNTs) was achieved via microwave-assisted reduction process in ethylene glycol as reported in the literature.<sup>S2</sup> The details were as follows: 40 mg of AP-CNTs and 2.13 mL  $\text{H}_2\text{PtCl}_6$  solution (19.3 mM) were mixed with 25 mL ethylene glycol. Then, the pH value of the solution was adjusted to 8-9 with KOH (1.0 M) aqueous solution and the mixture solution was

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ultrasonic treated for 30 min. The mixture was treated by microwave irradiation (800 W) for 10 min at 393 K and then diluted with double-distilled water, filtered through a Nylon 66 membrane and washed thoroughly with double-distilled water and acetone several times. The products were labeled as PtNPs/AP-CNTs

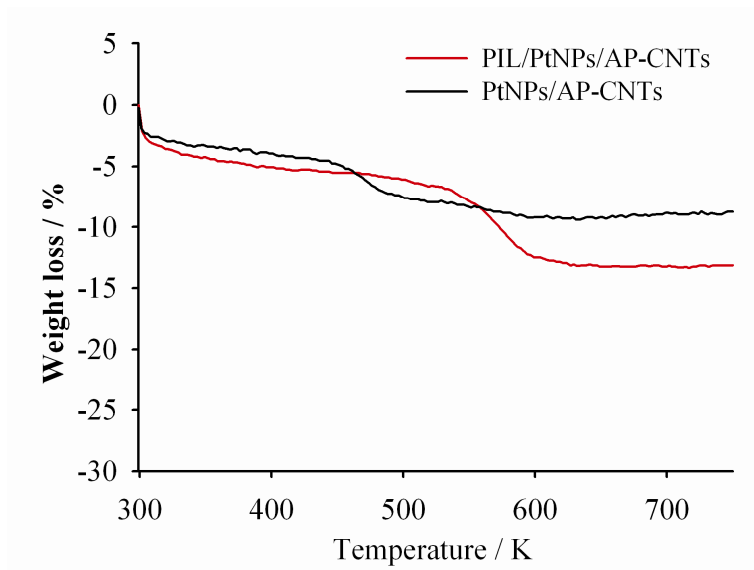
The corresponding loading mass of PtNPs on CNTs was investigated by inductively coupled plasma–atomic emission spectroscopy and is 15.75 wt. %. The obtained product was labeled as PtNPs/AP-CNTs and divided into two parts. One was used as the comparison sample and the other was treated with ILs.

1-vinyl-3-ethyl imidazolium bromide ([VEIM]Br) was synthesized according to the procedure reported previously.<sup>S3</sup> The formation of PIL thin layer on the surface of the PtNPs/AP-CNTs electrocatalyst was accomplished by the following procedure<sup>S4</sup>: a mixture of PtNPs/AP-CNTs (25 mg) and [VEIM]Br (5 mg) was grounded in an agate mortar for 30 min. After adding AIBN (1 mg), the mixture was ground for another 1 min, and then transferred to a 50 mL round-bottomed flask equipped with condenser and magnetic stirrer, refluxed for 16 hours at 353 K under vigorous stirring and N<sub>2</sub> protection. After that, the mixture was cooled down and diluted with double-distilled water, filtered through a Nylon 66 membrane and washed with double-distilled water, ethanol and acetone several times to thoroughly remove physically absorbed polymer and un-reacted [VEIM]Br monomer. The final products, labeled as PIL/PtNPs/AP-CNTs, were then dried in vacuum oven at 333 K to remove the residual solvent.

The PIL/PtNPs/AP-CNTs electrocatalyst were characterized by transmission electron microscopy (TEM, JEOL 3010, 200kV) and thermogravimetric analysis (TGA, NETZSCH STA 409 PC, 10 °C.min<sup>-1</sup> in N<sub>2</sub> atmosphere). The ESA and the electrochemical performance of the electrocatalysts were evaluated by cyclic voltammetry and chronoamperometry. All electrochemical measurements were performed on a CHI660B electrochemical workstation (Chenhua Instrument Company of Shanghai, China), except the ESA measurement (Autolab PGSTA12). A conventional three electrode glass cell was used with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the potentials reported herein were with respect to the SCE. Double-distilled water was used throughout.

