



# Functionalizing carbon nanotubes for effective electrocatalysts supports by an intermittent microwave heating method

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## ABSTRACT

In this work an efficient functionalizing method of carbon nanotubes (CNTs) by intermittent microwave heating (IMH) KOH media is reported. The performance of such modified CNTs as Pt electrocatalysts supports is demonstrated. FTIR spectrum and Raman spectrum are used to investigate the surface state of the CNTs. TEM technology is employed to study the dispersion of Pt particles for the prepared electrocatalysts. Meanwhile, cyclic voltammetry and chronopotentiometry measurements are adopted to investigate the corresponding activity and stability of the electrocatalysts. The results indicate that the CNTs functionalized by the IMH method in the form of 15s-ON/10s-OFF for pulse 20 repetitions used as electrocatalysts supports shows significantly higher activity and stability towards methanol electrooxidation in comparison with the CNTs decorated in other forms in the present study. The present method is simple and economic and displays a probability of mass production for supporting materials and electrocatalysts as well.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are a better choice for small-scale stationary and portable applications [1,2]. The predominant obstacle for their commercialization is the low durability and high cost of electrocatalysts [3]. Consequently, it is necessary to develop electrocatalysts with high performance and good durability. Whatever the case may be, Pt or Pt based electrocatalysts are still widely used with desirable performance in DMFCs due to its high activity and stability. However, Pt is rare in the earth, thereby great efforts are focused on reducing the use of Pt or improving its performance.

Carbon nanotubes (CNTs) have attracted growing interest as electrocatalysts supports for fuel cells due to their unique physico-chemical properties including their relatively high electrical conductivity, structural stability and corrosion resistance both in acid and basic solutions [4–6]. However, Pt particles can hardly be uniformly deposited on their inert graphitized surface. Considerable efforts have been made to modify the CNTs to enhance the

interaction between CNTs and metallic particles [4,5,7]. Among these methods, the surface oxidation is the most adopted one. Because in this case the amorphous carbon can be removed from CNTs and the end of CNTs can be opened, which make them facilitate for the mass transport [8,9]. Liu et al. [10] have used concentrated H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture to cut the highly tangled long ropes of CNTs into short and produced many carboxylic groups at the open end. Zhang et al. [7] have investigated the effect of chemical oxidation on the structure of CNTs by using different oxidants. KOH activation is also an effective route to improve the specific surface area and the pore size distribution of CNTs [11–15]. He et al. [11] have studied the performance of KOH activated CNTs supported Pt electrocatalysts. The corresponding results showed the activity towards oxygen reduction reaction is better than the as-received ones as electrocatalysts supports, but the process is time-consuming and with low efficiency.

Microwave irradiation has been widely used for the electrocatalysts synthesis due to its unique advantages of high heating efficiency [16,17]. In the previous studies [18,19], CNTs functionalized by intermittent microwave heating (IMH) H<sub>2</sub>O<sub>2</sub> solutions used as electrocatalysts supports were investigated, which showed better performance for methanol electrooxidation and oxygen reduction reaction than the as-received CNTs used as electrocatalysts supports. Here, the CNTs functionalized by IMH KOH media as electrocatalysts support is investigated. And the corresponding physico-chemical properties for the pretreated CNTs and their

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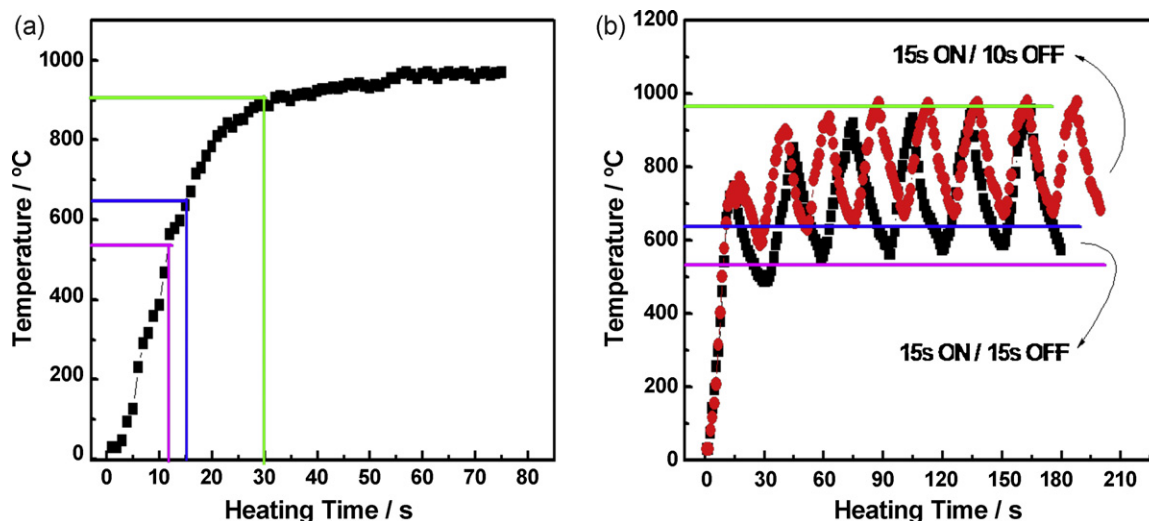


