

Supplementary Information

for

Enhancing catalytic performance of Pt-based electrodes with noncovalent interaction-induced functionalized carbon nanotubes-grafted matrix

By

Le Quynh Hoa,^{*a} Mun'delanji C. Vestergaard,^b Hiroyuki Yoshikawa,^a Masato Saito^a and Eiichi Tamiya^{*a}

^a Department of Applied Physics, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^b School of Materials Science & Centre of Graduate Education Initiative, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi City, Ishikawa 923-1292, Japan

Table of Contents

1. SEM images of COOH-MWCNTs grafted Pt/MWCNTs on carbon sheet	2
2. Quantification of electrochemical active surface area of Pt on different matrix	2
3. Zeta potential and size distribution profiles	3
4. ATR-FTIR of functionalized multi-walled carbon nanotubes	4
5. Electrochemical impedance spectroscopy (EIS) studies	5
6. Effect of scan rate on ethanol oxidation current density derived from grafted catalyst	5

1. SEM images of COOH-MWCNTs grafted Pt/MWCNTs on carbon sheet

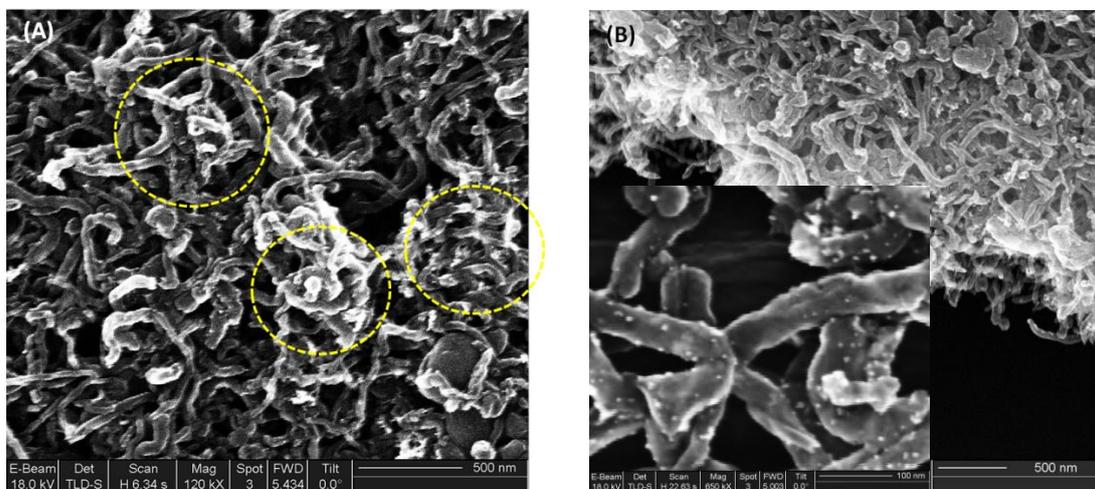


Fig. S1 SEM image of COOH-MWCNTs grafted Pt/MWCNTs on carbon sheet. Figure S1A shows 3 clusters of COOH-MWCNTs grafted Pt/MWCNTs and Figure 1SB shows the thickness of the whole catalyst layer on carbon sheet. The inset of Figure 1SB shows the Pt nanoparticles decorated on MWCNTs on carbon paper.

2. Quantification of electrochemical active surface area of Pt on different matrix

The electrochemical properties of Pt nanoparticles decorated on MWNTs then deposited on f-MWNTs modified glassy carbon electrodes have been investigated by CV as shown in Fig. 3A. The voltammetric features of all Pt/MWNTs with and without f-MWNTs supporting matrix reveal the typical characteristic of Pt metal with the adsorption and desorption (Q_{H-ads} and Q_{H-des}) of hydrogen between -0.2 and 0.1 V and the oxide formation and reduction in the 0.6 V to 1 V range and 0.3 to 0.5 V (vs. Ag/AgCl), respectively. Using the charge passed for hydrogen adsorption and desorption, the Pt areas were calculated electrochemically according to the following formula:

$$A = \frac{\sum Q_H}{Q_{ref}(Pt \text{ loading})}$$

A: Active surface area ($\text{cm}^2 \text{cm}^{-2}$)

$$\sum Q_H = Q_{H-ads} + Q_{H-des}$$

$$Q_{ref} = 0.21 \text{ mC cm}^{-2}$$

Pt loading for all electrodes: 0.05 mg cm^{-2}

As calculated from the data in Figure 2 (manuscript), the Q_{H-des} is $1.03\text{E-}04$ and Q_{H-ads} is $8.47\text{E-}05$. Thus, the final active surface area is $253.0786 \text{ (cm}^2 \text{cm}^{-2}\text{)}$. The calculation for

COOH-MWCNTs-g-Pt/MWCNTs and NH₂-R-MWCNTs-g-Pt/MWCNTs could not be done due to the change of redox pattern that diminish hydrogen adsorption and desorption regions.

