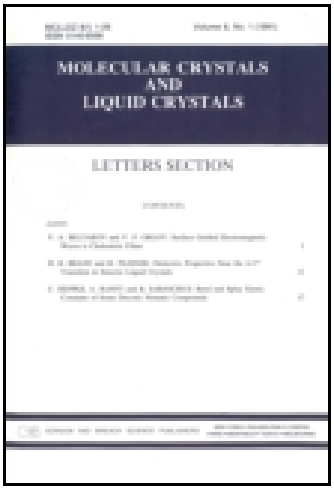

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Electron Beam Reduction Method for Preparing the Catalyst Layer in the Growth of Carbon Nanotubes

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In this paper, electron beam (e-beam) reduction method is applied for the catalyst layer preparation in the growth of carbon nanotubes (CNTs). A hot cathodic electron beam facility was employed to electron bombarding of catalyst layer before stage of CNTs growth. This new method leads to reducing the diameter of particles via sputtering and evaporating the surface of catalyst. The growth of CNTs was performed on the Fe catalyst layer with SiO_2 substrate in an environment of different mixed gases (H_2, NH_3 and C_2H_2) by thermal chemical vapor deposition (TCVD) system. The morphology of the electron beam reduced catalyst particles were probed by atomic force microscopy (AFM). All samples were analyzed by scanning electron microscopy (SEM) before and after growth of CNTs. SEM analyses clarified that the catalyst grains have been smaller under effect of electron beam bombardment.

Keywords Carbon nanotubes; catalyst; electron beam bombardment

Introduction

Nanomaterials based on carbon nanotubes (CNTs) have been widely studied for various applications due to their unique characteristics including small diameters, high electrical conductivity, high surface area to volume ratio, and outstanding mechanical and thermal properties [1,2]. Over the past decade, many techniques have been developed for the synthesis of CNTs, such as arc discharge [3,4] spray pyrolysis method [5], and chemical vapor deposition (CVD) [6–9]. CVD is the most cost effective and promising one among different methods. Currently, the formation of CNTs directly on the metal plate by CVD has attracted much attention [10]. This is because the metal plate can act as the substrate and a catalyst for the growth of the CNTs at the same time. One advantage of this approach is that the superior thermal and electrical conductivities of the metal substrate can improve the electrochemical efficiency of the CNTs/metal system. These products have the potential of being used as electrodes in field emission [11]. A thermal pyrolysis method, based on the CVD of hydrocarbons and transition metal catalysts, is attractive due to its scalability and ease of use. Generally, the pyrolysis method consists of evaporating the precursor and

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carrying it into a pyrolysis furnace. In this method, catalysts play an important role in the growth of CNTs, and typically, transition metals, such as Fe, Co, and Ni, are used as catalysts [12]. Nanoscaled catalyst particles are generally prepared from either physical or chemical methods. Laser ablation [4] and physical vapor deposition (PVD or sputtering) [13] are the commonly reported physical methods for catalyst fabrication. Therefore, control of the surface morphology of the catalytic metal is an essential ingredient before CNTs' growth. In this paper, we aim to prepare catalyst particles with a better distribution and investigate the effect of electron beam bombardment on the catalyst layer on the growth of CNTs. The growth CNTs structures were confirmed by Raman spectroscopy and were further characterized using SEM. The results were then compared and discussed.

Experimental

In this method, silicon (Si) wafers (110) were used as substrates and cleaned by ultrasonics for 10 min in acetone and alcohol baths consecutively and rinsed with distilled water. After cleaning, silicon plates were thermally oxidized at 800°C under atmosphere pressure in an electric furnace for 60 min. The furnace composed of a horizontal quartz glass tube with an internal diameter of 75 mm and a length of 1000 mm and pure Cr-Al as heating elements. After oxidation, pure Fe layer with 30-nm thickness was deposited as catalyst by magnetron sputtering system. Some of the specimens were directly bombarded by high energy electron beam ($I = 104$ μA, $V = 20$ kv, $t = 20$ s), emitted from Al cathode (anode is stainless steel). All of the samples were placed into the quartz reactor for growth stage. Samples were annealed in Ar gas ambient with a flow rate of 200 sccm (Standard Centimetre Cubic per Minute) into the quartz CVD reactor. Ar gas ambient prevents the oxidation of catalytic

