

Supporting information

Promoted aerobic oxidation of benzyl alcohol on CNT supported platinum by iron oxide

Chunmei Zhou,^a Yuanting Chen,^a Zhen Guo,^a Xin Wang,^{*a} and Yanhui Yang^{*a}

^aSchool of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

Experimental section

Materials and Equipment: Multi-walled carbon nanotubes (MWCNT) was purchased from Cnano Technology Ltd (purity: 97.1%, S_{BET} : 241 m²/g, bulk density: 0.05 g/cm³). Fe(NO₃)₃, HNO₃ (69%), HCl (36%), H₂SO₄ (98%), H₂PtCl₄, ethylene glycol (EG), benzyl alcohol (98%), benzaldehyde (98%) and benzoic acid (98%), toluene (99.9%) were provided by Sigma-Aldrich. All chemicals were used as received without further purification. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F, operated at 200 kV. The sample was suspended in ethanol and dried on holey carbon-coated Cu grids. X-ray Diffraction (XRD) patterns were recorded on a Bruker AXS D8Focus diffractometer using a Ni filtered Cu K α radiation ($\lambda = 0.154$ nm), operated at 40 kV and 40 mA. Diffraction data were collected between 20 and 80° (2 theta) with a resolution of 0.02° (2 theta). X-ray photoelectron spectroscopy (XPS) measurement was carried out on a VG Escalab 250 spectrometer equipped with an Al anode (Al K α = 1486.6 eV). The background pressure in the analysis chamber was lower than 1×10^{-7} Pa. Measurements were performed using 20 eV pass energy, 0.1 eV

step and 0.15 min dwelling time. The correction for the binding energies (BE) was carried out using the C 1s peak of adventitious C at 284.6 eV.

Synthesis: The pristine MWCNT was pretreated with concentrated HNO₃ at 120 °C for 2 h to remove the amorphous carbonaceous and metallic impurities as well as to introduce abundant surface oxygen functional groups for anchoring metal precursors. Platinum catalyst supported on MWCNT was prepared by a microwave-assisted polyol reduction method²: 0.1 g of CNT was immersed in 722 µl of H₂PtCl₄ (0.05 M) aqueous solution (20 mg/ml) and dried at 373 K in vacuum. EG (40 ml) was added to the above-mentioned Pt-CNT composite followed by sonicating for 10 min to afford a homogenous suspension. The said suspension was transferred into a three-neck flask with a condenser and placed in a microwave reactor (Sineo, MAS-II). A magnetic stirrer agitated the slurry, and an infrared sensor monitored the temperature inside the flask. The suspension was heated to 438 K in 0.5 min and kept at the same temperature for 1.5 min. After cooling to room temperature, the powder was filtrated and washed with deionized water, followed by drying at 373 K in vacuum. The as-synthesized catalyst was denoted as Pt/CNT and the expected Pt loading is 5 wt.% and confirmed by inductively coupled plasma (ICP) measurements.

Iron oxide catalyst supported on Pt/CNT was prepared by a reductive deposition precipitation (RDP) method² with a Fe loading of 3 wt.%: 0.1 g of Pt/CNT was stirred for 1 h under hydrogen (1.2 bar) in 20 ml of HCl (0.1M) followed by adding 5 ml of Fe(NO₃)₃ (0.1M) solutions. The mixture was stirred for another 30 min under hydrogen atmosphere. The slurry was filtered and the catalysts were dried overnight at 393 K in

the air. The obtained catalyst was denoted as FeO_x/Pt/CNT.

The preparation of PtFe/CNT catalyst was similar to that of Pt/CNT but in the presence of both Pt and Fe precursors. The Pt loading was kept at 5 wt.%, and the molar ratio of Pt to Fe was 1:2. To remove the iron oxides formed on the surfaces of PtFe alloy, 100 mg of PtFe/CNT sample was soaked in 20 ml of H₂SO₄ (0.5M) for 10 min, and the slurry was filtered and the catalyst was repeatedly washed by deionized water.