3. Zeta potential and size distribution profiles

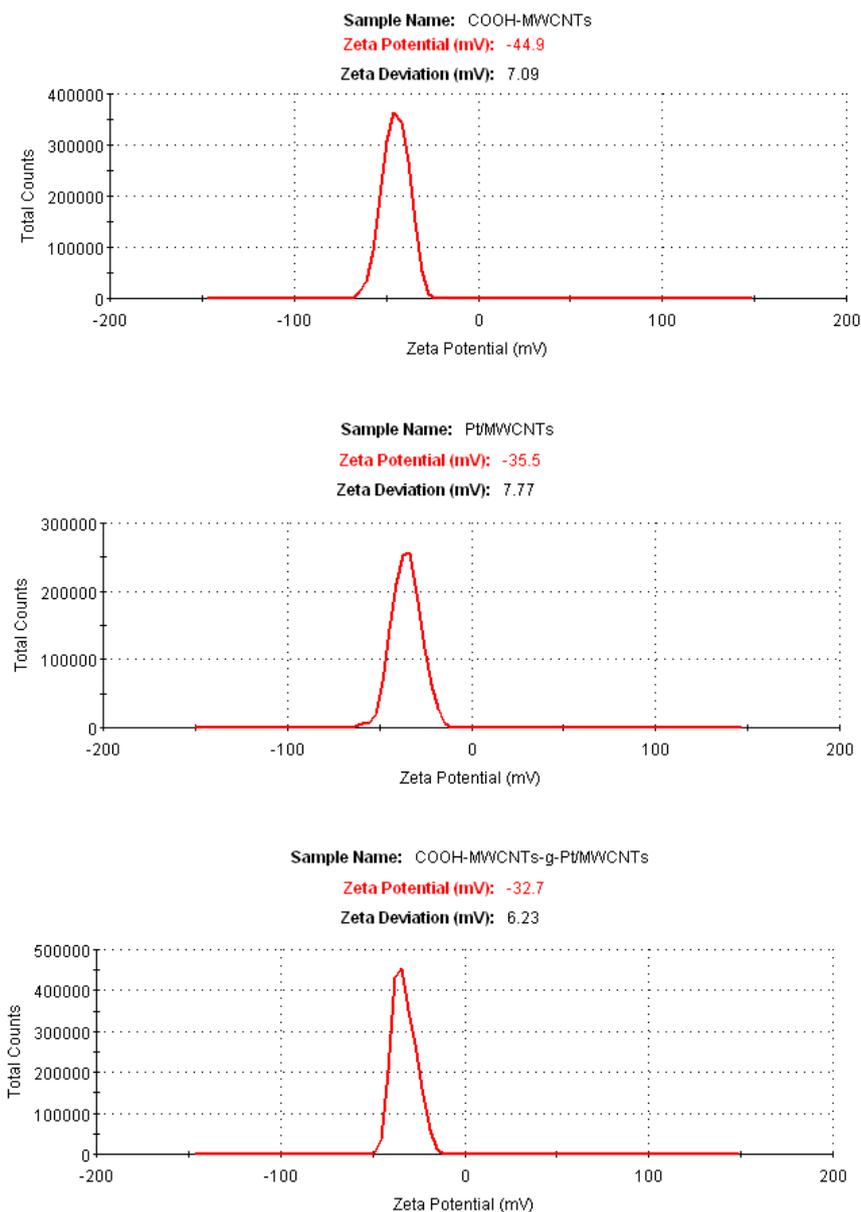


Fig. S2 Zeta potential distribution of COOH-MWCNTs, Pt/MWCNTs and COOH-MWCNTs-g-Pt/MWCNTs in water. The concentration of the catalyst was 0.1 mg/mL, and pH was ~7.

