Electronic Supplementary Information

Boron-doped Carbon Nanotube-supported Pt Nanoparticles with Improved CO Tolerance for Methanol Electro-oxidation**

*Shuangyin Wang, Thomas Cochell and Arumugam Manthiram**

Experimental Details

CVD growth of B-doped CNT (B-CNT). B-CNTs were prepared by a CVD method using toluene and ferrocene (1 wt. %) as sources for carbon and catalyst, respectively. Triethyl borate (TEB) was used as the B precursor. Briefly, a toluene solution (3 mL) containing 1 wt. % TEB and 1 wt. % ferrocene was injected, along with 50 cc of H_2 and Ar flow, at 780°C in a quartz tube furnace. After the growth processes, B-CNT was immersed into HCl solution to remove the residual Fe metal particles decomposed from ferrocene. CNT was also prepared following the similar procedure in the absence of TEB.

Synthesis of Pt/B-CNT and Pt/CNT. To deposit Pt nanoparticles on B-CNT and CNT at a given metal loading (25 wt. %), 20 mg of B-CNT (or CNT) was mixed with a stoichiometric amount of H_2PtCl_6 in ethylene glycol (EG) solution under ultrasonication. The pH of the reaction system was then adjusted to 1.25 by adding 2 M NaOH solution in EG dropwise, followed by refluxing the solution at 160 ℃ for 3 h to ensure the complete reduction of the metal salt. After the reaction, the pH was adjusted back to ~ 4. After the reaction was completed, the Pt/B-CNT and Pt/CNT products were obtained by filtrating the resultant solution and washing with a Nylon filter membrane followed by vacuum drying at 70 ℃ for 24 h.

Physical characterizations. STEM (Hitachi S-5500) was performed at 30 kV to observe the morphology of the as-prepared electrocatalysts: Pt/CNT and Pt/B-CNT. X-ray diffraction with Cu Kα was used to identify the crystalline phases. X-ray photoelectron spectroscopy (XPS, Krato) was used to analyze the surface composition of B-CNT and CNT. The structural changes in CNT on doping with boron were examined by Raman spectroscopy (Renishaw). The average crystallite size of Pt particles was estimated from the diffraction peak of Pt(200) using the Debye-Scherrer equation:

$$d = 0.9\lambda_{K\alpha 1}/\beta \cos\theta_{max}$$

in which d is the average size of the Pt particle, $\lambda K_{\alpha 1}$ is the X-ray wavelength (Cu K_α $\lambda K_{\alpha 1}$= 1.5418 Å), θmax is the maximum angle of the (200) peak, and β is the full-width at half-maximum in radians.

Electrochemical characterizations. The electrochemical measurements were performed with a three-electrode cell, using a glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and Pt foil as the counter electrode at room temperature. All potentials reported here are against the SCE reference electrode. To load the electrocatalysts onto GCE, the catalyst powder was dispersed in water to form a homogeneous ink (2 mg mL^{-1}) and then 40 μL of the ink was dropped onto GCE. After becoming dry, 5 μl of Nafion solution (0.05 %) was added to fix the catalysts on GCE. The CO stripping was performed in 0.5 M H_2SO_4 solution, which was first purged with nitrogen gas. The adsorption of CO on the electrocatalyst was carried out by bubbling CO gas through the electrolyte solution for 20 min, while the electrode was maintained at -0.15 V (vs. SCE). Afterwards, the electrolyte solution was purged with pure nitrogen for another 20 min to remove the residual CO from the electrolyte. The CO stripping CV curves and blank CV curves were obtained from

two consecutive scan cycles. The electrocatalytic activity for methanol oxidation was evaluated by CV in a 0.5 M H_2SO_4 + 0.5 M MeOH solution at a scan rate of 10 mV s^{-1}.