Electrochemical Performance Measurement: All the electrochemical performance tests were carried out at room temperature condition (25 °C) in a rotating disk electrode system using Autolab PGSTAT302 potentiostat. The working electrode was prepared by dropping 40 µl of the catalyst ink onto a glassy carbon electrode. The ink was prepared by ultrasonically mixing 2 mg of catalyst sample with 1 ml of 0.025 wt.% Nafion in deionized water solution. Pt foil and Ag/AgCl electrode (+0.197 V vs. NHE) were used as the counter and reference electrodes, respectively. All the potentials in the present study are given vs. the Ag/AgCl electrode. The cyclic voltammograms were first recorded in nitrogen purged 0.1 M of KOH at a scan rate of 50 mV/s until reproducible voltammograms were obtained. For the electrochemical active surface area (EAS) measurement, the average Coulombic charge (Q_H) of hydrogen adsorption and hydrogen desorption was used to calculate the Pt EAS of the electrodes, according to the equation of $EAS = Q_H/210 (\mu C/cm^2)/w$, in which 'w' represents the content of Pt in the catalysts³. Benzyl alcohol electro-oxidation was measured in 0.2 M of Ph-CH₂OH with 0.1 M of KOH as electrolyte at 50 mV/s. Oxygen electro-reduction was measured in 0.1 M of KOH saturated with oxygen by linear potential sweep at 10

mV/s.

Determination of dispersion (D) of Pt: The dispersion of Pt defined as the fraction of surface-active Pt atoms in all Pt atoms can be obtained:

$$D = \frac{EAS}{\frac{1}{M_{Pt}} \cdot (N_A \cdot 4\pi r_{Pt}^2)}$$

Where M_{Pt} is the atomic weight of Pt (195.09 g/mol), N_A is Avogadro constant (6.02E23) and r_{Pt} is the atomic radius (0.135 nm).

Catalytic reaction: The selective oxidation of benzyl alcohol using molecular O₂ was carried out in a bath-type reactor operated under atmospheric conditions: a three-necked glass flask (50 ml) pre-charged with 3 mmol of benzyl alcohol, 12 mg of catalysts (0.03 mmol of Pt), 15 ml of deionized water, as well as a stir bar, was heated to 75 °C by an oil bath, where a thermocouple was applied to control the temperature and a reflux condenser to condense the vapor of products. Oxygen flow was bubbled at 25 ml/min controlled by a mass flow meter into the mixture to initiate the reaction. After the reaction, the catalyst powder was filtered off, the liquid organic products were extracted with toluene (3×10 ml) and the supernatant (mixture of residual reactant, product and toluene) was analyzed using an Agilent gas chromatograph 6890 equipped with a HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silica-based supel cosil), and flame ionization detector (FID). Dodecane was the internal standard. The turnover frequency (TOF) was defined as the number of benzyl alcohol (BA) converted over one surface-active Pt atom per hour:

$$TOF(h^{-1}) = \frac{M_{BA} \cdot X}{M_{Pt} \cdot D \cdot t}$$

Where M_{BA} and M_{Pt} are the amount of BA and Pt in feed (mol), X is the conversion of

BA, D is the Pt dispersion calculated using electrochemical method and t is the reaction time (h).

Supplementary discussion:

As shown in Figure S1, Pt nanoparticles in FeO_x/Pt/CNT show identical distance between two adjacent Pt(111) lattice planes compared to Pt/CNT, which was further corroborated by XRD measurements. There is no shift of 2 theta value for Pt(111) diffraction peak for FeO_x/Pt/CNT compared to Pt/CNT, and the formation of PtFe bulk alloy in FeO_x/Pt/CNT is excluded. For PtFe/CNT, the lattice spacings of Pt(111) planes noticeably shrank, and the corresponding XRD peak also slightly shifts to a high angle, implying that Fe has alloyed with Pt during the catalyst preparation⁴.

The cyclic voltammetry (CV) curves of fresh catalysts (Figure S2) were recorded in 0.1 M of KOH to characterize the structure of different samples. Compared to CNT support, Pt/CNT presents two pairs of peaks on the potential range from -0.9V to -0.3V, attributing to the hydrogen desorption/adsorption for Pt(111) and Pt(110), respectively. For FeO_x/Pt/CNT, the Pt(110) peaks nearly disappear. The suppressed hydrogen desorption/adsorption peak on Pt (110) implies that FeO_x preferentially deposits on Pt(110) surfaces, which favors the selective hydrogenation of cinnamaldehyde towards unsaturated alcohol (Table S1). Pronounced redox peaks of iron oxides presented at ca. -0.35V and 0.45V suggest the presence of Fe²⁺ and Fe³⁺ oxides on the surface of fresh FeO_x/Pt/CNT⁵, respectively. Nonetheless, during the benzyl alcohol oxidation (Figure S3), the reduction peak of Fe₂O₃ (0.45V) disappears, implying that the oxidation state of Fe in the FeO_x/Pt/CNT is mainly

Fe²⁺ during the reaction.