Fig. 1. The relationship between the temperature and the heating time during the CMH (a) and IMH (b) processes.

supported Pt electrocatalysts for methanol electrooxidation are studied.

## 2. Experimental

### 2.1. Carbon nanotubes pretreatment

CNTs with diameters of 10–20 nm and purities of >95% (Shenzhen Nanotech. Co., Ltd., China) were used as-received. Such CNTs were physically mixed with concentrated KOH solutions with the KOH:CNTs mass ratio of 4:1. After drying at 110 °C, the mixture was heated in air atmosphere in a homemade program-controlled microwave oven (2000 W, 2.45 GHz) by IMH method in the form of 15s-ON/10s-OFF and 15s-ON/15s-OFF for pulse 20 repetitions. The other sample was treated with continuous microwave heating (CMH) for 5 min. Afterwards, the samples were washed with 5.0 mol L<sup>-1</sup> HCl aqueous solutions for 30 min and filtered until no Cl<sup>-</sup> could be detected by 1.0 mol L<sup>-1</sup> AgNO<sub>3</sub> solutions. After drying at 80 °C under vacuum for 24 h, the resulting black solids are denoted as CNTs-IMH1, CNTs-IMH2 and CNTs-CMH. And the as-received CNTs are used as reference and denoted as CNTs-pristine.

### 2.2. Catalyst preparation

The 20 wt.% Pt/CNTs electrocatalysts were easily and rapidly prepared by formic acid reduction method [20] as follows. 0.7 ml 18.0 mg ml<sup>-1</sup> chloroplatinic acid as the starting precursor was well mixed with 40.0 ml deionized water in an ultrasonic bath, and then 50.0 mg CNTs were added into the mixture. The well-dispersed slurry was obtained with stirring and ultrasonication for 15 min, and then 2.1 ml concentrated formic acid was added into the mixture. Subsequently, after impregnation for several hours, the resulting black solid samples were filtered, washed and dried at 80 °C for 12 h in a vacuum oven. The corresponding electrocatalysts are denoted as Pt/CNTs-IMH1, Pt/CNTs-IMH2, Pt/CNTs-CMH and Pt/CNTs-pristine.

### 2.3. Catalyst characterization

Fourier transform infrared spectroscopy (FTIR) measurements were carried out on all the CNTs samples using a Nicolet 5700 spectrometer (Thermo, USA). Raman spectroscopy measurements were performed on a Renishaw Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser with the wavelength of 514.5 nm. X-ray

diffraction (XRD) measurements were carried out on a D/Max-III (Rigaku Co., Japan) using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm), and operating at 40 kV and 30 mA. The  $2\theta$  angular regions between 20° and 90° were explored at a scan rate of 10° min<sup>-1</sup> and the 64–72° angle range was finely scanned at 1° min<sup>-1</sup> in order to obtain the crystal size of Pt according to the Scherrer equation [21,22]. TEM investigations were carried out in a JEOL JEM-2010 (HR) at 200 kV to get information of the particle size distribution of Pt particles in the electrocatalysts. The histograms of the prepared electrocatalysts were made by randomly measuring more than 300 particles. The specific surface area of CNTs before and after modification was quantified by the Brunauer–Emmett–Teller (BET) technique using a ChemBET-3000 (Quantachrome, USA) analyzer.

