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ScienceDirect
Applied Surface Science 254 (2008) 1700–1704
applied surface science
www.elsevier.com/locate/apsusc

Preparation of carbon nanosheets deposited on carbon nanotubes by microwave plasma-enhanced chemical vapor deposition method

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Received 11 June 2007; received in revised form 12 July 2007; accepted 14 July 2007
Available online 20 July 2007

Abstract

Carbon nanosheets were synthesized by microwave plasma-enhanced chemical vapor deposition method on carbon nanotubes substrate which was treated by hydrogen plasma. The results showed that the diameters of carbon nanotubes first got thick and then ''petal-like'' carbon nanosheets were grown on the outer wall of carbon nanotubes. The diameters of carbon nanotubes without and with carbon nanosheets were 100–150 and 300–500 nm, respectively. Raman spectrum indicated the graphite structure of carbon nanotubes/carbon nanosheets. The hydrogen plasma treatment and reaction time greatly affected the growth and density of carbon nanosheets. Based on above results, carbon nanosheets/carbon nanotubes probably have important applications as cold cathode materials and electrode materials.

Keywords: Carbon nanotubes; Carbon nanosheets; Chemical vapor deposition

1. Introduction

Since they were found by Iijima in 1991 [1], carbon nanotubes (CNTs) have been synthesized by different methods and considerable investigations have also been made due to their exceptional properties and extensive applications. For example, CNTs can be applied as cold cathode materials, light-invisible materials, electrode materials, catalyst supports and reinforced composites [2]. Especially, they are expected to be applicable to large-scale integration technologies and so on [3–6].

Recently, another carbon nanomaterials – carbon nanosheets, have been synthesized by several groups [7–16]. The high surface-to-volume ratio and sharp edges of carbon nanosheets are attractive for fuel cells and microelectronic technologies. Especially, carbon nanosheets are probably good candidate as field emitters due to their unique geometrical structure [9,10]. Having reported, carbon nanosheets can be grown on Si, SiO_2, Al_2O_3 and different metal substrates, and they can also be synthesized without catalyst. However, by far, carbon nanosheets synthesized on CNTs have not been reported. The synthesis of carbon nanosheets on CNTs will be significative for the preparation and application of other C–C composites. Furthermore, CNTs/carbon nanosheets may have more exceptional field emission performance than individual carbon nanosheets or CNTs.

In this paper, ''petal-like'' carbon nanosheets were synthesized on CNTs by microwave plasma-enhanced chemical vapor deposition (MPECVD) method without catalyst. Before the growth of carbon nanosheets, CNTs were treated by hydrogen plasma. The morphology and microstructure of carbon nanosheets were characterized by scanning electron microscope (SEM) and Raman spectroscope. Finally, the growth mechanism of carbon nanosheets on CNTs was discussed.

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0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2007.07.131

2. Experiments

First, CNTs were synthesized by floating catalyst method, using C_2H_2 as carbon source, N_2 as carrier gas and ferrocene as catalyst precursor. Before the growth of carbon nanosheets, CNTs were purified by the solutions of H_2SO_4 and HNO_3 ($V_{H_2SO_4} : V_{HNO_3} = 3 : 1$).

Using MPECVD method, purified CNTs were treated by hydrogen plasma for about 5 h. First, the powder of CNTs was dispersed onto a salver of Al_2O_3. The temperature of the substrate was controlled by microwave power and process pressure and measured by thermocouple. The microwave power increased gradually from 800 W. After it increased to 1600 W and the pressure was 6.14 kPa, H_2 was introduced and the flow rate was 100 sccm. Then using treated CNTs as template, carbon nanosheets were grown on the outer walls of CNTs. The microwave power was 800 W, the pressure of chamber was 13.25 kPa and the flow rate ratio of CH_4:Ar:H_2 was 2:40:2 sccm. The reaction time was 3 and 6 h, respectively.

