Supporting Information

Unique reactivity in Pt/CNT catalyzed hydrolytic dehydrogenation of ammonia borane

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1 Catalysts preparation

1.1 Synthesis of Pt/AC and Pt/CNTs catalysts

Activated carbon (AC), purchased from Sinopharm Chemical Reagent Co. Ltd, was first dispersed into water, and then treated at 80 ^{o}C for 3 h. The slurry was filtrated, and dried at 120 ^{o}C for 12 h. The as-obtained AC samples and pristine close carbon nanotubes (CNTs, purchased from Beijing Cnano Technology Limited) were used to immobilize Pt catalysts. Four different Pt loadings (i.e., 0.5, 1.5, 2.0 and 3.0 wt%) were prepared by incipient wetness impregnation with an aqueous solution of H_2PtCl_6 (Sinopharm Chemical Reagent Co. Ltd) onto AC and CNTs supports. The precursors of Pt/AC and Pt/CNTs catalysts were dried in stagnant air at room temperature and ambient temperature for 12 h and then at 120 ^{o}C for 12 h.

1.2 Synthesis of Pt/CNTs-HT, Pt/CNTs-O and Pt/CNTs-O-HT catalysts

Pristine close CNTs were treated by high temperature of 800 ^{o}C under Ar atmosphere for 2 h, acid oxidation of 8 M HNO_3 (65%, Shanghai Lingfeng Chemicals) mixed with 8 M H_2SO_4 (98%, Shanghai Lingfeng Chemicals) in an ultrasonic bath of 60 ^{o}C for 2 h, and acid oxidation followed by high temperature, respectively. The as-obtained samples were labelled as CNTs-HT, CNTs-O and CNTs-O-HT, respectively. Three kinds of Pt/CNTs-HT, Pt/CNTs-O and Pt/CNTs-O-HT catalysts were prepared using the same procedure mentioned in Section 1.1.

2 Characterization

Raman spectra were measured on a Raman microscope (LabRAM HR, Horiba JY, France). TGA experiments under Ar gas flow were carried out on SDT-Q600 thermobalance (TA Instruments) by heating up to 800 ^{o}C at a heating rate of 10 ^{o}C·min^{-1}, in which the surface concentration of oxygen groups on carbon supports was analyzed. XPS analysis of Pt nanocatalysts was performed on a Kratos XSAM-800 instrument using Al K_{α} (hυ=1486.6 eV) X-ray as the excitation source, in which the samples were stored under Ar atmosphere at room temperature before the XPS analysis. The binding energy of C1s (284.6 eV) was taken as a reference to correct the binding energy of the samples. Fourier transform infrared (FTIR) spectra were measured with Nicolet (Thermo Scientific) instrument using KBr plates. Pt particle sizes were recorded by transmission electron microscope (TEM, JEOL JSM 2010, Japan). The surface areas and pore volumes of carbon supports were measured on ASAP 2020 (Micromeritics, USA) at 77 K after out-gassing the samples at 190 ^{o}C and 1 mmHg for 6 h.

3 Catalytic tests

Activity test of the hydrolytic dehydrogenation of ammonia borane (AB, purity of 97%, purchased from Aldrich) over Pt nanocatalysts was carried out at 30±0.5 or 25±0.5 ^{o}C under atmospheric pressure. Prior to the reaction, the precursors of the as-prepared Pt nanocatalysts were reduced by pure H_2 of 60 mL·min^{-1} at 250 ^{o}C for 2 h and then purged with pure Ar. After reduction, the catalysts were passivated for 20 min and then stored in an inert atmosphere. The volume of H_2 generation was measured by the displacement method.

Typically, a certain amount of the reduced Pt nanocatalysts were placed in a three-necked round-bottom flask (50 mL) with an outlet tube connected with a gas washing bottle filled with water for collecting the hydrogen evolved. The catalysis reaction was conducted once injecting AB aqueous solution (5 mL, C_{AB}=0.01 g/mL and $n_{Pt}/n_{AB}=4.7\times10^{-3}$) from syringe. An electronic balance was used to calculate the volume of water discharged which could be converted into the volume of hydrogen.

Table S1 N_2-BET results of carbon supports and properties of Pt catalysts.

