

# Fabrication of high surface area graphitic nanoflakes on carbon nanotubes templates

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## Abstract

Graphitic nanoflakes were fabricated on the carbon nanotubes templates for increasing the surface area utilizing bias assisted microwave plasma enhanced chemical vapor deposition (MWPECVD). The analysis of morphologies and structures were achieved by means of scanning electron microscopy and transmission electron microscopy. The surface area of graphitic nanoflakes, carbon nanotubes (CNTs) and graphitic nanoflakes/CNTs were 57.44 m<sup>2</sup>/g, 90.31 m<sup>2</sup>/g and 130.96 m<sup>2</sup>/g from BET measurement, respectively. The cyclic voltammetry was used to calculate the active area of platinum catalysts in 1 M sulfuric acid from hydrogen adsorption peak. An enhancement of activity could be observed from the calculation of CV results. This may be attributed to the small particle size and high dispersion of platinum particles coated on graphitic nanoflakes/CNTs. These high surface area materials could be used as catalysts supports or electrode for fuel cell applications.

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**Keywords:** Graphitic nanoflakes; High surface area; Template; Cyclic voltammetry

## 1. Introduction

To the intention of worldwide environmental protection, the research of new source with a low degree of power consumption, pollution and a high efficiency is required and most urgent thing to do. With a high power density and low pollution, fuel cell is esteemed as a new power source to the next generation to replace fossil oil. However, the major obstacle to fuel cell development is the problem of catalyst utility [1]. Low utility of noble metal catalysts will be correspondingly raised a high cost of fuel cell production. In light of this, most research was put their focus on using carbon related materials as the catalyst supports to improve the utility and the activity of catalysts [2–4]. Carbon appears with various atomic structures in nature. Zero-dimensional carbon, such as fullerence, was identified by Kroto et al. [5], also led to the discovery of carbon nanotubes [6]. One-dimensional carbon, such as carbon nanotube, exhibit amazing behaviors and attracts a lot of attention. According

to its extraordinarily high aspect ratio and high surface area, carbon nanotubes have been widely applied in proton exchange membrane fuel cell and direct methanol fuel cell recently [7–9]. Although two-dimensional carbon such as graphite, has already been studied widely and extensively. The unusual petal-like graphitic nanoflakes have been widely applied in these years [10,11]. The petal-like graphitic nanoflakes which were first reported by Ebbesen and Ajayan in 1992 were the byproduct of synthesizing carbon nanotubes [12]. Several groups used graphitic nanoflakes as field emitter in these years [10,13]. However, graphitic nanoflakes could be also served as catalyst supports or hydrogen absorption due to their large surface-to-volume ratio. Consequently, it is interesting to combine these one-dimensional and two-dimensional carbons to get higher surface area to improve the dispersion of catalysts and reduce the loading of catalysts.

In this study, two dimensional graphitic nanoflakes were grown on carbon nanotube templates by using two steps method to increase the surface area of carbon nanotubes. At the same time, we demonstrated the electrocatalytic properties of these materials via cyclic voltammetry. This supporting material with high surface area is essential to either improve

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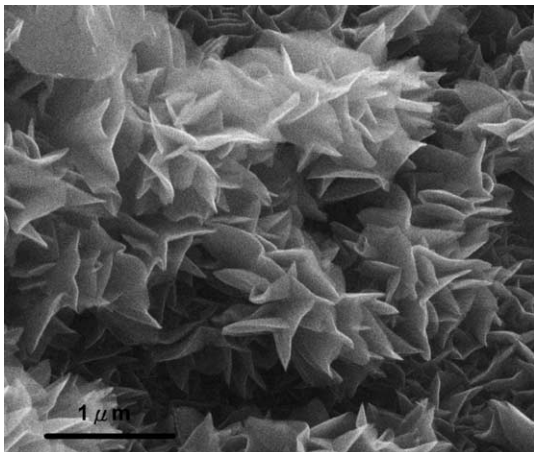


Fig. 1. SEM micrograph of graphitic nanoflakes grown on silicon substrate.

the dispersion of catalysts or reduce the loading of catalysts in the application of fuel cell.