The oxidation states of Fe in fresh PtFe/CNT and FeO_x/Pt/CNT catalysst were also analyzed by XPS (Figure S4). The existence of both Fe²⁺ and Fe³⁺ is verified. Nevertheless, FeO_x/Pt/CNT possesses larger abundance of Fe³⁺ than PtFe/CNT, indicating the higher oxidation state of Fe in this particular catalyst.

The CV measurement for electro-oxidation of benzyl alcohol on Pt-based catalysts was conducted the first time, and two oxidation peaks (ca. -0.1V and 0.25V, respectively) was found. Control experiments were then conducted to identify to the origin of the peaks. Figure S5 shows the CV curves of the electro-oxidation of benzyl alcohol, benzaldehyde and benzoic acid on Pt/CNT. No relevant oxidation peaks were observed in the potential range of interest on the CV curve of benzoic acid. For benzaldehyde, the CV curve presents only a peak near 0.2V, suggesting that benzaldehyde would be oxidized to benzoic acid around 0.2V. Thus, for the CV curve of benzyl alcohol, the first peak (-0.10V) can be ascribed to the oxidation of benzyl alcohol to benzaldehyde, and the second peak (0.25V) is due to the oxidation of benzaldehyde to benzoic acid.

The activity for the electro-oxidation of benzyl alcohol was determined form the CV curve (Figure S6) by the amount of exchanged charge (peak area) from Ph-CH₂OH to Ph-CHO, denoted as Q_{Ph-CHO}. The selectivity for the electro-oxidation of benzyl alcohol was determined by: (Q_{Ph-CHO} - Q_{Ph-COOH})/ Q_{Ph-CHO}.

The formation of PtFe alloy was also evidenced using cinnamaldehyde hydrogenation as shown in Table S1. PtFe/CNT and Pt/CNT show similar TOF, suggesting that the surfaces of PtFe/CNT are dominated by Pt atoms. Nevertheless, PtFe/CNT possesses a

better selectivity towards C=O hydrogenation, which can be explained by the enriched electron density over Pt due to the electronic interaction between metallic Fe phase and Pt. It can also be observed from Table S1 that the introduction of FeO_x onto Pt/CNT dramatically improves both selectivity and TOF.

The open circuit potential (OCP) shown in Table S2 is employed to characterize the adsorption of substrates⁶⁻⁸. CNT presents weak adsorption of benzyl alcohol and benzaldehyde. The OCP of benzyl alcohol for FeO_x/Pt/CNT is lower than the other two catalysts, implying the stronger adsorption of benzyl alcohol on the interface of FeO_x/Pt. Pt/CNT and PtFe/CNT show similar adsorption strength of benzyl alcohol, while PtFe/CNT shows the weakest adsorption of benzaldehyde among all the Pt-based catalysts, suggesting that low adsorption strength of reaction intermediates contributes to the high selectivity and enhanced stability of PtFe/CNT sample.

Direct TEM observation was performed to examine the mean particle size and particle size distribution of the catalysts and study the potential particle size effect on the catalytic activity. It is shown in Figure S7 that the average sizes of Pt for Pt/CNT (3.7 nm) and FeO_x/Pt/CNT (3.5 nm) are similar. The average Pt size for PtFe/CNT is slightly larger (4.4 nm), which is caused by alloying Pt with Fe, which is also confirmed by XRD results. Thus Pt particle size effect for these samples can be excluded.

References

1. Z. Guo, Y. T. Chen, L. S. Li, X. M. Wang, G. L. Haller, Y. H. Yang, *J. Catal.*, 2010, **276**, 314-326.

2. J. H. Bitter, A. J. Plomp, D. M. P. van Asten, A. M. J. van der Eerden, P. Maki-Arvela, D. Y. Murzin, K. P. de Jong, *J. Catal.*, 2009, **263**, 146-154.
3. A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, *J. Power Sources*, 2002, **105**, 13-19.
4. W. Z. Li, W. J. Zhou, H. Q. Li, Z. H. Zhou, B. Zhou, G. Q. Sun, Q. Xin, *Electrochim. Acta.*, 2004, **49**, 1045-1055.
5. Y. L. Wang, S. H. Ye, J. K. Bo, Y. Y. Wang, F. Wu, *J. Electrochem. Soc.*, 2009, **156**, A572-A576.
6. J. W. Long, R. M. Stroud, K. E. Swider-Lyons, D. R. Rolison, *J. Phys. Chem. B*, 2000, **104**, 9772-9776.
7. H. Varela, B. C. Batista, E. Sitta, M. Eiswirth, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6686-6692.
8. J. F. E. Gootzen, A. H. Wonders, A. P. Cox, W. Visscher, J. A. R. van Veen, *J. Mol. Catal. A-Chem.*, 1997, **127**, 113-131.