Supports	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pt loading (wt %)	Pt particle size by TEM (nm)	
				Size range	Average size[a]
AC	-	-	0.5	0.9-3.4	1.6±0.2
			1.5	0.7-3.4	2.1±0.4
			2.0	1.3-3.9	2.3±0.3
			3.0	1.6-5.3	3.0±0.4
CNTs	202	1.17	0.5	0.4-2.7	1.0±0.3
			1.5	0.6-2.3	1.4±0.1
			2.0	0.4-2.7	1.5±0.2
			3.0	0.6-4.7	1.9±0.7
CNTs-HT	-	-	0.5	0.4-1.8	1.0±0.1
CNTs-O	225	1.64	1.5	0.6-3.3	1.6±0.6
CNTs-O-HT	221	1.40	1.5	0.4-1.9	1.0±0.1
			2.0	0.4-3.9	1.1±0.4
			3.0	0.6-3.0	1.3±0.2
			4.5	0.4-3.7	1.6±0.4

[a] Estimated by the equation $d_n=\sum n_i d_i/\sum n_i$ based on the random size of 200 particles.

Table S2 I_D/I_G values of AC, CNTs, CNTs-O and CNTs-O-HT supports.

Carbon support	I_D/I_G
AC	2.15
CNTs	1.13
CNTs-O	1.26
CNTs-O-HT	1.41

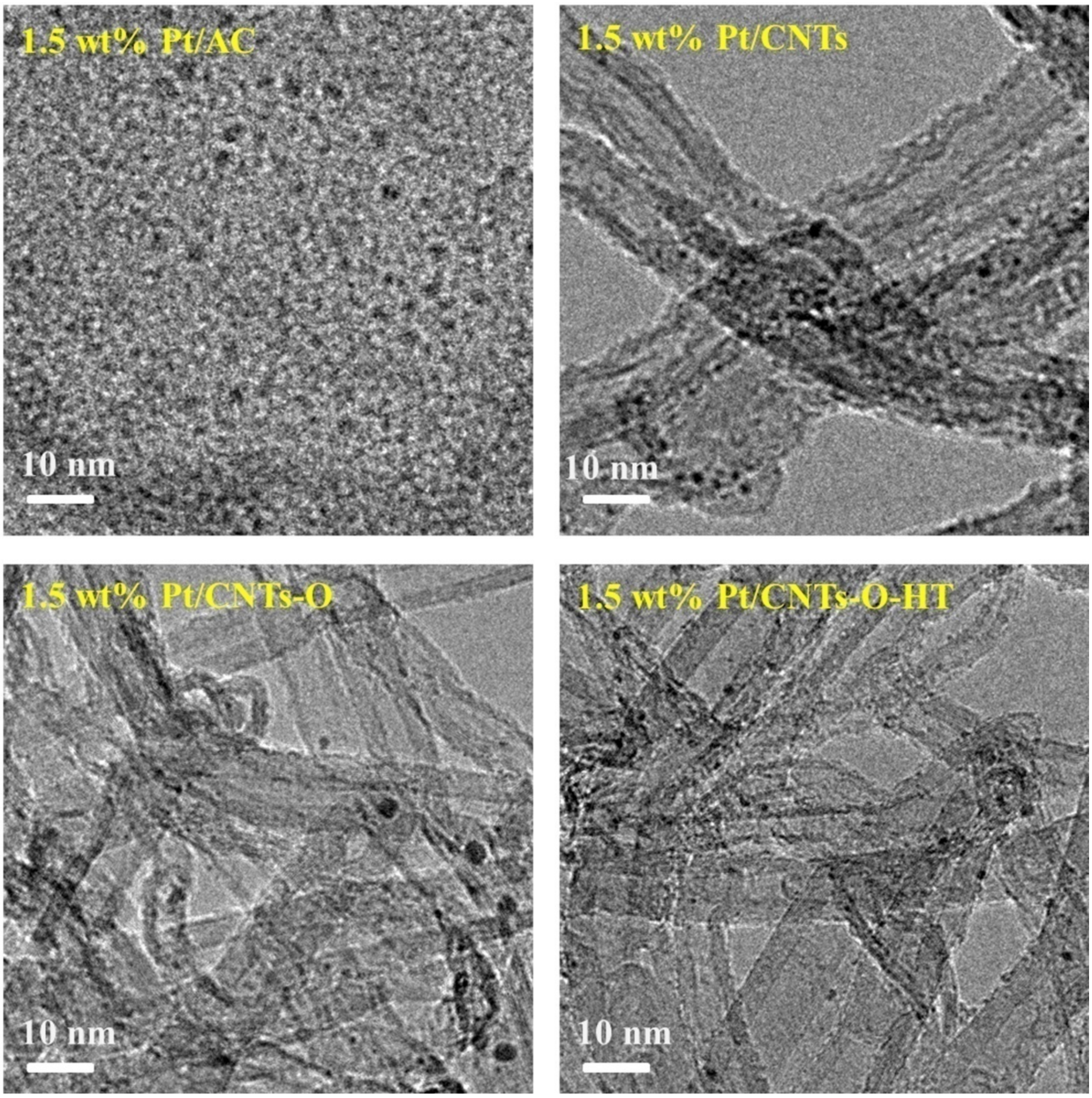

Figure S1 Representive TEM images of Pt/AC, Pt/CNTs, Pt/CNTs-O and Pt/CNTs-O-HT catalysts with Pt loading of 1.5 wt%.

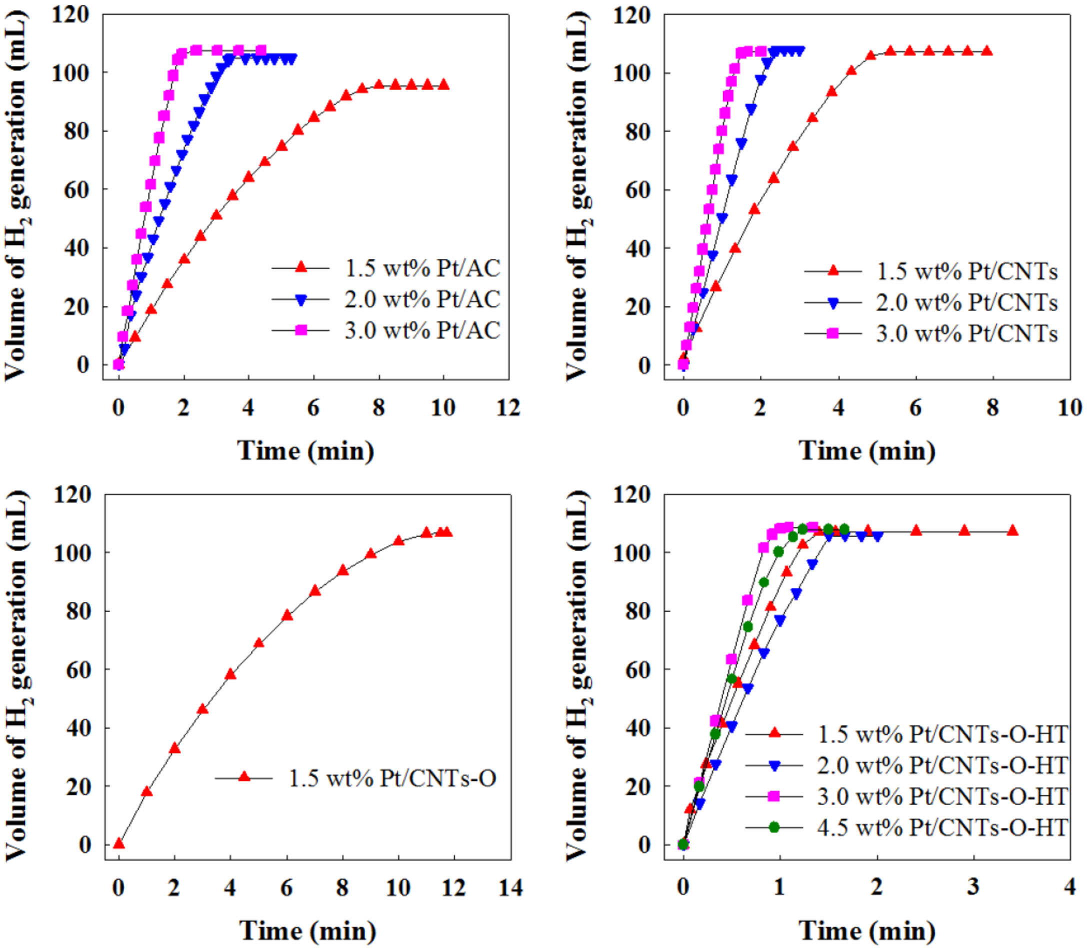

Figure S2 Volume of H_2 generation from AB hydrolysis as a function of time over Pt/AC, Pt/CNTs, Pt/CNTs-O and Pt/CNTs-O-HT catalysts. Reaction conditions: 30 ^{o}C, $n_{Pt}/n_{AB}=4.7\times10^{-3}$ and $C_{AB}=0.01$ g/mL.