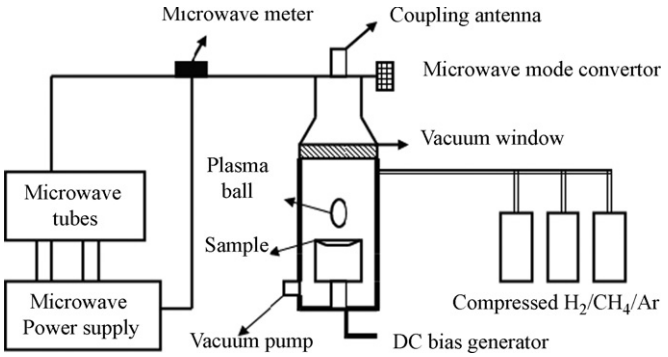

Fig. 1. Schematic diagram of MPECVD system.

Finally, the gases and power supply were shut. The purity of gases used in our experiment was above 99.5%. The MPECVD equipment was shown in Fig. 1 and the experimental parameters were shown in Table 1, in which sample A is CNTs and samples B and C are carbon nanosheets.

Table 1
Experimental parameters for the treatment of CNTs and the growth of carbon nanosheets

Samples	Microwave power (W)	Pressure (kPa)	H_1 (sccm)	Ar (sccm)	CH_4 (sccm)	Temperature (K)	Reaction time (h)
A	1600	6.14	100	–	–	1023	5
B	800	13.25	2	40	2	923	3
C	800	13.25	2	40	2	923	6