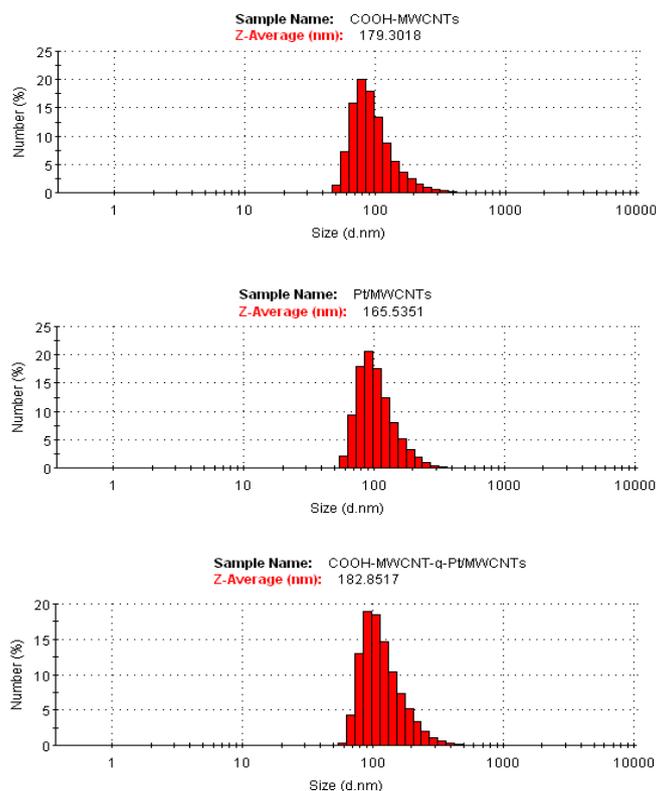


Fig. S3 Size distribution of COOH-MWCNTs, Pt/MWCNTs and COOH-MWCNTs-g-Pt/MWCNTs in water. Concentration of the catalyst was 0.1 mg/mL, and pH was ~ 7

4. ATR-FTIR of functionalized multi-walled carbon nanotubes

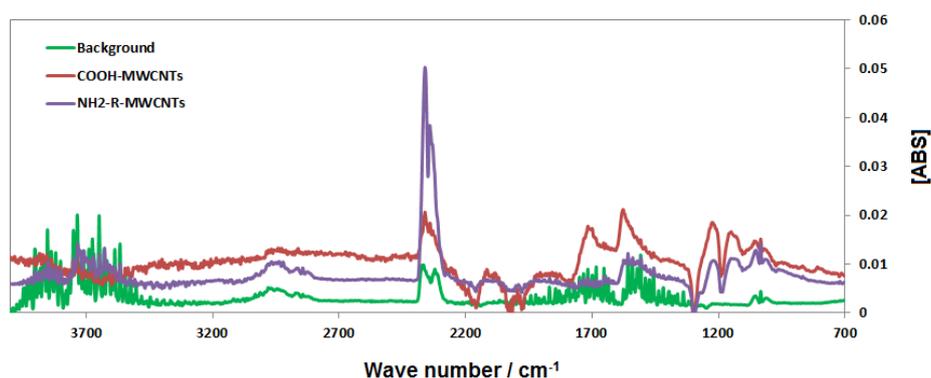


Fig. S4 FTIR-ATR spectra of COOH-MWCNTs compared with NH₂-C₂H₄-MWCNTs as a thin layer on diamond detecting surface. The background sample is measured under cleaned diamond surface which features the peaks of water and CO₂.