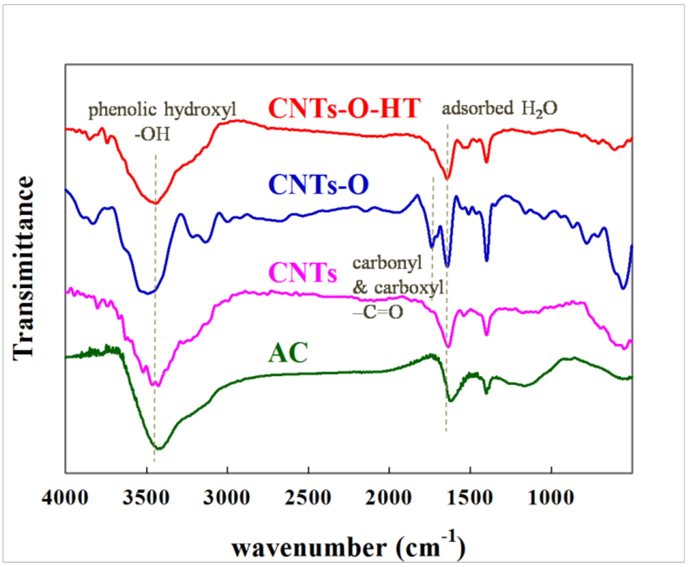

Figure S3 FT-IR spectra of AC, CNTs, CNTs-O and CNTs-O-HT supports.

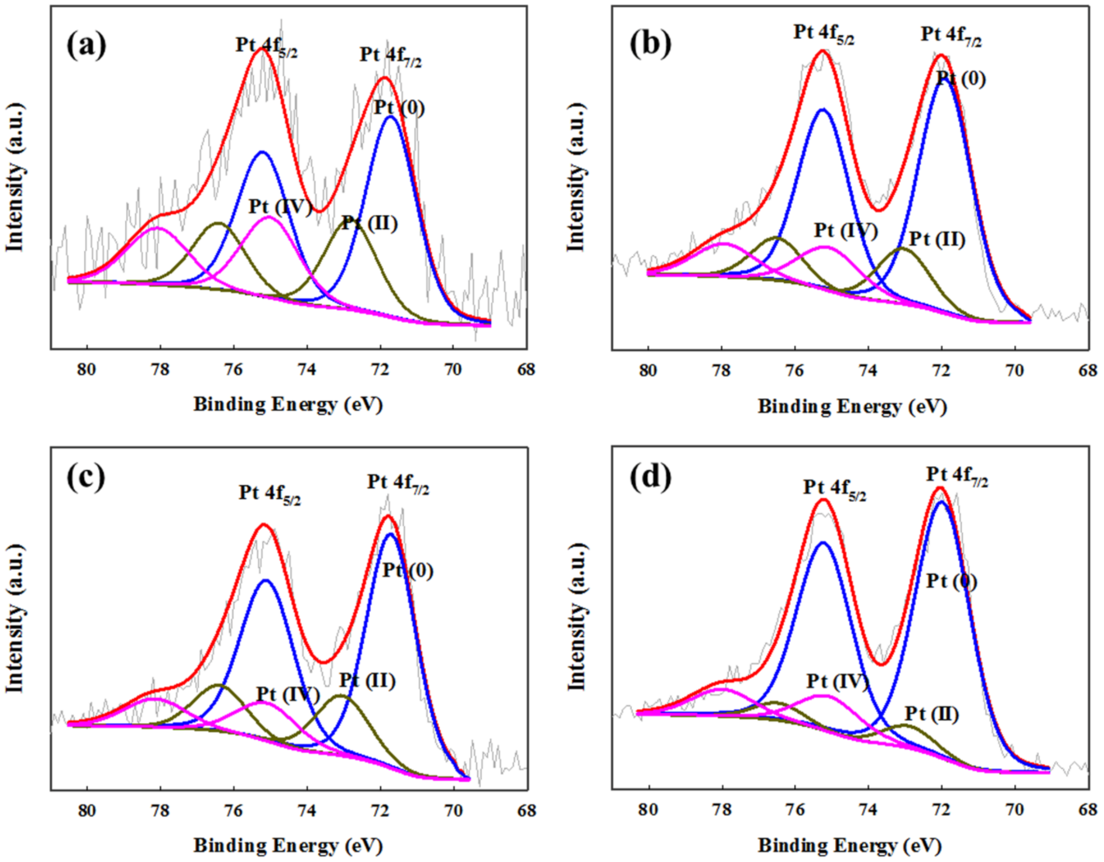

Figure S4 Typical XPS Pt 4f spectra of 1.5 wt% Pt/AC (a), 1.5 wt% Pt/CNTs (b), 1.5 wt% Pt/CNTs-O (c) and 1.5 wt% Pt/CNTs-O-HT (d) catalysts.