Electrochemical measurements were conducted on PARSTAT 2263 (Princeton Applied Research, USA) and Biologic VMP3 (Science Instrument, France) instruments in a thermostat-controlled standard three-electrode cell at room temperature using a saturated calomel electrode (SCE) as the reference electrode and a platinum foil (1 cm  $\times$  1 cm) as the counter electrode. A glass carbon (GC) disk electrode with a diameter of 5.0 mm was used as the substrate for the electrocatalysts thin film in the electrochemical measurements. The thin film working electrode was prepared as follows: a mixture containing 5.0 mg electrocatalysts, 1.8 ml ethanol and 0.2 ml Nafion solution (5.0 wt.%) were dispersed in an ultrasonic bath for 10 min to obtain a well-dispersed ink. The ink was then quantitatively transferred onto the surface of the GC electrode by a micropipette, and dried under an infrared lamp to obtain the thin electrocatalysts film. The estimated loading was 0.13 mg cm<sup>-2</sup> for each electrocatalysts in this study. Cyclic voltammeters (CVs) were carried out in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solutions with and without 1.0 mol L<sup>-1</sup> CH<sub>3</sub>OH deaerated with high-pure nitrogen gas. It should be noted that all the potentials are referred to the saturated calomel electrode (SCE).

## 3. Results and discussion

The temperature curves during the CMH and IMH process are shown in Fig. 1. As displayed in Fig. 1(a), the temperature keeps increasing with time in the CMH mode. The final temperature depends on the nature of CNTs and the output power of microwave oven, which is approximately 1000 °C. The principle of IMH method can be explained by the results as showed in Fig. 1(b). The temperature can be readily controlled as required by simply altering the heating and pause time during the IMH process. The longer

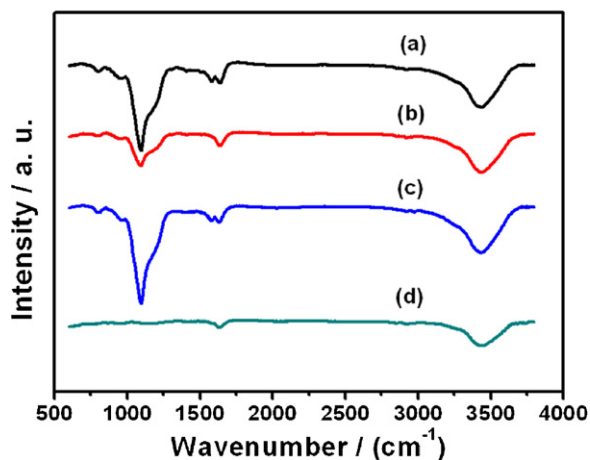


Fig. 2. FTIR spectrums of (a) CNTs-IMH1, (b) CNTs-IMH2, (c) CNTs-CMH, and (d) CNTs-pristine.

heating time results in the higher temperature. The pause time determines the low temperature limit, which means, the shorter the pause time results in the higher low temperature limit [16]. Specifically, the maximum and minimum temperatures for IMH in the form of 15s-ON/10s-OFF are approximately 1000–650 °C, and 1000–550 °C for IMH in the form of 15s-ON/15s-OFF. There are at least two advantages of IMH method. The first is to enhance the possibility to control the temperature at a desired range. The second is the flexible alternation of heating modes which would change the crystal structure in the formation process [16].

The surface state of CNTs was characterized by FTIR measurements and the results are displayed in Fig. 2. The band at 1636 cm<sup>-1</sup> is attributed to OH stretching vibration. The band at 1094 cm<sup>-1</sup> corresponds to C–O stretching vibration. From the FTIR spectrum, it is obviously that there are many oxygen-containing functional groups distributing on the surface of CNTs-IMH1, CNTs-IMH2 and CNTs-CMH. Compared to the pristine CNTs, it can be deduced that the CNTs have been successfully modified by KOH in high temperature. Such functionalization could be attributed to the strong oxidizing property of KOH, especially under the microwave heating conditions. Microwave heating can rapidly heat the mixture to a relatively high temperature. It is well known that as electrocatalysts supports, the oxygen-containing groups on CNTs are beneficial to enhance the hydrophilicity of CNTs, which is useful to improve the dispersion of electrocatalysts. Meanwhile, it could stabilize metallic particles by enhancing the bonding interaction between the metallic particles and the CNTs [11,19].

In order to further investigate the surface state of the CNTs, Raman spectrum was employed and the results are shown in Fig. 3. All the CNTs samples have similar Raman scattering patterns. The peak at 1356 cm<sup>-1</sup> is assigned to the disordered graphite (D-line) and the peak at high frequency of ~1580 cm<sup>-1</sup> corresponds to the splitting of the E<sub>2g</sub> stretching mode of graphite (G-line). The intensity ratio of D-line to G-line can be used as an indicator for the structural integrity of the sp<sup>2</sup>-hybridized carbon atoms [23,24]. Based on the Raman curves, it can be calculated that the intensity ratio of the D-line to G-line is 0.83, 0.86, 0.73 and 1.13 for CNTs-IMH1, CNTs-IMH2, CNTs-CMH and CNTs-pristine. Obviously, the difference in the ration comes from the different pretreatments, which are closely related to the temperature. As the temperature increases, the graphitization degree of CNTs becomes higher, which is a desirable property since the degree of graphitization is a key factor affecting the electrical conductivity and stability of electrocatalysts.