Table S1 Hydrogenation results of CALD over different catalysts by using 2-propanol as solvent. (Please refer to our previous paper¹ for experiment conditions and calculation method)

Catalysts	Conv.%	Select. of CALC %	Select. of HALD%	Select. of HALC %	Others ^a %	TOF ^b h ⁻¹
Pt /CNT	44.6	25.6	41.5	20.5	12.3	2000

FeOx/Pt/CNT	77.4	70.2	6.6	19.1	4.1	4900
PtFe/CNT	24.5	33.5	34.9	13.1	18.4	1753

^a Based on the characterization of GC–MS, the other by-products include 1-(3-propoxyprop-1-enyl)benzene, cinnamyl formate, cinnamic acid, benzyl cinnamate, 4,4-diphenylcyclohexa-1,5-dienyl acetate and some condensation products which cannot be identified by our GC–MS due to their large molecular weights.

^b TOF is defined as the number of converted CALD molecules in 1 h over one active site; the number of active sites (Pt atoms exposed on the surface of particles) is determined by EAS value. Reaction time is 1 h.

Table S2 Open circuit potentials for different samples in N₂ purged 0.2 M substrate +

0.1 M KOH solution

Catalysts	OCP ^a / V		
	- ^b	Benzyl alcohol	Benzaldehyde
CNT	-0.09	-0.12	-0.11
Pt /CNT	0.02	-0.53	-0.53
FeOx/Pt/CNT	0.05	-0.65	-0.52
PtFe/CNT	0.05	-0.56	-0.49

^a with a deviation of ± 0.02 V.

^b 0.1 M KOH solution without substrate.