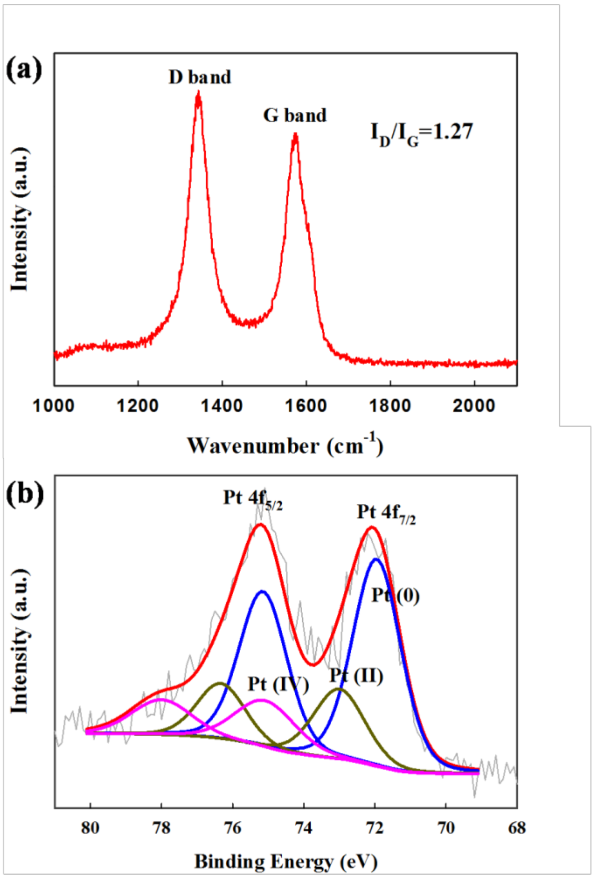

Figure S5 Raman spectrum of CNTs-HT support (a) and XPS Pt 4f spectrum of 0.5 wt% Pt/CNTs-HT catalyst (b).

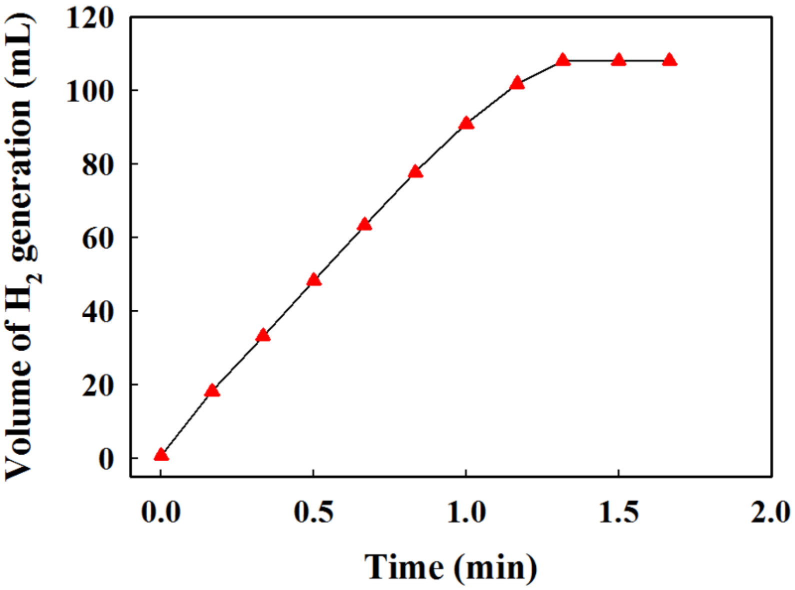

Figure S6 Volume of H_2 generation from AB hydrolysis as a function of time over 3.0 wt% Pt/CNTs-O-HT catalyst. Reaction conditions: 25 °C, $n_{Pt}/n_{AB}=4.7\times10^{-3}$ and $C_{AB}=0.01$ g/mL.