Fig. 4 presents the XRD results of the prepared electrocatalysts. All the samples show the typical characteristics of crystalline Pt

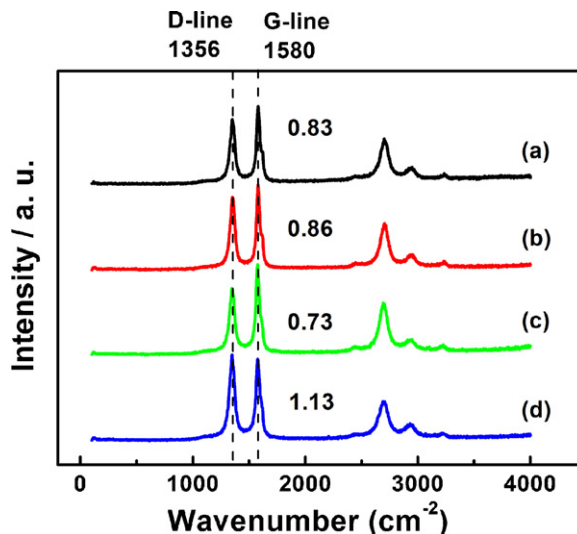
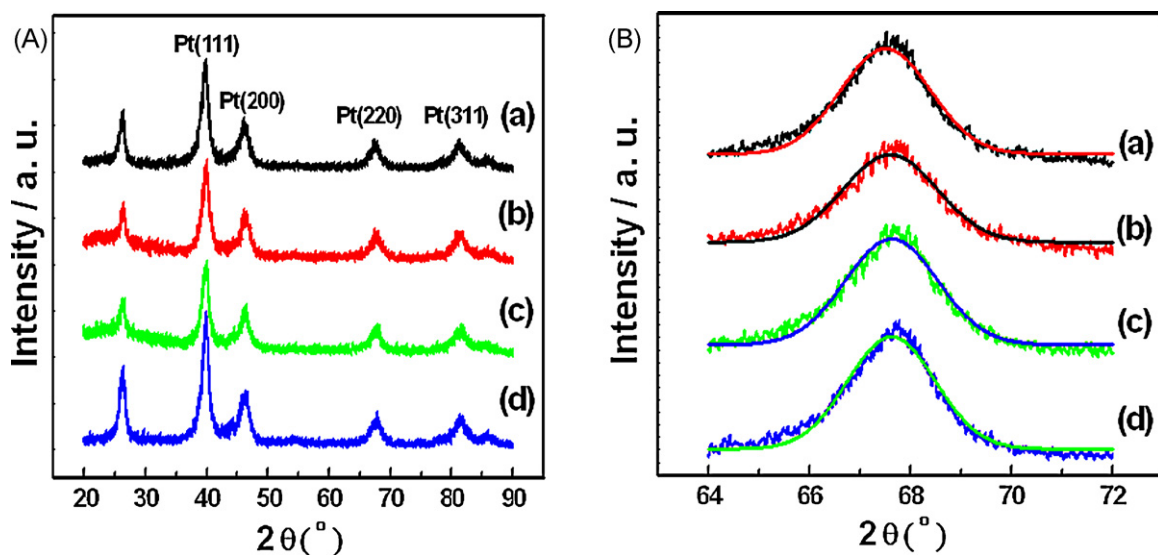


Fig. 3. Raman spectrums of (a) CNTs-IMH1, (b) CNTs-IMH2, (c) CNTs-CMH, and (d) CNTs-pristine.

face centered cubic (fcc) structure. The diffraction peaks at 2θ of 39.6°, 46.3°, 67.4° and 81.6° are assigned to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) facets of Pt. The fitted (2 2 0) plane is used to calculate the crystal size according to the Scherrer equation [21,22]. And the average crystal size of Pt/CNTs-IMH1, Pt/CNTs-IMH2, Pt/CNTs-CMH and Pt/CNTs-pristine are 4.0 nm, 4.0 nm, 4.1 nm and 4.0 nm. There is almost no difference in the size of Pt particles loaded on the above four different supports, proving the functionalization procedure and the graphitization degree of the supports do not affect the Pt particle size in this study. This is meaningful for comparing the effect of CNTs pretreated via different procedures.