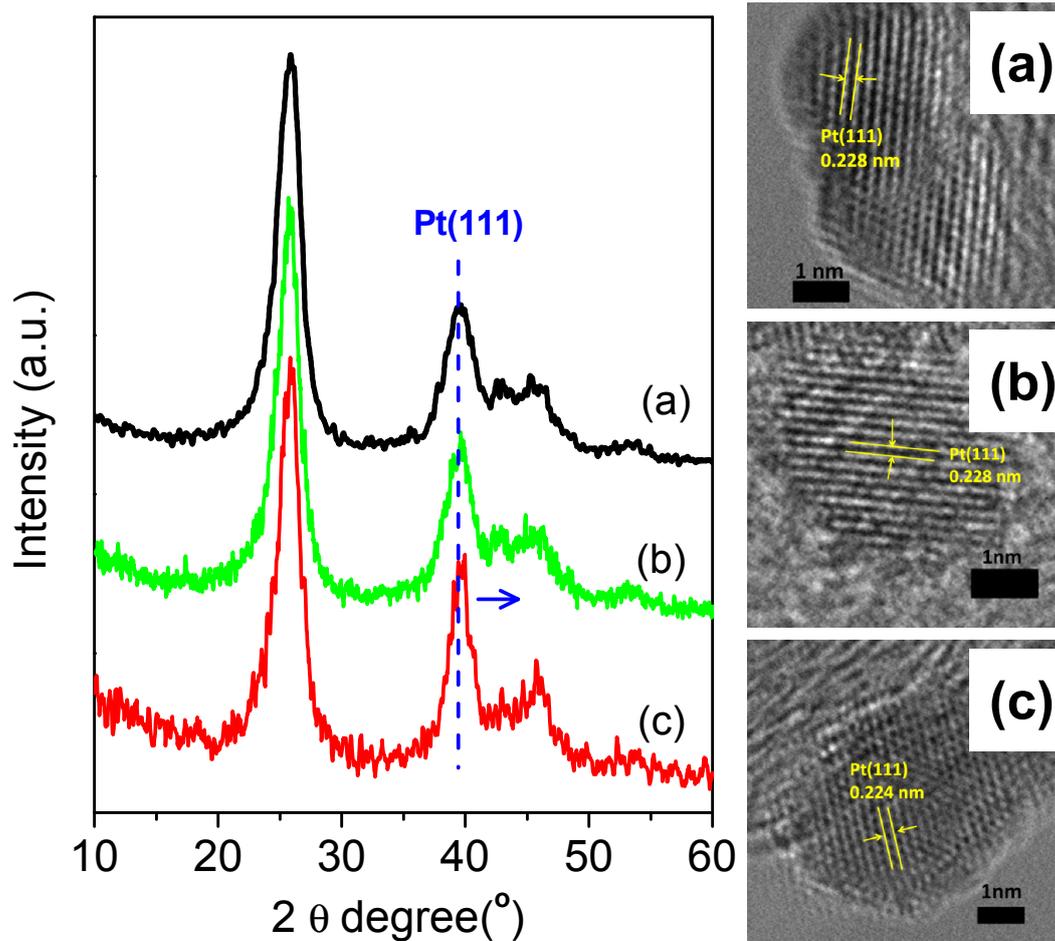


Fig. S1 XRD patterns (left) and HRTEM images (right) of Pt/CNT (a), FeO_x/Pt/CNT (b) and PtFe/CNT (c)

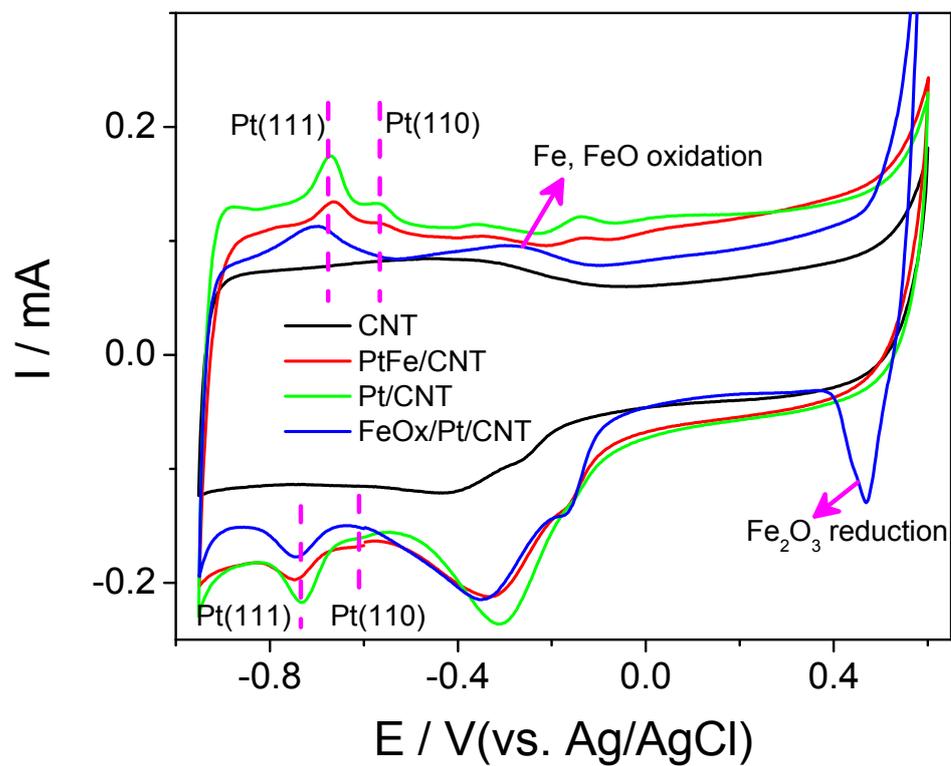


Fig. S2 Cyclic voltammograms (50mV/s) for different samples in N_2 purged 0.1 M KOH, under room temperature