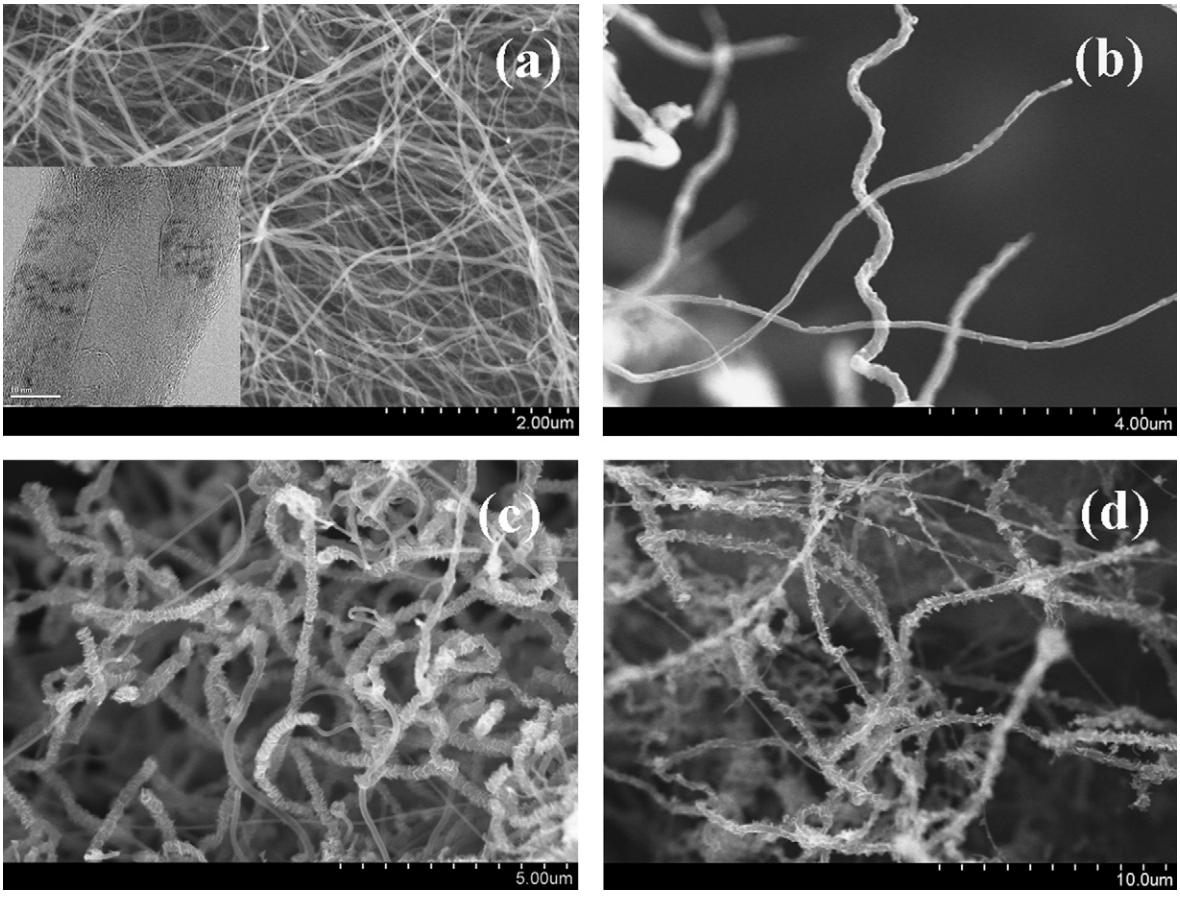

Fig. 2. SEM images of CNTs (a), CNTs/carbon nanosheets for 3 h (b) and for 6 h (c and d) with H_2 treatment.

The morphology of CNTs and CNTs/carbon nanosheets was characterized by Hitachi S-4800 SEM with accelerating voltage of 15 kV. The microstructure of CNTs and CNTs/carbon sheets was analyzed by Jobin Yvon HR800 Raman spectroscope with an Ar^+ laser ($\lambda = 488$ nm).

3. Results and discussion

Fig. 2(a) shows the SEM image of CNTs synthesized by floating catalyst method. It can be seen that the diameters of CNTs are about 40 nm, several are about 60 nm. In the inset of Fig. 2(a), the high-resolution transmission electron microscope image shows that CNTs are multi-walled CNTs. Fig. 2(b–d) shows the SEM images of carbon nanosheets grown on treated CNTs. After CNTs were treated by MPECVD method, the diameter of CNTs was larger than that of untreated CNTs, which can be found at the location of without carbon nanosheets. When the reaction time is 3 h, the diameter of obtained products is about 150 nm, and hardly petal-like carbon nanosheet is grown on them (Fig. 2(b)). When the reaction time is 6 h, at the high-density region of carbon nanosheets, the diameter is about 400 nm. However, at the low-density region of carbon nanosheets, the diameters are different. Some are about 300 nm and others are about 400 nm.

Fig. 3 shows the high-resolution SEM images of carbon nanosheets grown on treated CNTs substrate for 6 h. In Fig. 3(a), petal-like carbon nanosheets are vertical to the surface of CNTs and they all have the sharp tips. Fig. 3(b) shows the image of CNTs with and without carbon nanosheets, it can be seen clearly that the diameter of CNTs without carbon nanosheets is about 100 nm. After carbon nanosheets are grown, the diameter increases to about 500 nm. It can be evaluated that the length of carbon nanosheets is about 200 nm, which is the vertical distance from CNTs surface. Fig. 3(c and d) shows the SEM images of single CNT with carbon nanosheets. It can be found from Fig. 3(c) that carbon nanosheets are very thin and have semicircular structure. However, in Fig. 3(d), the carbon nanosheets have semiellipticlike structure and sharp tip.

Furthermore, the experiment has also been performed for the growth of carbon nanosheets on CNTs without hydrogen treatment. The SEM images of products are shown in Fig. 4. When the reaction time is 3 h, the diameters of obtained products are about 80–100 nm and some particles are covered on them. When it increases to 6 h, the products are similar to the result for the growth of 3 h except the diameter of about 400 nm. The results indicate that the hydrogen plasma treatment is important for the growth of carbon nanosheets. Therefore, we concluded that hydrogen etching formed the surface defects of CNTs and provided the growth sites of carbon nanosheets.