The TEM images and the Pt particle size distribution histograms of Pt/CNTs-IMH1 and Pt/CNTs-pristine are given in Fig. 5. The Pt particles are uniformly distributed on the surface of CNTs-IMH1. What's more important, there are more Pt particles supported on CNTs-IMH1 than that on CNTs-pristine. And the Pt loading that quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer, Germany) are 78.1%, 77.8%, 76.0% and 61.3% for Pt/CNTs-IMH1, Pt/CNTs-IMH2, Pt/CNTs-CMH and Pt/CNTs-pristine. This means the CNTs modified by IMH method are favorable for depositing Pt particles. The reason could be attributed to the IMH treatment could produce some oxygen-containing groups and micropores on the surface of CNTs [11]. The BET surface area of CNTs-IMH1 and CNTs-pristine that quantified by the Brunauer–Emmett–Teller (BET) technique are 197.3 and 122.9 m<sup>2</sup> g<sup>-1</sup>. The higher BET surface area of CNTs-IMH1 is a direct proof of micropores in CNTs made by the functionalization process.

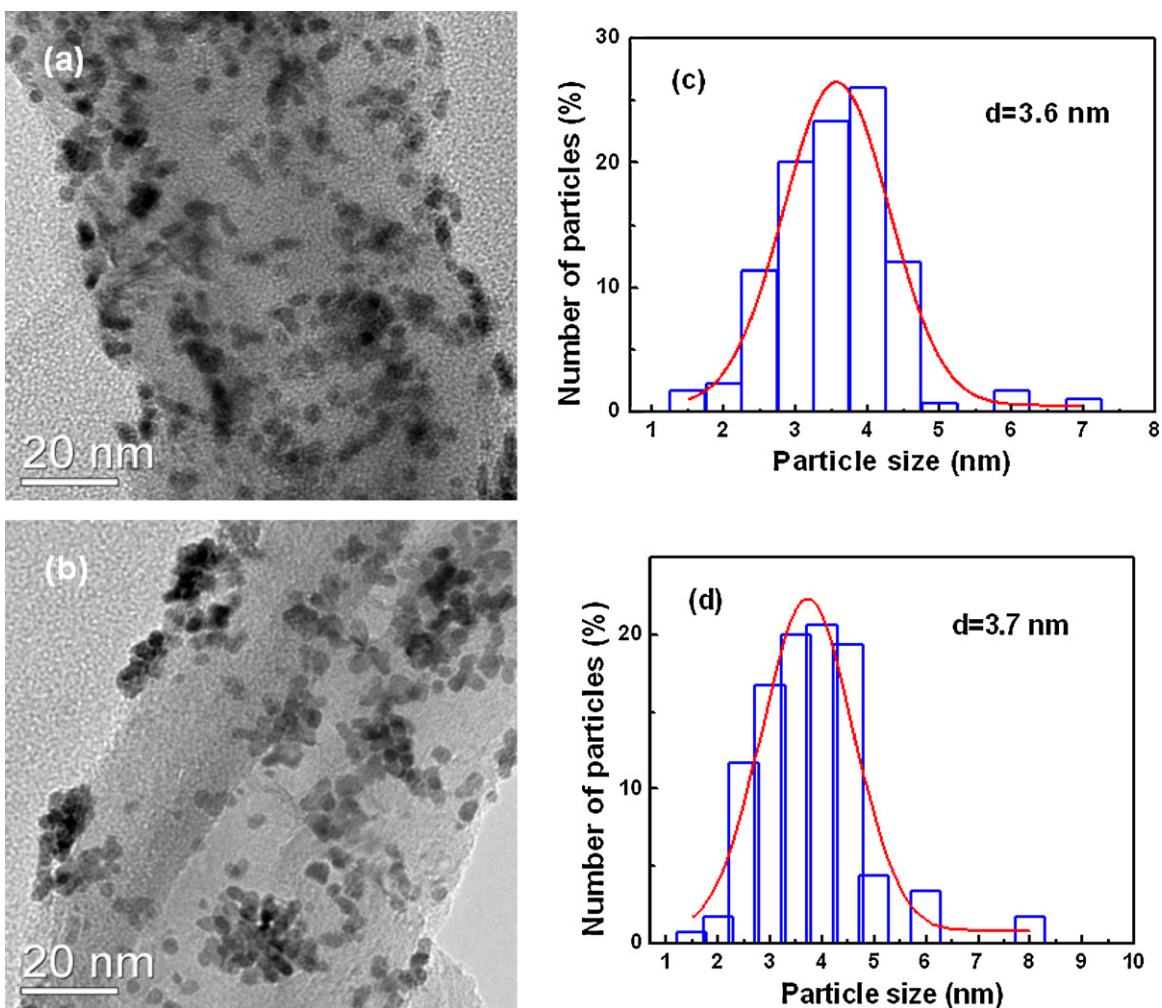
The methanol electrooxidation performance of the prepared electrocatalysts is evaluated. Fig. 6(A) and (B) shows the CVs of the electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solutions without and with 1.0 mol L<sup>-1</sup> CH<sub>3</sub>OH. By integrating the hydrogen adsorption/desorption charges according to the CVs in Fig. 6(A), the electrochemical surface area (ESA) of the electrocatalysts can be calculated [25]. The charges, Q<sub>H</sub>, of Pt/CNTs-IMH1, Pt/CNTs-IMH2, Pt/CNTs-CMH and Pt/CNTs-pristine are 2.93 mC cm<sup>-2</sup>, 2.41 mC cm<sup>-2</sup>, 2.19 mC cm<sup>-2</sup> and 1.85 mC cm<sup>-2</sup>, respectively. It is clear the Pt/CNTs-IMH1 has the largest ESA, which is 1.58 times higher compared to that of Pt/CNTs-pristine. The corresponding peak current density for methanol electrooxidation is proportional to the ESA as shown in Fig. 6(B). The Pt/CNTs-IMH1 shows the best performance for methanol electrooxidation and the specific peak current density is 2.60 times higher than Pt/CNTs-pristine. Considering the Pt loadings and the Pt particle sizes on these various