## **2. TGA characterization of PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs nanohybrids**

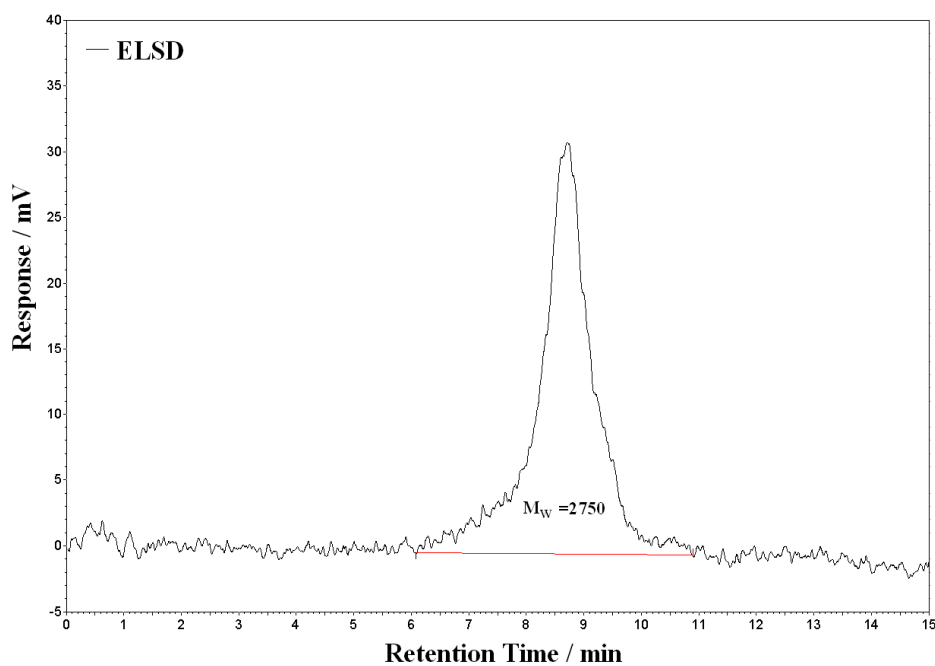
The weight percentage of the PIL on the PtNPs/AP-CNTs surface was determined using thermogravimetric analysis (TGA). TGA was performed on a NETZSCH STA 409 PC at a heating rate of 10 °C.min<sup>-1</sup> in N<sub>2</sub> atmosphere and the corresponding results are shown in Figure S1. In the temperature range of 600 - 750 K, the difference in weight loss of the PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs nanohybrids is the amount of PIL layer in the PIL/PtNPs/AP-CNTs nanohybrids and about 5 wt %.



**Figure S1. The thermogravimetric analysis of PIL/PtNPs/AP-CNTs and PtNPs/AP-CNTs nanohybrids**

### 3. GPC characterization of PIL/PtNPs/AP-CNTs

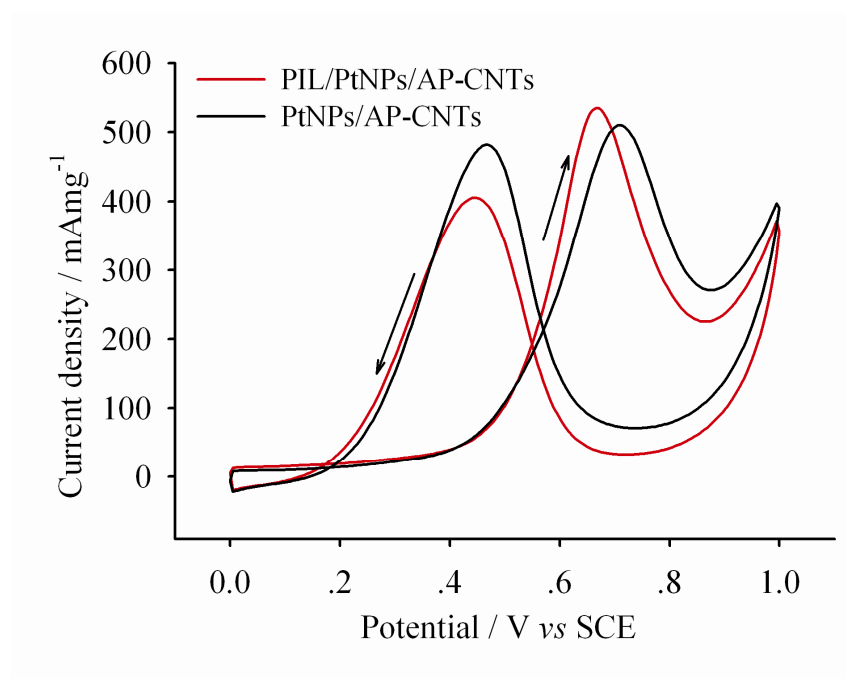
The PIL on the PtNPs/AP-CNTs surface was also confirmed by gel permeation chromatography (GPC, Jordi Gel DVB)<sup>S5</sup>. The PIL/PtNPs/AP-CNTs electrocatalysts were dispersed in tetrahydrofuran, ultrasonic treated for 30 min and filtrated. Then, the filtrate were used for GPC characterization and the corresponding results are shown in Figure S2. The weight average molecular weight ( $M_w$ ) of PIL in PIL/PtNPs/AP-CNTs is 2750. This confirms the existence of PIL film on the PtNPs/AP-CNTs surface because the molecular weight of ionic liquid monomer ([VEIM]Br) is 203.