## 2. Experimental

Carbon nanotubes, synthesized by bias assisted microwave plasma enhanced chemical vapor deposition, were used as the templates for growing graphitic nanoflakes. The Fe was first deposited on silicon as catalysts for growing carbon nanotubes and petal-like graphitic nanoflakes by using ion-beam sputter. After that, the prepared substrate was under a series cleaning

procedures using acetone, ethanol, and de-ionized water, and then pure nitrogen was introduced to dry the prepared substrate. The chamber was evacuated at pressure about  $10^{-2}$  Torr by a rotary pump.  $H_2$  and  $CH_4$  were chosen as the reactive gases with a ratio of 4/1 and the working pressure was 10 Torr. The microwave power of 300 W was applied and the temperature reached up to 700 °C. The carbon nanotubes were synthesized on the Fe-deposited substrates under the condition of applying  $-100$  V negative bias. Nevertheless, the growth of petal-like graphitic nanoflakes required two successive steps of applying 10 min negative bias and then 10 min positive bias by MWPECVD. In order to extend the surface area of carbon nanotubes, we try to synthesize petal-like graphitic nanoflakes on the side-wall of carbon nanotubes with following procedures. At beginning, carbon nanotubes were grown on the silicon substrate with about 20  $\mu\text{m}$  in length and 20 nm in width. After the growth of carbon nanotubes, another thin iron layer was deposited on the carbon nanotubes templates for synthesizing petal-like graphitic nanoflakes on the side-walls of carbon nanotubes. Eventually, the petal-like graphitic nanoflakes were synthesized on the side-wall of carbon nanotubes by using two steps method.

The characterization of morphologies was achieved by means of scanning electron microscopy (Hitachi S4700I and JEOL 2500) after deposition. The nanostructures of these carbon-related nanomaterials were investigated by high resolution transmission electron microscope (Philips Tecnai-

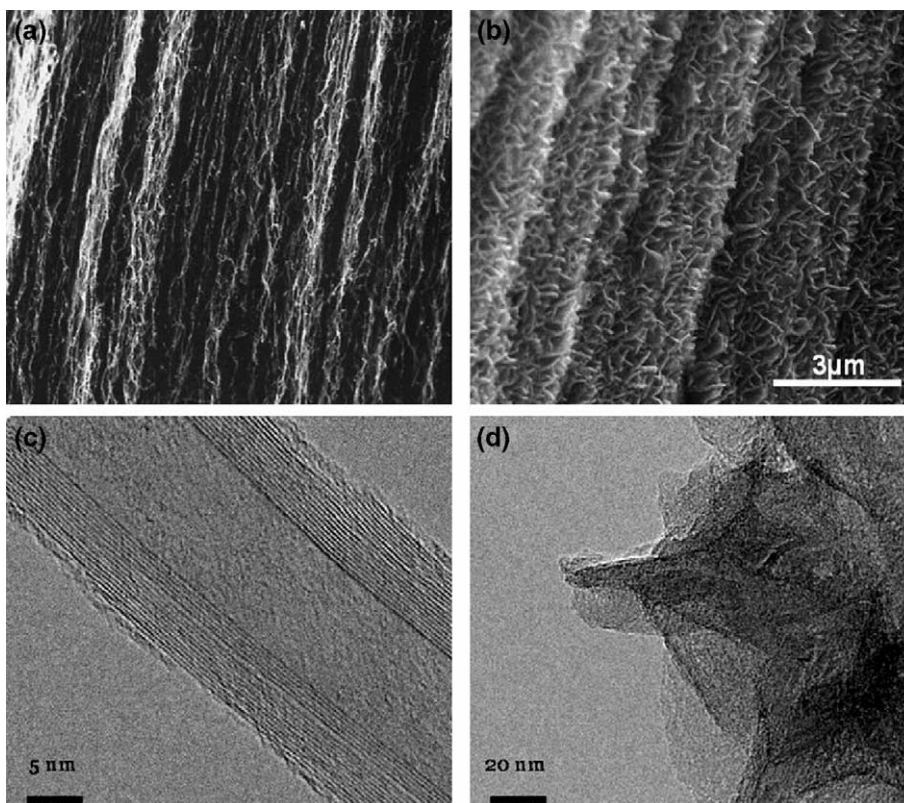


Fig. 2. (a) and (b) are the SEM images of carbon nanotubes before and after growing graphitic nanoflakes on it. (c) and (d) are HRTEM images of carbon nanotubes and graphitic nanoflakes.

