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Microwave-assisted chemical modification of carbon nanohorns: Oxidation and Pt deposition

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Abstract

Minimum irradiances necessary to chemically modify carbon nanohorns by microwave radiation were investigated using XPS, TEM, and Raman spectroscopy. Only 150 W min, equivalent of operating a home-use microwave oven for less than 10 s, is sufficient to oxidize nanohorns, with the result that nearly all materials used for this study become dispersible in polar solvents. Also, irradiation of less than 250 W min is enough to deposit Pt particles on the nanohorns by the polyol method, with a unique property that Pt particles are deposited mostly at the horn ends.

1. Introduction

A single-walled carbon nanohorn (SWNH) is made of a single graphene sheet rolled to a conical shape, with polygons of carbon atoms other than hexagons to close its pointing end [1]. Its diameter ranges from 2 to 5 nm and the length is ~40 nm. SWNHs typically form a 100 nm wide spherical aggregate of the secondary structure as if each cone radiates from the central region. The structure of the part where cones are united is not known. Laser ablation of graphite produces uniformly sized SWNHs with a trace amount of graphitic impurities without using metal catalyst [2]. High purity of the as-grown sample and the secondary structure make SWNHs better suited for applications such as catalyst supports [3–5] and drug delivery [6,7] than single-walled carbon nanotubes (SWCNTs). Yet, its chemical characteristics are similar to SWCNTs because both materials are based on a graphene sheet. Highly extended uniform π-electron surfaces provide no pores for other molecules to enter inside; they have low chemical reactivity and show poor wettability against most materials. Therefore, it is necessary for many applications to control surface properties of SWNHs.

In contrast to SWCNTs, where varieties of chemical methods are studied to modify their surface properties, oxidation seems to be the only reaction reported so far for SWNHs except for a recent report on azomethine ylides [8]. SWNHs have been oxidized by either treating with concentrated HNO_3 or heating in CO_2 or O_2 at high temperatures in order to increase pore volumes or support metal catalysts [9–11]. The former method leaves unwanted acids that require removal and the latter costs energy. We have previously shown that SWCNTs are heated efficiently by microwave radiation and demonstrated that microwave irradiation is a practical technique for chemical and mechanical modification [12,13].

Being encouraged by chemical similarity of SWNHs and SWCNTs, we have examined in the present study if the same methodology is applicable to SWNHs. In particular, we focus on the minimum irradiances necessary to modify the surface properties of SWNHs, because prolonged acid treatments or higher temperature annealing are known to open large pores and corrugate the wall [14]. Such a severe modification obviously changes surface properties and may cause significant damages on the structure. As we expected that extensive microwave irradiation causes irreversible

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structural changes on SWNHs, we examined two independent chemical modification schemes in this paper. The first microwave oxidation of SWNHs showed that only 150 W min was sufficient to improve dispersibility up to 25 times that of the as-grown sample. Then we examined the second example, Pt nanoparticles directly synthesized with SWNHs by polyol decomposition. It was found in this case that less than 250 W min was sufficient and that most Pt particles were formed at the pointing ends of SWNHs.

2. Experimental

High purity SWNHs were granted from NEC Corporation. In a typical experiment, 10 mL glass tube containing 1.5 mg of the as-grown SWNH was gently placed in a microwave reactor (Discover System, CEM) and 2455 MHz radiation was applied for a controlled time at a given microwave power. After allowing the sample to cool down to room temperature, 0.3 mg of the irradiated SWNHs was taken out and dispersed in 4 mL of tetrahydrofuran (THF). The mixture was sonicated in a bath sonicator for 1 min and was centrifuged at 3000*g* for 10 min. The absorbance at 400 nm of the supernatant was used as a measure of the dispersed amount. A small amount of the irradiated SWNHs was also examined by X-ray photoelectron spectroscopy (XPS) (Shimazu ESCA-1000, Mg X-rays). The Raman spectra (Nicolet AlmegaXR) were taken on the powdered SWNHs using 532 nm excitation.

For the Pt synthesis, 40 mg of SWNHs was added to a 25 mL ethylene glycol solution containing 0.4 mL of 0.4 M KOH and 1.0 mL of 0.05 M $H_2PtCl_6 \cdot 6H_2O$ and sonicated for 30 min. A 2.0 mL of the mixture was transferred to a glass tube and the microwave at 250 W was applied for 1 or 2 min. After irradiation, the SWNHs were collected on a Teflon filter, washed thoroughly with water, and dried for further examinations.

3. Results and discussion

The relative dispersed amount at 80 W irradiation is plotted against the irradiation time in Fig. 1a. Also plotted is the oxygen concentration of irradiated SWNHs measured by XPS. The dispersibility is clearly improved as the irradiation time is extended. The dispersed amount is increased nearly 25 times in comparison with the as-grown sample. The dispersed amount appears to saturate, because it corresponds to nearly complete dispersion of the used material. Starting with a larger amount of SWNHs may give a still higher saturated amount.