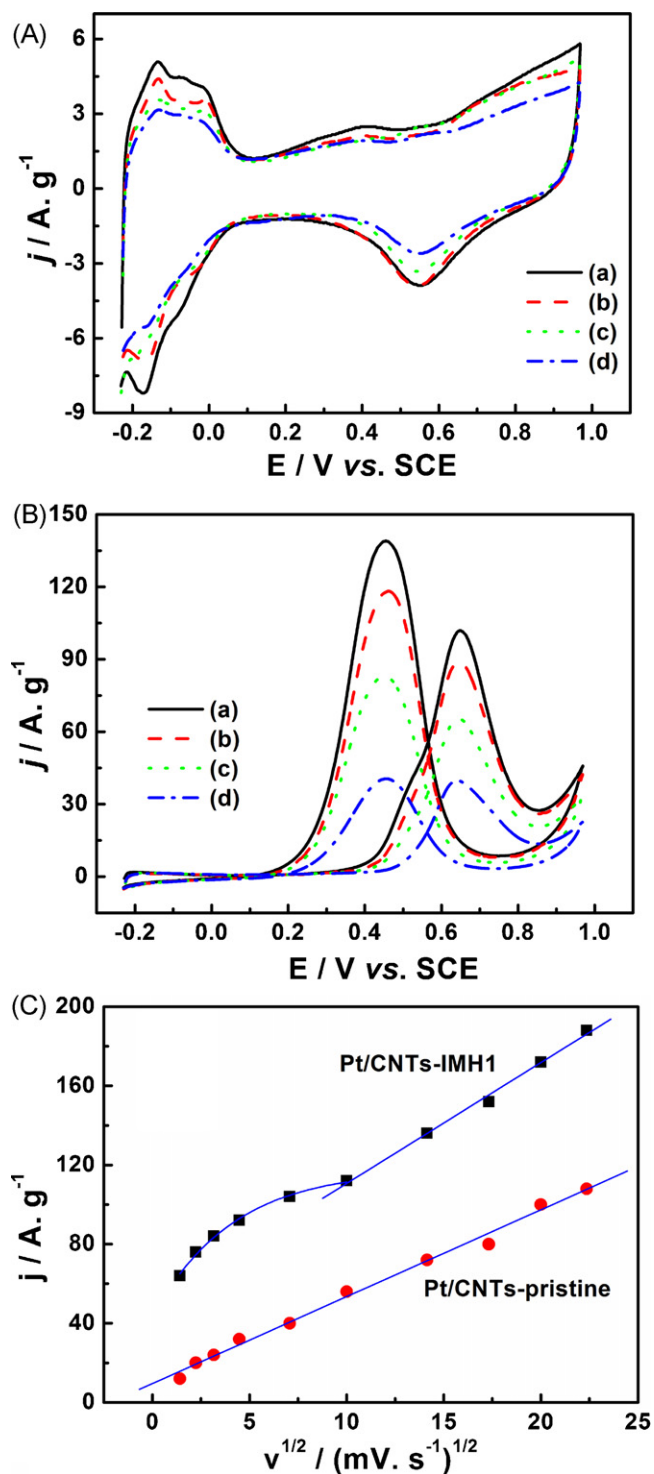
**Fig. 4.** (A) XRD patterns of Pt/CNTs-IMH1 (a), Pt/CNTs-IMH2 (b), Pt/CNTs-CMH (c) and Pt/CNTs-pristine (d) at a scan rate of  $10^\circ \text{ min}^{-1}$ . (B) The corresponding Pt (2 2 0) peaks at a scan rate of  $1^\circ \text{ min}^{-1}$ .