20). The surface area was measured by Brunauer Emmett Teller method (BET). The analysis of electrocatalytic properties of carbon nanomaterials have been done by cyclic voltammetry (CH Instrument 614B). The fabrication of platinum was carried out by using polyol method. The solvents of polyol method included glycol, PVP 4000, and  $\text{PtCl}_6$  with a concentration of 0.01 M. Cyclic voltammetric tests of the electrocatalytic activity over the Pt/graphitic nanoflakes, Pt/CNTs, and Pt/graphitic nanoflakes/CNTs with a Pt loading of 23% were performed in a conventional three-electrode test cell. The working electrode was a  $0.25 \text{ cm}^2$  thin Pt foil placed on carbon nanomaterials. A platinum wire was served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The carbon nanomaterials were measured in 1M  $\text{H}_2\text{SO}_4$  solution with a scanning rate of 50 mVs.

### 3. Result and discussions

In our case, the graphitic nanoflakes shown in Fig. 1 were synthesized on iron deposited silicon substrate under two successive steps of applying 10 min negative bias and then 10 min positive bias. The change of electrical field which result in anisotropic growth of carbon atoms would grow graphitic nanoflakes instead of carbon nanotubes. As can be seen from Fig. 1, the graphitic nanoflakes which have hundreds of nanometers in width and several nanometers in thickness are uniformly grown on the substrate. Fig. 2(a) and (b) were the micrographs of carbon nanotubes and graphitic nanoflakes/CNTs. The surface area of graphitic nanoflakes, carbon nanotubes and graphitic nanoflakes/CNTs were  $57.44 \text{ m}^2/\text{g}$ ,  $90.31 \text{ m}^2/\text{g}$  and  $130.96 \text{ m}^2/\text{g}$  from BET measurement, respectively. The enhancement of surface area by using carbon nanotubes as the templates could clearly be found. Fig. 2(c) and (d) displays HRTEM images of carbon nanotubes and graphitic nanoflakes/CNTs. The outer and inner diameters of carbon nanotube are about 10 nm and 20 nm which can be observed from Fig. 2(c). The fringes of graphitic sheets can clear be seen on carbon nanotubes which incorporate with some amorphous carbon on the out shell of the nanotubes. For

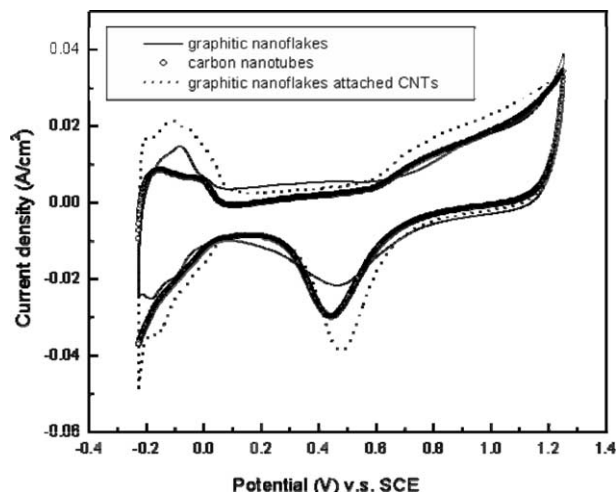


Fig. 4. Cyclic voltammograms of Pt/graphitic nanoflakes, Pt/CNTs, and Pt/graphitic nanoflakes/CNTs at 50 mV/s in 1 M  $\text{H}_2\text{SO}_4$  aqueous solution.

testing the electrocatalytic properties, Pt nanoparticles were synthesized on graphitic nanoflakes, carbon nanotubes and graphitic nanoflakes attached carbon nanotubes by polyol method. Fig. 3 depicts the TEM images of platinum nanoparticles dispersed on (a) carbon nanotubes and (b) graphitic nanoflakes attached carbon nanotubes.