This improved dispersibility is a result of oxidation, as evidenced by a similar trend exhibited by the oxygen concentration curve. Oxygen-containing groups make SWNHs more polar and lead to better dispersibility in THF. There are two points to be noted: the oxygen concentration of the as-grown sample fluctuated significantly by each measurement (from 3% to 9%), which indicated the presence of organic contaminants. On the contrary, the irradiated samples gave reproducible values (within 1.5%) on repetitive measurements. This means that irradiation at the initial stage effectively cleans the surface of SWNHs. The amount of additional oxygen introduced by the microwave radiation is estimated to be ~5%. Another point is a drop of the oxygen concentration at the longest irradiation. In the case of SWCNTs, carboxylic acids are known to decompose at lower temperatures than ether or quinone groups [15]. We speculate that the prolonged irradiation raises the temperature of SWNHs high enough to decompose carboxylic acids, resulting in a reduced oxygen content. The remaining oxygen-containing groups, such as ether and quinone, are expected to provide sufficient polarity to make SWNHs still dispersible in THF.

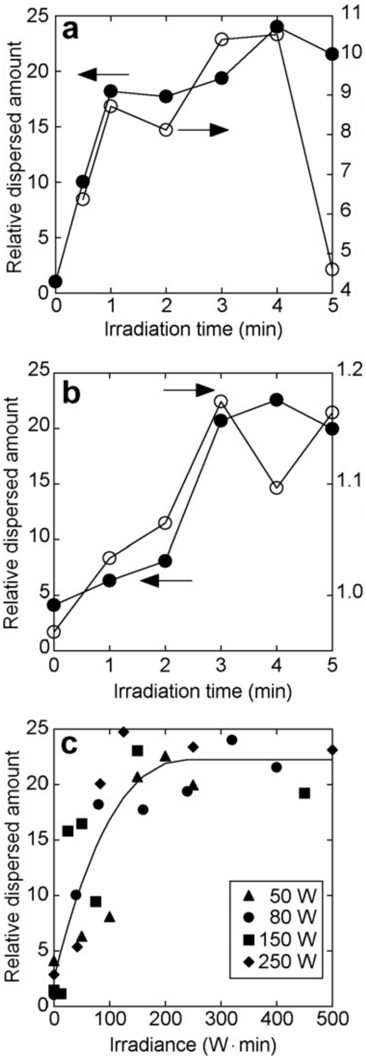

Fig. 1. (a) Relative dispersed amount of SWNHs in THF (closed circles) and oxygen concentration (open circles) for various irradiation times at 80 W. (b) Relative dispersed amount (closed circles) and the ratio of the band intensities (open circles) for various irradiation times at 50 W. (c) Relative dispersed amount plotted against irradiance for all conditions.

The extent of reaction is also studied by Raman spectroscopy. The Raman spectra of SWNHs generally consist of a G-band around 1580 cm^{-1} and a D-band around 1325 cm^{-1} in similar intensities. The G-band is assigned to axial vibration of the sp^2 carbons comprising graphitic hexagons, and the D-band is considered to be the sp^3 carbons as well as amorphous carbons. Thus, the ratio of D- to G-band intensities, I_D/I_G, gives a measure of the extent of oxidation. Fig. 1b shows the dispersibility and the I_D/I_G ratio at 50 W irradiation for various time intervals. Similar dependences indicate that the dispersibility is enhanced due to oxidation, in agreement with the XPS results.

A close inspection of the dispersibility curves shown in Figs. 1a and b reveals that it takes a shorter time by 80 W irradiation to improve the dispersibility than 50 W. In fact, previous SWCNT studies [12,13] indicate that the irradiance (microwave power times irradiation time) is a relevant quantity in microwave chemistry. Fig. 1c summarizes all data as a function of the microwave irradiance. As expected, the dispersed amounts at different powers fall onto a single curve. This suggests that the temperature during irradiation is an important factor [12]. Technically, the temperature of SWNHs during irradiation depends not only on irradiance but on the amount and packing of the SWNHs in the glass tube as well. In the present experiment, the latter factor was kept constant. Regardless of the microwave power, approximately 150 W min is sufficient to improve dispersibility. Irradiation made nearly all irradiated SWNHs dispersible, demonstrating high efficiency of the microwave process.