**Figure S2 GPC curve of PIL/PtNPs/AP-CNTs**

#### **4. Cyclic voltammograms of methanol Oxidation on PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs electrocatalysts**

The electrochemical performance of PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs electrocatalysts toward electro-catalytic oxidation of methanol was evaluated by cyclic voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.0 M CH<sub>3</sub>OH aqueous solution at a scan rate of 50 mV.s<sup>-1</sup> at ambient temperature. The results are shown in Figure S3. The data about peak current and peak potential of methanol oxidation on two electrocatalysts are summarized in Table S1.



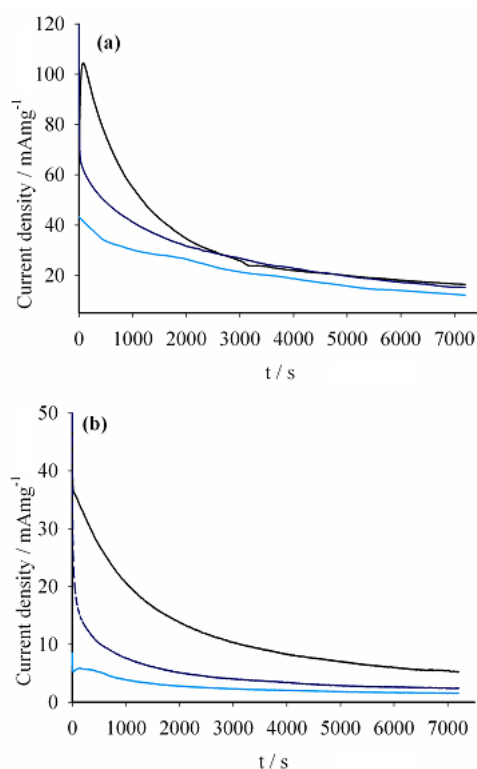
**Figure S3** Cyclic voltammograms of the PIL/PtNPs/AP-CNTs and PtNPs/AP-CNTs electrocatalysts in nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> +1.0 M CH<sub>3</sub>OH aqueous solution at a scan rate of 50 mV.s<sup>-1</sup>.

**Table S1** The data about peak current and peak potential of methanol oxidation on PIL/PtNPs/AP-CNTs and PtNPs/AP-CNTs electrocatalysts

Electrode	Forward	Forward	Reverse	Reverse
	peak current	peak	peak current	peak
	(mA.mg <sup>-1</sup> )	potential (V)	(mA.mg <sup>-1</sup> )	potential (V)
PtNPs/AP-CNTs	510.42	0.710	481.83	0.470
PIL/PtNPs/AP-CNTs	535.03	0.670	405.69	0.450

#### 4. Chronoamperometric results of methanol oxidation on PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs electrocatalysts

The electrochemical performance of PtNPs/AP-CNTs and PIL/PtNPs/AP-CNTs electrocatalysts toward electro-catalytic oxidation of methanol was evaluated by chronoamperometry in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.0 M CH<sub>3</sub>OH aqueous solution and the corresponding results are shown in Figure S4. The chronoamperometry experiments were carried out continuously for 2 hours, then the electrolyte solution was replaced with fresh solution and the chronoamperometry experiment was performed again. We did the chronoamperometry experiments for three times (6 hours).



**Figure S4 Chronoamperometric results of the PIL/PtNPs/AP-CNTs (a) and PtNPs/AP-CNTs (b) electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.0 M CH<sub>3</sub>OH aqueous solution. From top to down, 1 period, 2 period, 3 period.**

**Table S2 The data of the electrochemical surface area (ESA) of PIL/PtNPs/AP-CNTs and PtNPs/AP-CNTs electrocatalysts before (ESA1) and after (ESA2) chronoamperometry experiments for three periods (6hours).**

Electrocatalyst	ESA1(m <sup>2</sup> .g <sup>-1</sup> Pt)	ESA2(m <sup>2</sup> .g <sup>-1</sup> Pt)
PtNPs/AP-CNTs	39.10	5.63
PIL/PtNPs/AP-CNTs	40.20	39.30

**References:**

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