In order to verify the conclusion, Raman spectrums of CNTs with and without hydrogen treatment are characterized and compared. Generally, Raman spectrums of CNTs have two

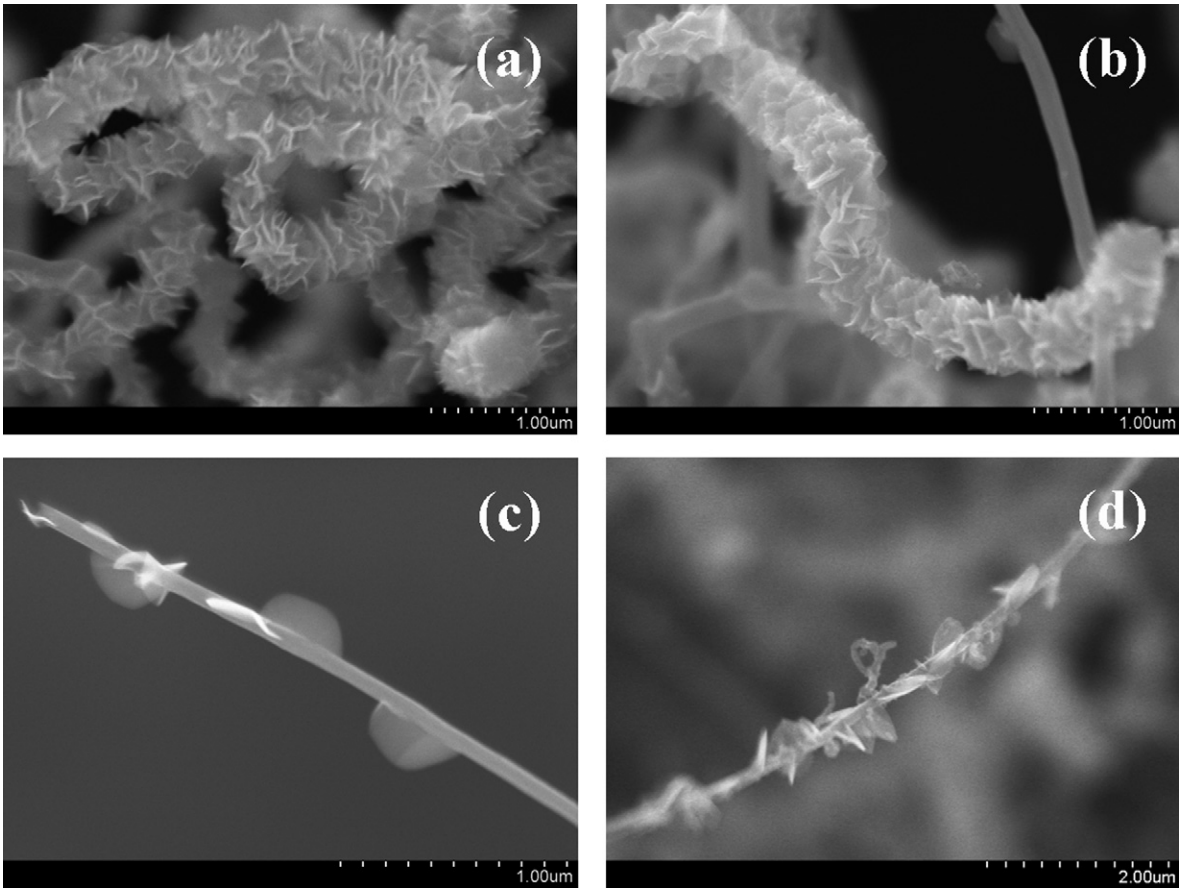

Fig. 3. High-resolution SEM images of CNTs/carbon nanosheets for 6 h with H_2 treatment.