supports are similar, the difference in the performance can only be ascribed to the surface characteristic of supports. The Pt/CNTs-IMH shows higher performance than Pt/CNTs-CMH. The reason could be attributed to the graphitization difference between these two

kinds of supports. As we know, the higher graphitization will lead to the poor hydrophilicity, which hinders the fine dispersion of the Pt particles and the prepared electrocatalysts. As discussed above, the graphitization degree of CNTs increased with the increasing of

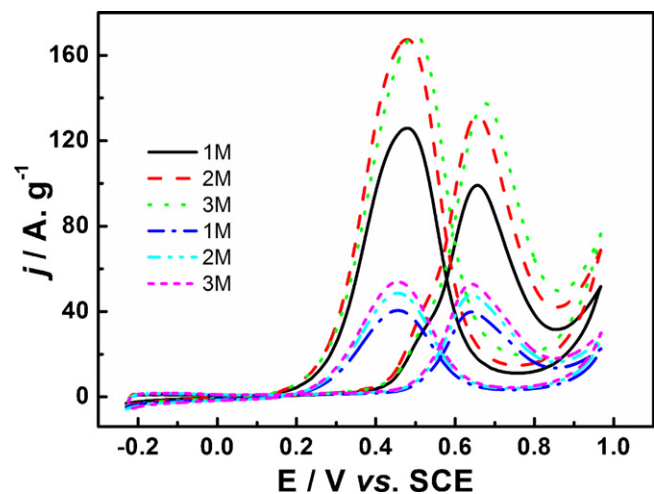


**Fig. 5.** TEM images of Pt/CNTs-IMH1 (a) and Pt/CNTs-pristine (b) and the corresponding particle size distribution histograms of Pt/CNTs-IMH1 (c) and Pt/CNTs-pristine (d).



**Fig. 6.** The CVs curves of the prepared electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solutions without (A) and with (B) 1.0 mol L<sup>-1</sup> CH<sub>3</sub>OH at a scan rate of 50 mV s<sup>-1</sup>. (C) Plots of the peak current density as a function of the square root of the scan rate on Pt/CNTs-IMH1 and Pt/CNTs-pristine.

temperature. The CNTs-CMH possess the highest graphitization degree as observed from Raman spectrum. Consequently, the CNTs-CMH might not be the ideal support for loading Pt particles. Meanwhile, so far as the Pt/CNTs-IMH1 and Pt/CNTs-IMH2 are concerned, the former shows higher activity, proving this procedure could result in better functionalization and graphitization on the surface of CNTs.

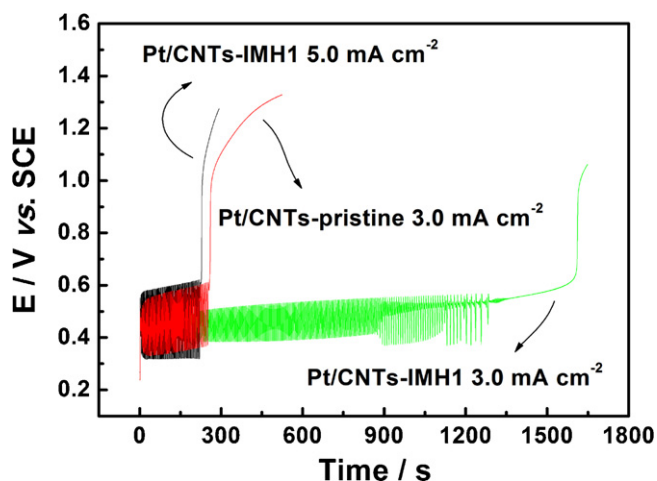


**Fig. 7.** The Pt/CNTs-IMH1 and Pt/CNTs-pristine in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solutions contain different concentration of methanol at a scan rate of 50 mV s<sup>-1</sup>.