5. Electrochemical impedance spectroscopy (EIS) studies

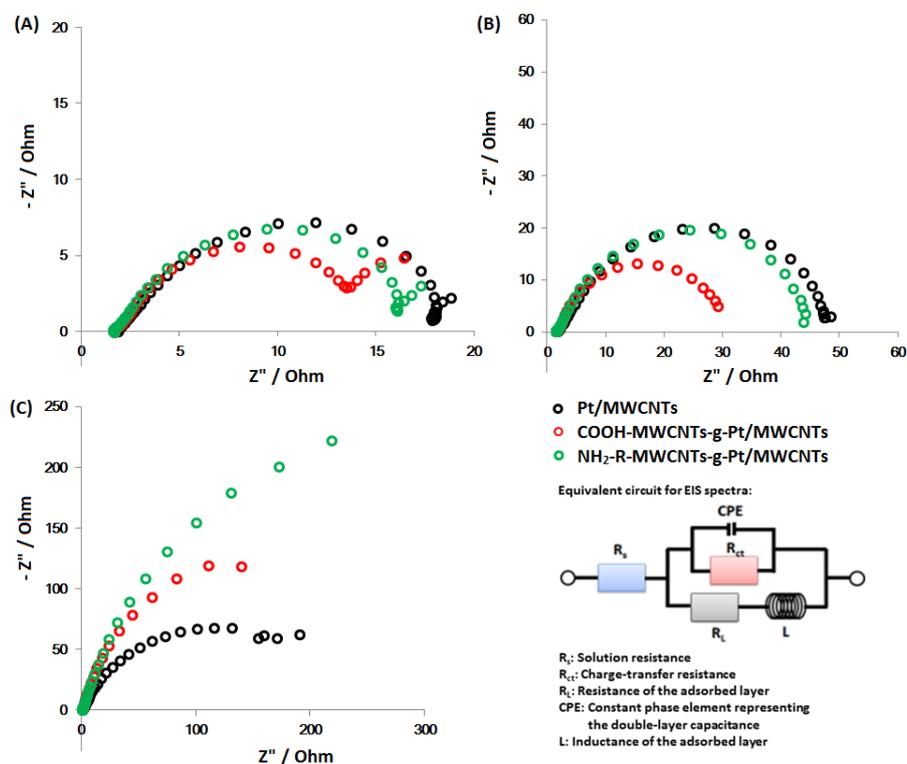


Fig. S5 EIS of f-MWCNTs supported Pt/MWCNTs in C₂H₅OH 1 M and H₂SO₄ 0.5 M at 0 mV (4A); 300 mV (4B) and 600 mV (4C) and the equivalent circuit.

6. Effect of scan rate on ethanol oxidation current density derived from grafted catalyst

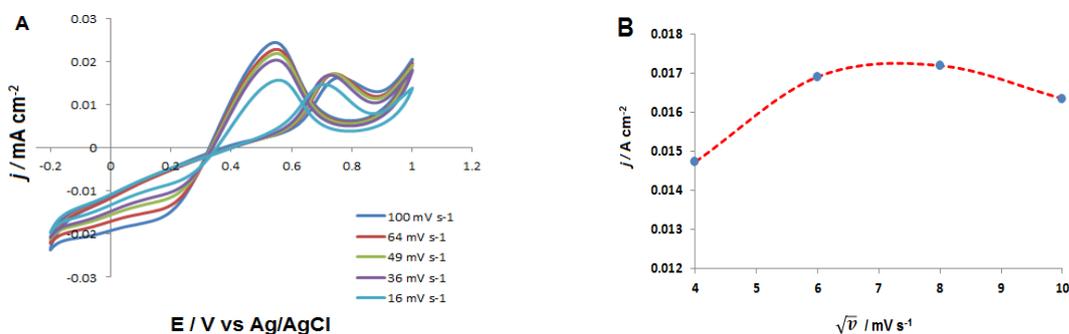


Fig. S6 Effect of scan rate dependence of COOH-MWCNTs-g-Pt/MWCNTs on ethanol oxidation current density. (A) The CVs of COOH-MWCNTs-g-Pt/MWCNTs on carbon

substrates at different scan rates and (B) the dependence of oxidation current density on scan rate. The electrolyte is C₂H₅OH 1 M, H₂SO₄ 0.5 M.

$$i_p = (\text{Constant}) n(\alpha n_a)^{1/2} A C D^{1/2} \nu^{1/2}$$

Where n is the number of electron; n_a is the number of electron involved in the charge-transfer step; A is the electrode area (cm²); C is the concentration (in mol cm⁻³); D is the diffusion coefficient (in cm² s⁻¹), ν is the scan rate (V s⁻¹); i_p is the peak current and α is the transfer coefficient.

By studying the effect of scan rate on the ethanol oxidation current density, we further investigated the reason behind the significant variation of peak current at a lower scan rate (Fig. 8A). For linear diffusion, the peak current (i_p) varies with $\nu^{1/2}$, however in the case of grafted structure when the scan rate (ν) is increased, the oxidation current density shows a non-linear relationship suggesting that there is mass-transfer limitation for this structural catalyst. We propose that the grafted structure forms cluster(s) around Pt active sites, and that these create a retard of reactant inside these clusters. Although the clustered structure allows the reactant species to gain a lower activation energy and promotes further oxidized, it creates somewhat difficulty for a fresh ethanol molecular to penetrate and start a new reaction on the inner Pt active site.