Supplementary Results

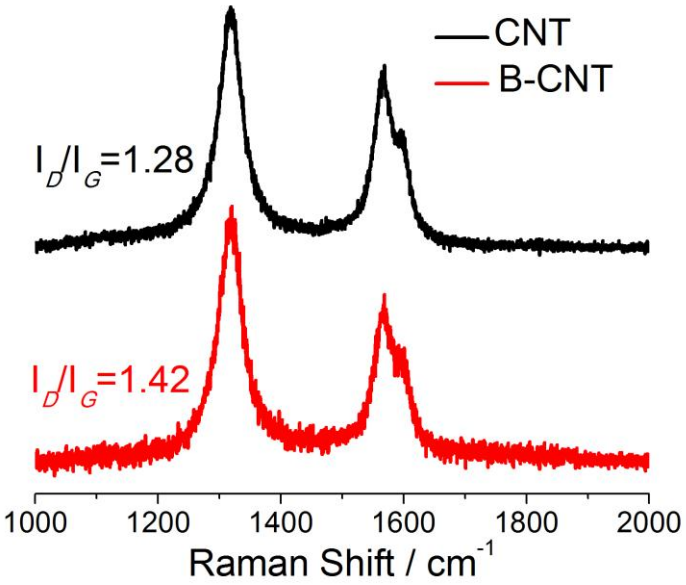

Figure S1. Raman spectra of CNT and B-CNT.

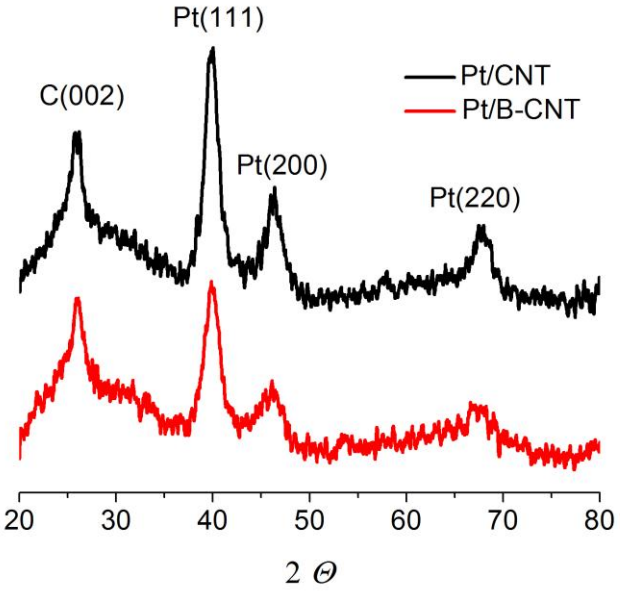

Figure S2. XRD patterns of Pt/CNT and Pt/B-CNT.

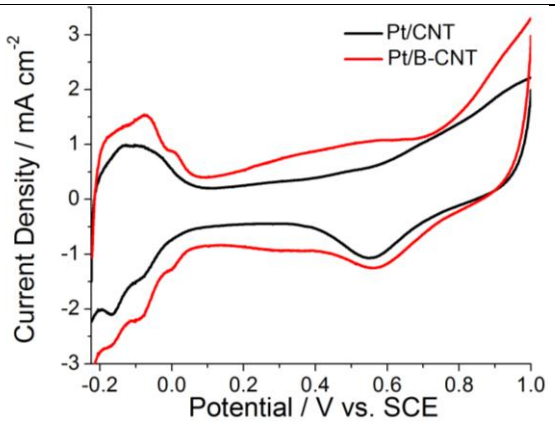

Figure S3. CV curves of Pt/CNT (black) and Pt/B-CNT (red) in 0.5 M H_2SO_4 at a scan rate of 10 mV s^{-1}.

Table S1. Summary of the electrochemical data from Figure 3-4 and Figure S3.

		CO Stripping	Methanol Oxidation	
Catalyst	ESA / m^2 g^{-1}	Peak Potential / V	Peak Potential / V	Peak Current / mA cm^{-2}
Pt/CNT	40.6	0.56	0.62	7.8
Pt/B-CNT	55.7	0.53	0.59	13.6