The mass transport property on the electrode was investigated by correlating the anodic peak density for methanol electrooxidation during the forward potential cycling at different scan rates. The relationship between peak current density and scan rate on the Pt/CNTs-IMH1 and Pt/CNTs-pristine are presented in Fig. 6(C). It is obviously that the peak current densities of both electrocatalysts increase with the scan rate. However, the Pt/CNTs-IMH1 has a larger slope than the Pt/CNTs-pristine, which shows better activity towards methanol electrooxidation. In addition, there is a liner relationship above the scan rate of 100 mV s<sup>-1</sup> for Pt/CNTs-IMH1, while it shows a liner relationship at all scan rate for Pt/CNTs-pristine. This means the methanol electrooxidation is more favorable on Pt/CNTs-IMH1 than that on Pt/CNTs-pristine. The reason could be attributed to the larger BET of CNTs-IMH1, which is beneficial to the mass transport.

To further compare the mass transport properties, the performance of Pt/CNTs-IMH1 and Pt/CNTs-pristine were also investigated in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solutions containing different concentrations of methanol. As displayed in Fig. 7, the activity of both electrocatalysts increases as the methanol concentration increases. Especially as the concentration of methanol increases from 1.0 mol L<sup>-1</sup> to 2.0 mol L<sup>-1</sup>, the peak densities of Pt/CNTs-IMH1 increase 33.4% from 99.3 A g<sup>-1</sup> to 132.5 A g<sup>-1</sup>. While, the peak densities of Pt/CNTs-pristine increase 21.6% from 40.2 A g<sup>-1</sup> to 48.9 A g<sup>-1</sup>. This further confirms that the CNTs-IMH1 facilitates the mass transport.

For methanol electrooxidation, the CO poisoning-resistance is also very important, since the CO-like by-products generated during the methanol electrooxidation will occupy the active sites of Pt and consequently decrease its activity towards methanol electrooxidation [26–28]. Chronopotentiometry measurements were employed to investigate the CO poisoning-resistance of Pt/CNTs-IMH1 and Pt/CNTs-pristine, and the results are displayed in Fig. 8. The potential oscillation is a typical phenomenon on Pt due to the poisoning by CO-like by-products formed during the dehydrogenation of methanol [29]. Under a constant current density, while the potential is higher than the onset-potential for methanol electrooxidation, the methanol could be electrooxidized. On the other hand, the potential would increase with the formation of intermediate species, such as CO<sub>ads</sub>, CH<sub>3</sub>OH<sub>ads</sub>, and CHO<sub>ads</sub> [26], which would accumulate on the surface of Pt and make Pt poisoned. In this process, while the potential further increases to a certain high value, the intermediates could be electrooxidized. Once the Pt surface is refreshed, the corresponding potential would decrease. The adsorption/desorption process would terminate while the Pt



**Fig. 8.** The chronopotentiometry curves of methanol oxidation on Pt/CNTs-IMH1 and Pt/CNTs-pristine at different current densities in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  aqueous solutions with  $1.0 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ .

particles in the electrocatalysts do not have any activity, and the potential would keep increase till more than 1.23 V, under which the water could be electrolyzed. The longer time the potential reaches 1.23 V, the more stable the electrocatalysts are. As the results displayed, the potential oscillation time observed on Pt/CNTs-IMH1 is much longer than that on Pt/CNTs-pristine at the current density of  $3.0 \text{ mA cm}^{-2}$ . And the oscillation time of Pt/CNTs-IMH1 at  $5.0 \text{ mA cm}^{-2}$  is even comparable to that of Pt/CNTs-pristine at the current density of  $3.0 \text{ mA cm}^{-2}$ , which proves a much higher stability. We believe that such high stability predominantly originates from the better graphitization and functionalization of the CNTs which enhance the interaction between the Pt particles and the CNTs.

#### 4. Conclusions

An efficient way to functionalize CNTs by intermittent microwave heating method (IMH) is developed in the present study. And the Pt particles can be uniformly loaded on the modified CNTs. Cyclic voltammetry and chronopotentiometry results indicate that the CNTs functionalized by IMH KOH in the form of 15s-ON/10s-OFF for pulse 20 repetitions possess significantly higher activity and stability towards methanol electrooxidation in comparison with the CNTs treated in other forms. The intermittent microwave heating method is simple and economic, and can be potentially applied to mass production of supporting materials and related electrocatalysts as well.

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