The particle size of Pt/CNTs ranged from 3 to 10 nm. However, the Pt/graphitic nanoflakes/CNTs show smaller particle size and better dispersion than Pt/CNTs. The electrocatalytic properties of platinum supported carbon nanotubes and graphitic nanoflakes attached carbon nanotubes were investigated by CV. Fig. 4 shows CV of Pt supported carbon materials in 1 M  $\text{H}_2\text{SO}_4$  solution with a scan rate 50 mV/s. Based on the hydrogen adsorption wave capacitor [14], the active area of Pt supported graphitic nanoflakes, carbon nanotubes and graphitic nanoflakes attached carbon nanotubes were  $5.22 \text{ cm}^2$ ,  $12.23 \text{ cm}^2$ , and  $17.37 \text{ cm}^2$ , respectively. The calculated results of these materials are summarized in Table 1. The symbols  $S$ ,  $Q_{\text{H}}$ , and  $S_{\text{Pt}}$  represent surface area, charge of H-adsorption, and active area of Pt, respectively. It could be clearly observed

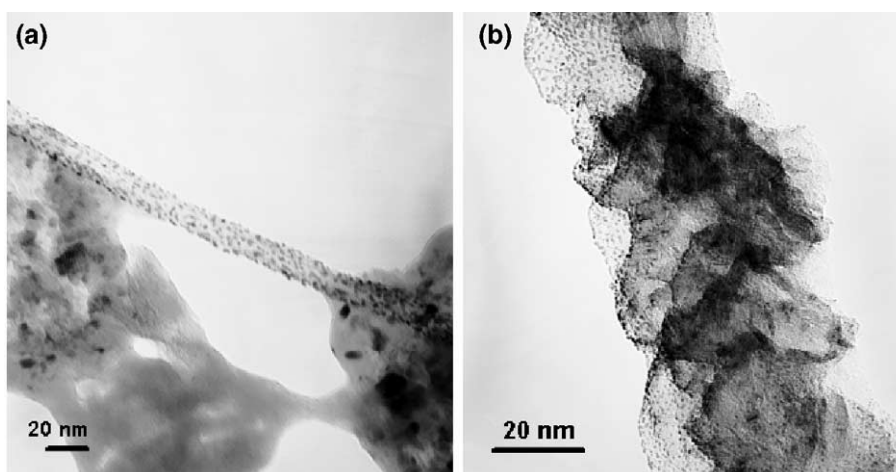


Fig. 3. TEM images of Pt supported (a) carbon nanotubes and (b) graphitic nanoflakes/CNTs.

Table 1

Comparison of properties of graphitic nanoflakes, carbon nanotubes and graphitic nanoflakes attached carbon nanotubes

Sample	Wt.%	$S$ (m <sup>2</sup> )	$Q_H$ (mC)	$S_{Pt}$ (cm <sup>2</sup> )
Graphitic nanoflakes	23	57.44	1.09	5.22
Carbon nanotubes	23	90.31	2.56	12.23
Graphitic nanoflakes attached carbon nanotubes	23	130.96	3.64	17.37

that the growth of graphitic nanoflakes on carbon nanotubes could not only increase the surface area of carbon nanotubes, but increase the activity of Pt catalysts.

This may be attributed to the small particle size and high dispersion of platinum particles coated on graphitic nanoflakes/CNTs. This shows good potential application in fuel cells.

#### 4. Conclusion

We demonstrated an approach to synthesize high surface area graphitic nanoflakes on carbon nanotubes templates using a two steps method by MWPECVD system. The graphitic nanoflakes can be produced by a successive procedure of negative bias to positive bias. The surface area of as-grown multi-wall carbon nanotubes and graphitic nanoflakes were 90.31 m<sup>2</sup>/g and 57.44 m<sup>2</sup>/g from BET measurement. Furthermore, the surface area of graphitic nanoflake/carbon nanotubes is 130.96 m<sup>2</sup>/g. The results of CV also show the improvement of electrocatalytic properties of Pt supported graphitic nanoflakes/carbon nanotubes. This may be attributed to the small particle size and high dispersion of platinum particles coated on graphitic nanoflakes /CNTs from TEM observation.

The enhancement of high surface area of carbon nanotubes could be used as catalyst supports or other fields that require the use of high surface area.

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