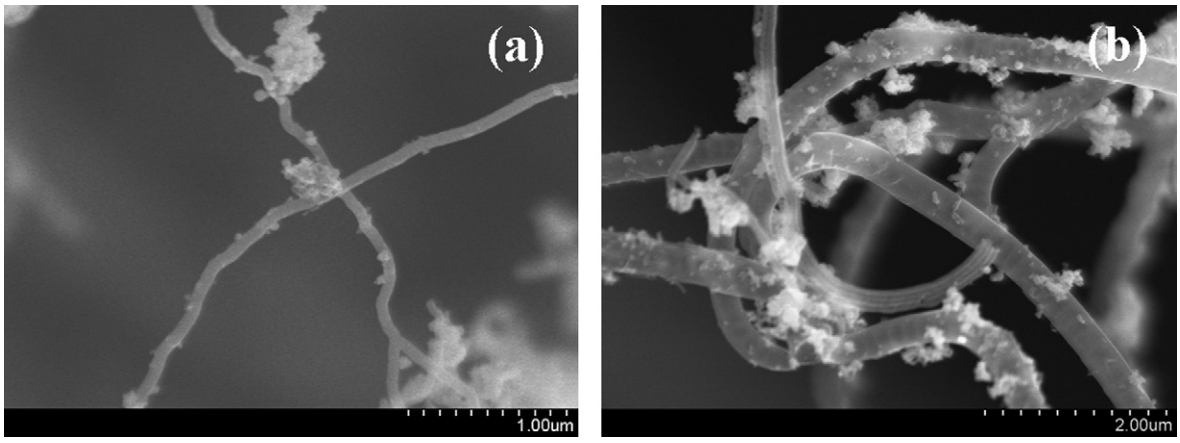

Fig. 4. SEM images of CNTs/carbon nanosheets for 3 h (a) and 6 h (b) without H_2 treatment.

strong peaks at about 1350 and 1580 cm^{-1}, commonly known as the D and G bands. The peak at 1580 cm^{-1} corresponds to an E_{2g} mode of graphite, which is due to the sp^2-bonded carbon atoms in a two-dimensional hexagonal graphitic layer. The D band at about 1350 cm^{-1} is associated with the presence of defects in the hexagonal graphitic layers [17,18]. Furthermore, the intensity ratio of D and G peaks shows the graphitization degree and crystal quality of CNTs. The ratio of I_D/I_G is smaller, the graphitization degree is higher or the crystal defect is less. In Fig. 5, the ratios of I_D/I_G of CNTs with and without hydrogen treatment is 0.87 and 0.57, respectively, which indicates the hydrogen treatment increases the disorder and defects of CNTs.

The microstructures of CNTs/carbon nanosheets are also analyzed by Raman spectrums. The results show that CNTs/carbon nanosheets are graphitic structure, and disordered structure is increased, which was compared with that of CNTs. It can also be seen that on treated CNTs substrate, the I_D/I_G of CNTs/carbon nanosheets is 1.09 and 1.01, respectively, which corresponds to the growth time of 3 and 6 h. However, on untreated CNTs substrate, the I_D/I_G of CNTs/carbon nanosheets is 1.15 and 1.22, respectively, which corresponds to the growth time of 3 and 6 h. The data suggests that with hydrogen treatment, CNTs/carbon nanosheets have better graphitization degree along with the increase of reaction time. But without hydrogen treatment, the obtained products have worse graphitization degree along with the increase of reaction time (Fig. 6).