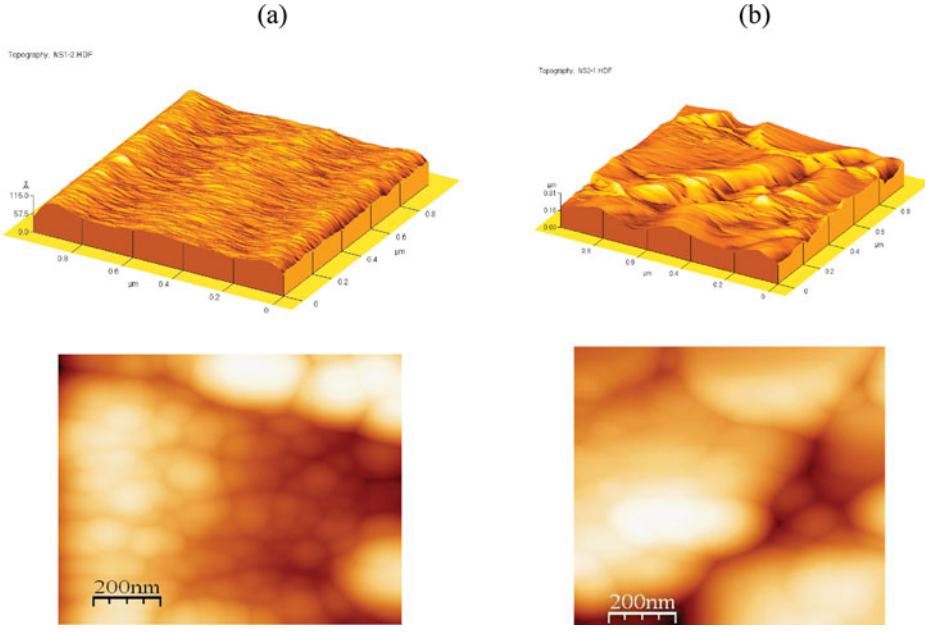

Figure 1. 2D and 3D AFM images of Fe catalyst: (a) without pretreatment; (b) bombarded with electron beam.

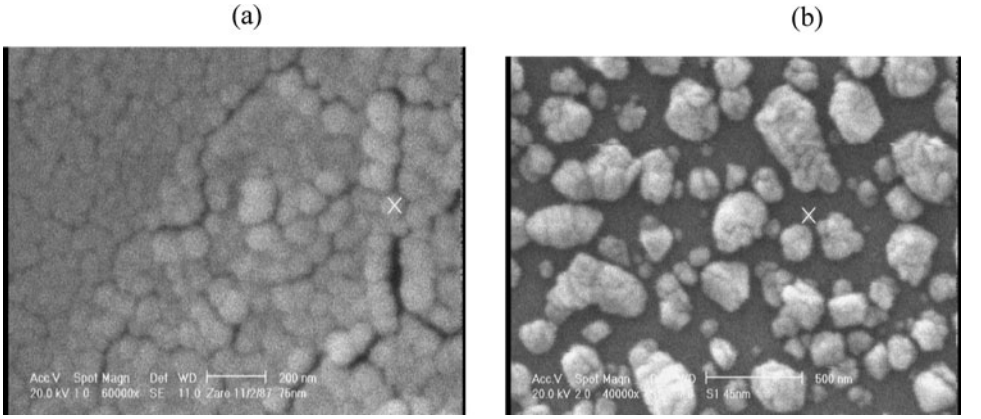

Figure 2. SEM images of Fe catalyst: (a) without any pretreatment; (b) bombarded with electron beam.

metal while increasing the temperature to 400°C. Then Ar flow was switched to H_2 as an etching and diluting gas while the samples are heated to reduction temperature at 700°C. Samples were processed by NH_3 and H_2 gases with a flow rate of 100 sccm at 700°C for 10 min. The CNTs were grown using C_2H_2 gas added to the previous mixture of gases with a flow rate of 20 sccm at 800°C. The gases with purity of 99.5% were employed in the experiment. After growth, Ar was flowed on the samples that were cooling down slowly to room temperature. All substrates were analyzed by atomic force microscopy (AFM) to investigation of surface morphology before growth of CNTs. Raman spectroscopy using an Nd:Ylf laser (532) and scanning electron microscopy (SEM, LEO.440i, 15–20. KV) were employed to confirm the graphite formation of CNTs.

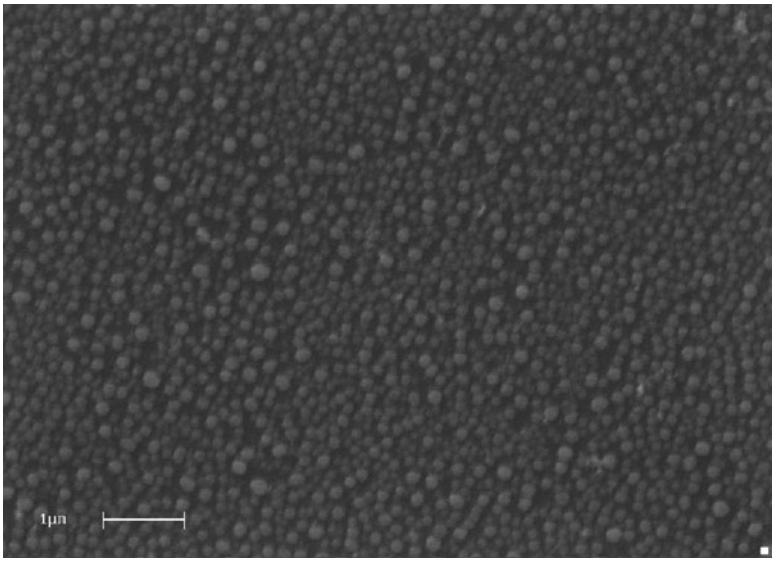

Figure 3. SEM image of Fe catalyst layer after reduction process.