One of the expected uses of SWNHs is a metal catalyst support for fuel cell applications. Microwave radiations have been used to deposit Pt nanoparticles on SWCNTs by the polyol method [16]. Thermal decomposition of polyol (ethylene glycol in the present case) produces species that reduces Pt salt to afford metallic Pt colloids. We applied 250 W radiation for 2 min to the aqueous reaction mixture containing polyol, Pt salt and SWNHs, with concentrations adjusted for 20 wt% loading. We also obtained a similar result with 1 min irradiation, so the minimum irradiance is probably smaller. Transmission electron microscopy (TEM) (Fig. 2a) shows that metal nanoparticles are deposited on SWNHs. XPS (Fig. 2b) reveals that the nanoparticles are metallic Pt (70.9 and 74.4 eV). The average particle diameter is 3.6 nm and most of the particles fall within 1 nm range (Fig. 2c). These size and distribution are typical for the Pt nanoparticles synthesized by the polyol method [16].

Fig. 2d is a histogram of a number of particles vs. the distance from an estimated center as measured on TEM micrographs. Since TEM images is a 2D projection of a 3D object, the particle distribution should be parabolic if Pt nanoparticles are distributed only at the pointing ends of a SWNH

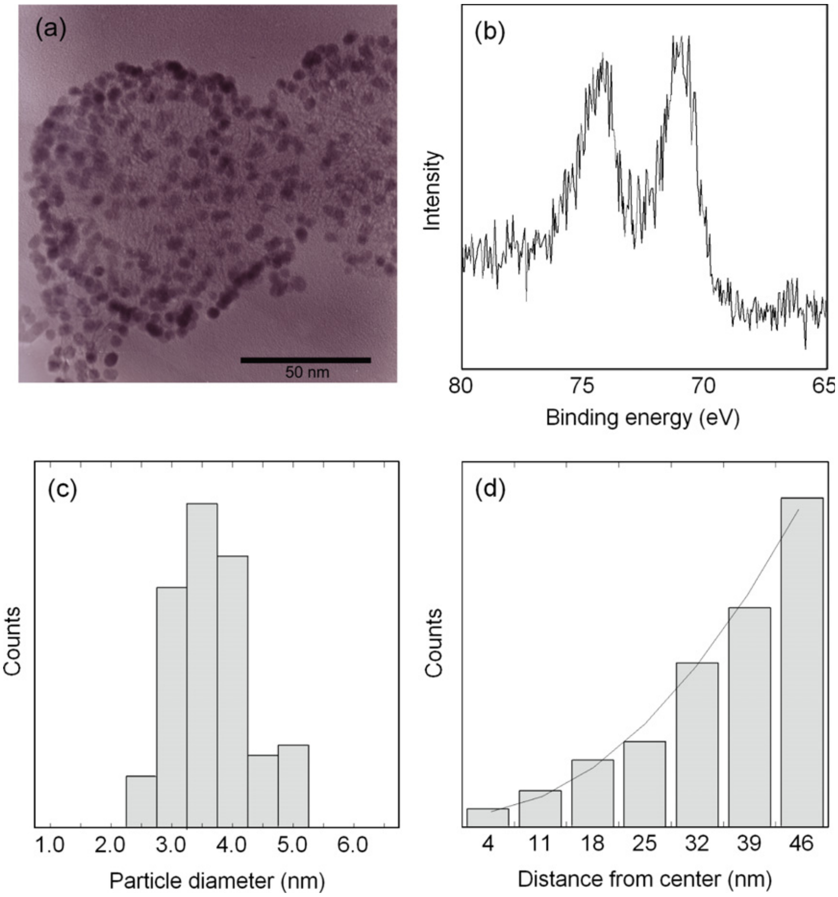

Fig. 2. (a) TEM image of Pt supporting SWNHs. (b) XPS spectrum of Pt supporting SWNHs. (c) Diameter distribution of Pt particles on SWNH. (d) A histogram of a number of Pt particles against the distance from the center of the SWNH imaged in TEM. The solid line is a parabolic function of the distance.

sphere. The histogram, which fits well with a parabolic curve, indicates that the Pt nanoparticles are located mostly at the horn ends. Microwave radiation heats both ethylene glycol and SWNHs. In the present short time intervals of irradiation, in which convection and thermal diffusion are insignificant, SWNHs are heated faster than ethylene glycol in bulk. Although a SWNH is smaller than the wavelength, the near-field radiation can still be focused at the pointing end. In this case, thermal decomposition of ethylene glycol is enhanced near the horn end, where Pt synthesis should occur faster than other regions. Furthermore, the same focusing effect oxidizes the horn end faster than other parts of the SWNH, with additional reactivity gained by non-hexagonal carbons at the horn end. These two enhancement factors explain the observed particle distribution.

4. Conclusion

Only 150 W min of irradiance has a significant effect on dispersibility, and less than 250 W min is sufficient to deposit Pt nanoparticles. The oxidation involves no unwanted acid or high power. The present study demonstrates that microwave irradiation is a simple and highly efficient method to modify the surface properties of SWNHs. It also reveals a possibility of radiation focusing effect at horn ends.

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