Based on above results, it can be concluded that hydrogen treatment of CNTs and reaction time greatly affected the morphology of carbon nanosheets. Before the growth of carbon nanosheets, the hydrogen plasma treatment increased the disorder and surface defects of CNTs, which was favorable for the deposition of carbon nanosheets. In the process of hydrogen treatment, some C–C bonds were replaced by C–H bonds; some were broken due to the plasma bombardment. Originally, along with the broken C–C bonds, the non-crystalline carbon and graphite layers with sp^2 structure covered the outer wall of CNTs. With the increase of reaction time, the outer wall of CNTs was thicker and thicker. When the reaction time was 3 h, the protuberant structure began to form on thick outer wall of CNTs. However, when the reaction time was up to 6 h, the petal-like carbon nanosheets covered the surface of CNTs. Therefore, at the beginning of reaction, the growth of carbon nanosheets and non-crystal carbon are both present. After the surface of

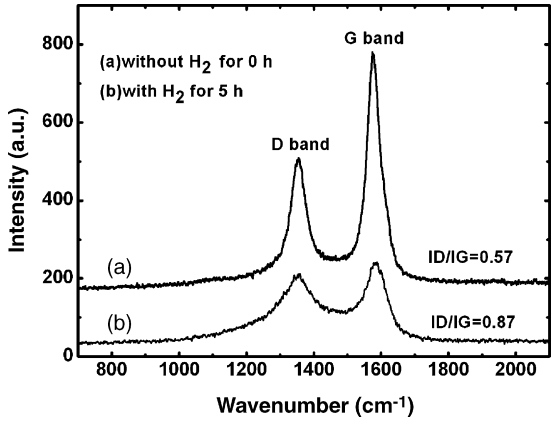

Fig. 5. Raman spectrums of CNTs without (a) and with H_2 treatment (b).

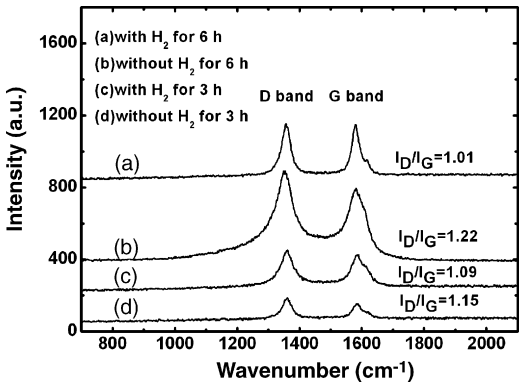

Fig. 6. Raman spectrums of CNTs/carbon nanosheets for 6 h (a) and 3 h (c) with H_2 treatment and for 6 h (b) and 3 h (d) without H_2 treatment.

CNTs was basically covered, the non-crystal carbon films stopped to grow. However, the sheet-like structure had the predominance of upward growth. Ultimately, the protuberant carbon nanosheets were formed. The density of carbon nanosheets is related to the surface defects of CNTs, which came from the hydrogen plasma treatment and the quality of CNTs. The defects of CNTs are more, the density of carbon nanosheets is larger.

Finally, we consider that the synthesis of carbon nanosheets can be attributed to the hydrogen plasma treatment and reaction time. The broken C–C bonds provided the interface transition between CNTs and carbon nanosheets. The long reaction time was favorable for the formation of carbon nanosheets. Based on these results, CNTs/carbon nanosheets may be good candidate as cold cathode materials and nanoelectric devices interconnection materials.

4. Conclusions

Microwave plasma-enhanced chemical vapor deposition method has been employed for the synthesis of carbon nanosheets on CNTs substrate. The obtained carbon nanosheets were characterized by SEM and Raman spectra. The results showed that the diameters of CNTs/carbon nanosheets ranged from 300 to 500 nm. The petal-like carbon nanosheets were very thin and had semicircular and sharp structure. The hydrogen plasma treatment of CNTs broke the C–C bonds, which provided the growth sites of carbon nanosheets. The growth of carbon nanosheets went through two stages, the synchronous growth of carbon nanosheets and non-crystal carbon and the alone growth of carbon nanosheets. Therefore, the long reaction time is the key for the preparation of carbon nanosheets on CNTs substrate.

Acknowledgements

This research work was supported by the National Natural Science Foundation of China (NSFC, Grants Nos. 50072029 and 50572101).

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