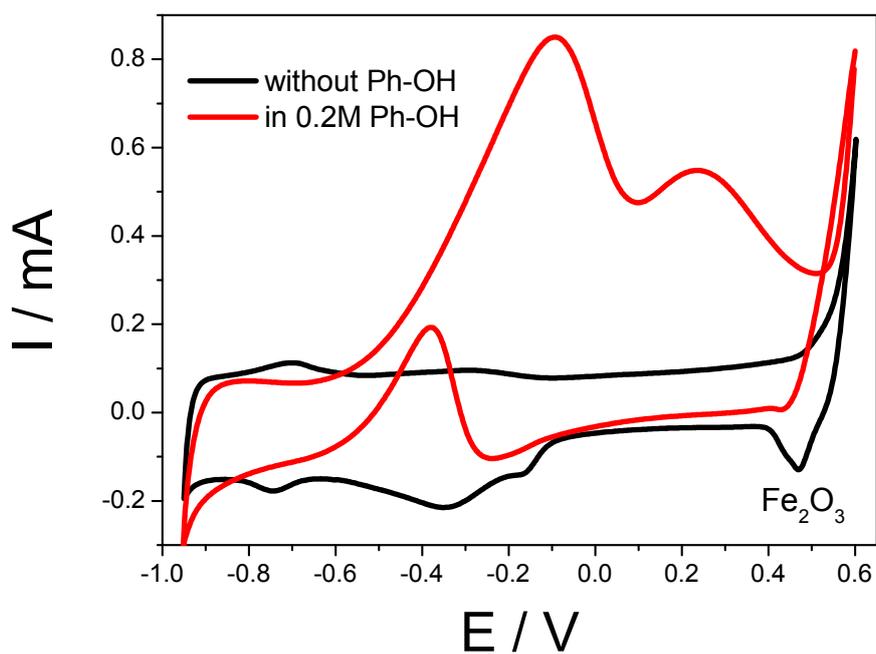


Fig. S3 Cyclic voltammograms (50mV/s) for FeO_x/Pt/CNT in 0.1M KOH and in 0.1M KOH + 0.2 M benzyl alcohol