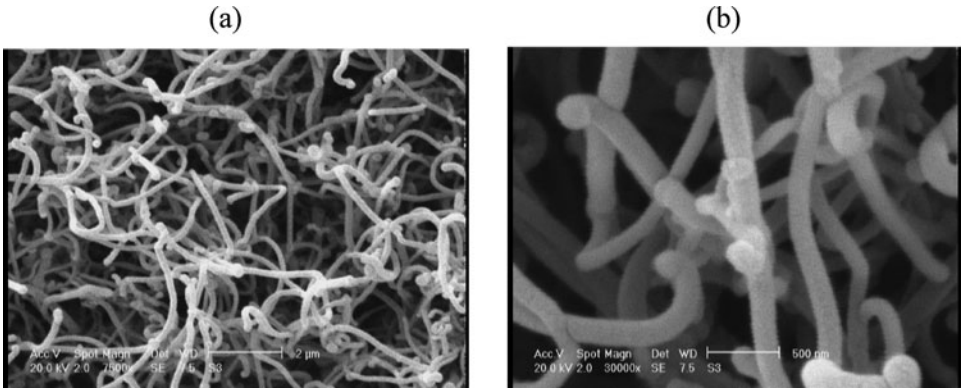

Figure 4. Morphologies of CNTs synthesized at 800°C for 30 min (not pretreated samples): (a) low magnification; (b) high magnification.

Results and Discussion

The morphology of the electron beam-prepared catalyst particles has been analyzed with AFM. We observed that electron beam bombardment has an effective influence on Fe-layer morphology during pretreatment. Due to the electron beam impact, the particles of catalyst undergo reduction processes, which subsequently leads to reduce the size of nanoscaled catalyst particles. The collision of energetic electrons leads to sputtering effect and the formation of islands on the surface. Figure 1(a) shows AFM image of catalyst-coated substrates without any pretreatment, and Fig. 1(b) shows AFM image of catalyst-coated substrates after electron beam bombardment. The average roughness of not pretreated sample is 6.36Å while the average roughness of substrates bombarded with electron beam is 212Å. Figure 2(a) shows SEM images of not pretreated catalyst-coated substrate. The size of an arbitrarily chosen particle is about 75 nm. Figure 2(b) shows SEM image of pretreated sample by electron beam bombardment. Figure 2(b) shows that electron beam bombardment leads to separation of adhered Fe particles but the particles are still agglomerated. However, it seems that electron beam bombardment makes smaller diameter

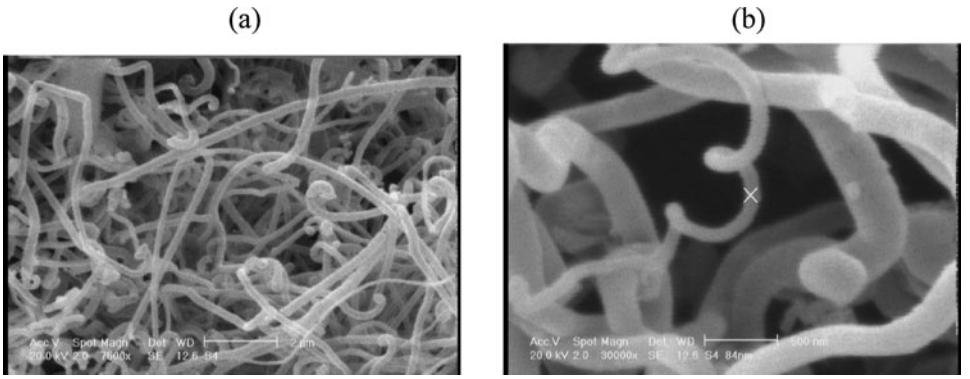

Figure 5. Morphologies of CNTs synthesized at 800°C for 30 min (pretreated samples by electron beam bombardment): (a) low magnification; (b) high magnification.