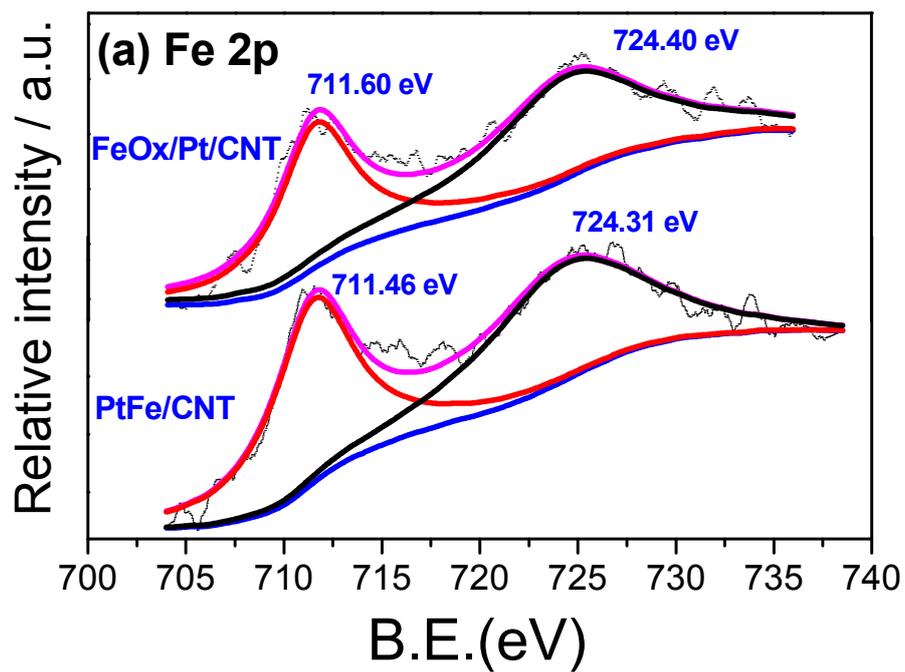


Fig. S4 Fe 2p XPS spectra of FeO_x/Pt/CNT and PtFe/CNT

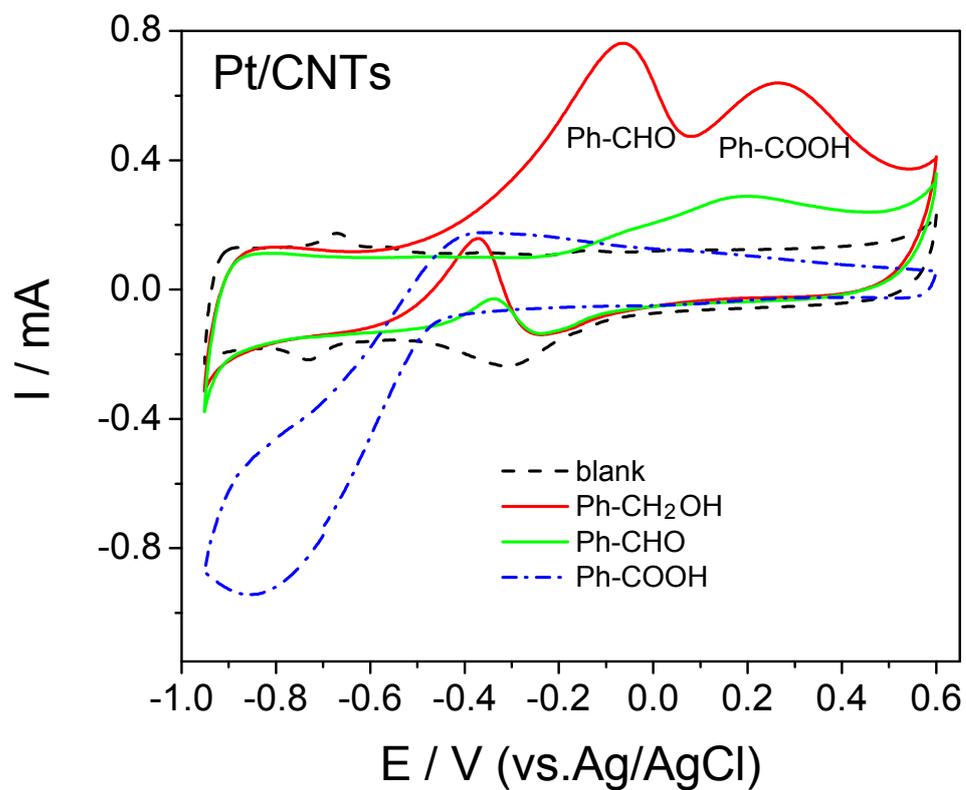


Fig. S5 Cyclic voltammograms (50mV/s) for Pt/CNT in 0.1M KOH and 0.2 M different reactants, under room temperature, with N₂ saturated

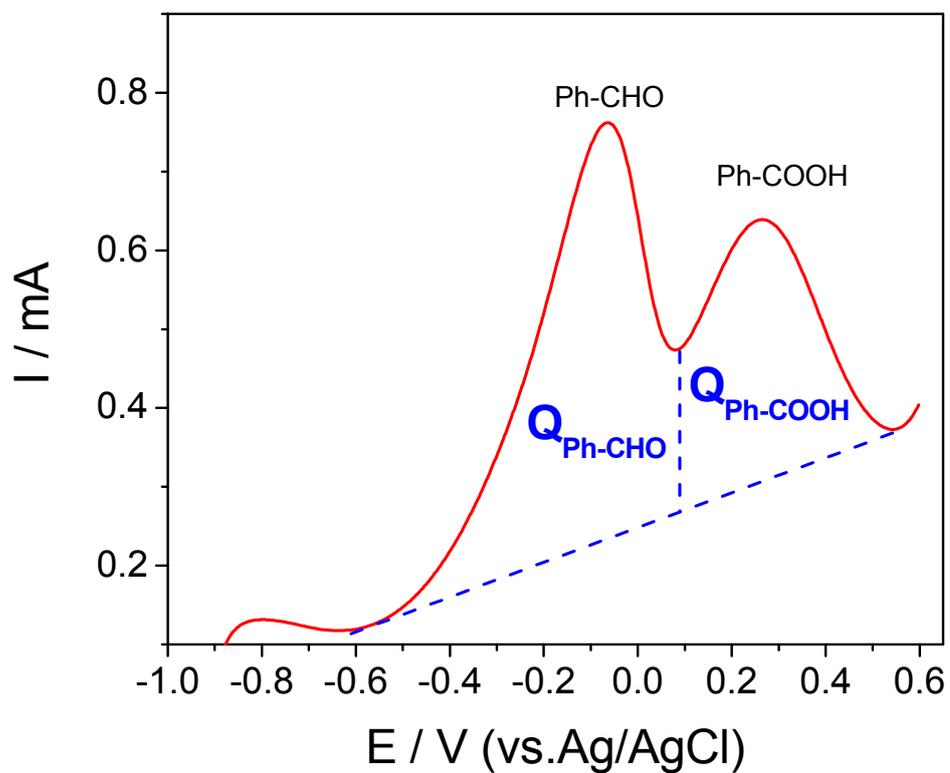


Fig. S6 Potentiodynamic current of benzyl alcohol electro-oxidation on Pt/CNT in 0.1M KOH and 0.2 M benzyl alcohol, under room temperature, with N₂ saturated, scan rate = 50mV/s