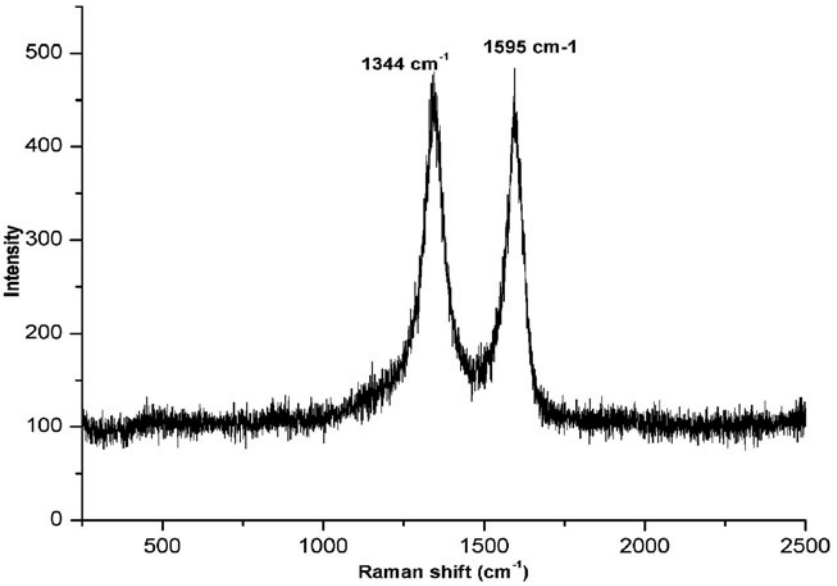

Figure 6. Raman spectra of CNTs synthesized by TCVD at 800°C: not pretreated samples.

of Fe particles; some particles with 45 nm in size can be identified in Fig. 2(b). According to Fig. 3, the agglomerated Fe particles separate from the reduction process of samples at 700°C in H_2 and NH_3 ambient, and this process leads to obtaining a high density of nucleation sites for CNTs growth. We observed a clear satisfactory effect of electron beam on formation of better growth of CNTs. SEM images of CNTs grown on the samples

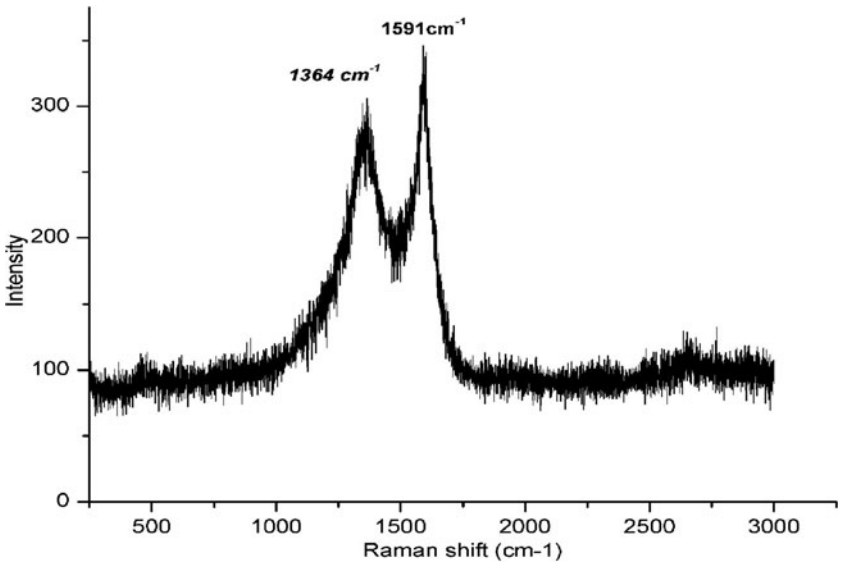

Figure 7. Raman spectra of CNTs synthesized by TCVD at 800°C: pretreated samples by electron beam bombardment.

without pretreatment by electron beam have been shown in Figures 4(a) and (b) with different magnification. The growth of CNTs on pretreated substrates by electron beam is seen in SEM images of samples with different magnification in Figure 5(a) and (b). Figures 6 and 7 show Raman spectra of CNTs synthesized at 800°C; there are two peaks observed, one at about 1600 cm^{-1} and the other at about 1335 cm^{-1}. The peak at 1600 cm^{-1} is the *g*-peak arising due to the ordered graphite crystalline structure [14]. Existence of G-band and D-band indicates the growth of CNTs. A comparison between Figs. 6 and 7 implies that CNTs grown on samples pretreated by electron beam have a higher quality due to higher I_G/I_D.

Conclusions

Carbon nanotubes (CNTs) were synthesized on Fe-coated silicon substrates by thermal CVD using C_2H_2, NH_3, and H_2 gases at 800°C. Electron beam bombardment exerts a great effect on the particles size of the Fe catalyst. SEM images show that CNTs have been grown on samples pretreated by electron beam as well as not pretreated samples. Raman spectra of samples clarified high quality of CNTs grown on samples pretreated by electron beam due to higher I_G/I_D ratio.

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