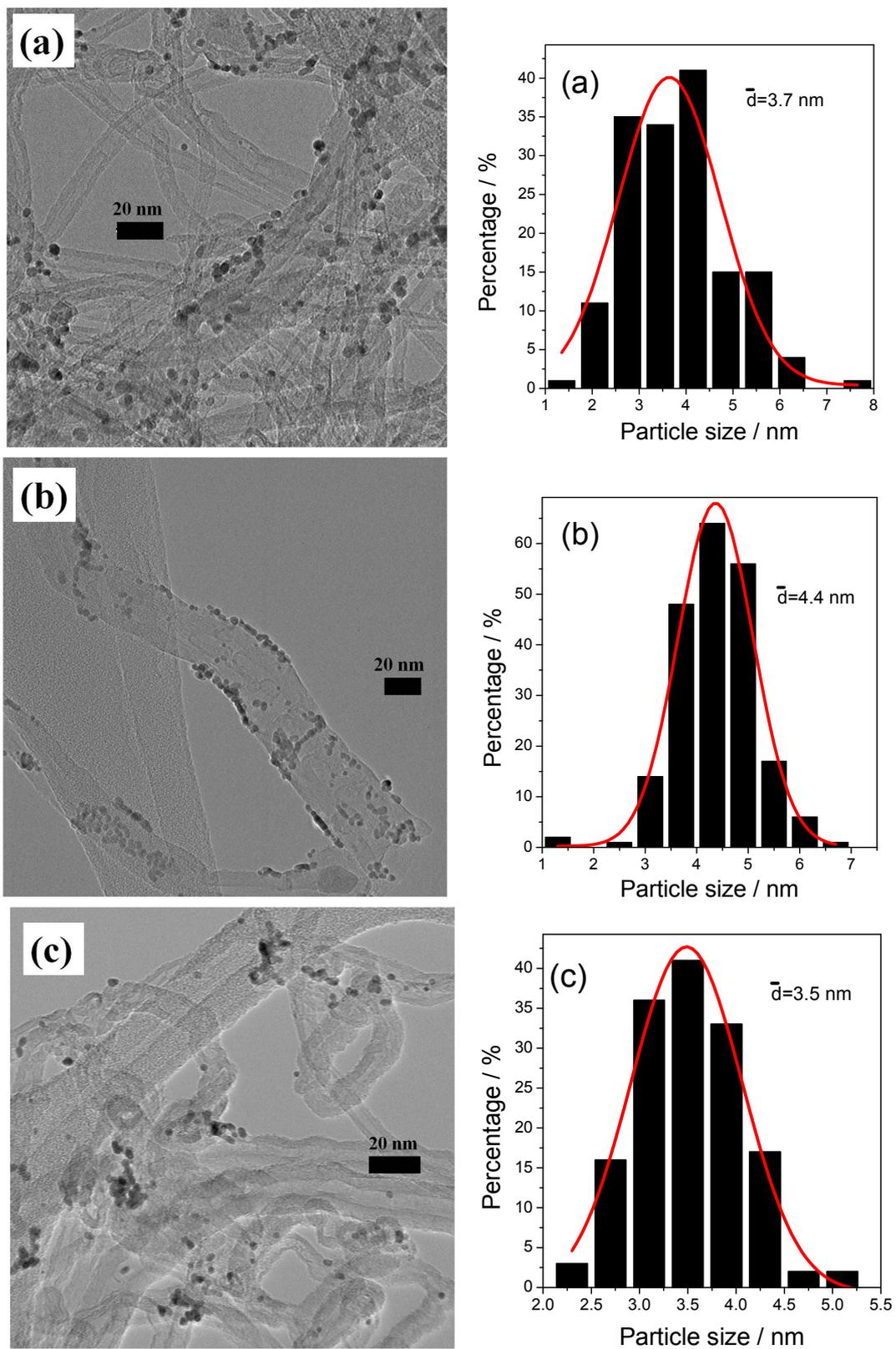


Fig. S7 TEM micrographs and size distributions: (a) Fe/CNT; (b) PtFe/CNT; (c)

FeO_x/Pt/CNT