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Carbon nanotubes decorated by graphitic shells encapsulated Cu nanoparticles

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Abstract Carbon nanotubes (CNTs) decorated by graphitic shells encapsulated Cu nanoparticles were fabricated by low-energy hydrocarbon ion deposition with using Cu as hold substrate at 900°C. Scanning electron microscopy shows that the surface of CNTs becomes very coarse by hydrocarbon ion treatment. The investigation of transmission electron microscope shows that the full surfaces of CNTs are coated by dense graphitic shells encapsulated Cu nanoparticles. The graphitic shells consist of 7–10 layers and the size of Cu core is 1–2 nm.

1 Introduction

Carbon nanotubes (CNTs) have been considered one of the most promising materials for field emission application, nanoscale electronic and optoelectronic devices, due to their high electrical conductivity, high aspect ratio "whisker-like" shape for optimum geometrical field enhancement, and remarkable thermal stability [1]. Modifications of the nanotubes could provide diverse technological applications ranging from wiring in integrated circuits and nanoscale components to composite materials by organizing them after functionalization [2, 3]. Recently, carbon-encapsulated metal nanoparticles have attracted much attention for their wide promising application. The novel structure of the encapsulating second phase inside carbon shells can immunize the encapsulated species against environmental degradation effects while retaining their intrinsic properties, and also offers an opportunity to investigate a dimensionally confined system [4]. Some metal could be compatible with the organism due to the effect of encapsulating carbon layer. The carbon-encapsulated magnetic metal nanocapsules exhibited good microwave absorption properties because of their special core/shell structure [5, 6]. In addition, carbon-encapsulated metal nanoparticles could be applied in the magnetic record materials,fine ceramics and so on. It is believed that the synergistic combination of CNTs and carbon-encapsulated metal nanoparticles could give rise to materials with novel properties, which could be used advantageously in applications such as information technologies, biomedicines and radar-absorbing materials.

Various techniques have been developed to synthesize carbon-encapsulated metal nanoparticles, including standard and modified carbon arc techniques [7], tungsten arc technique [8], magnetron and ion-beam co-sputtering [9], high-temperature annealing of the mixtures of carbon-based materials and metal precursors [10], catalytic carbonization process [11], catalytic chemical vapor deposition and pyrolysis of organometallic compounds [12, 13]. Up to now, CNTs modified by the carbon shells encapsulated metal nanoparticles have been achieved by above-mentioned techniques. In general, the carbon shells encapsulated metal nanoparticles are on the cap of the CNTs, and the size of carbon-encapsulated metal nanoparticles materials is in agreement with the diameter of CNTs, typically several tens nm [14–18]. One important parameter of modification is the degree of CNTs functionalization, that is, the degree of CNT coverage with carbon-encapsulated metal nanoparticles materials. The size of carbon-encapsulated metal nanoparticles would be smaller for the investigation of the dimensionally confined system. Therefore, there is still

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a challenge for fabricating the CNTs coated by high-density carbon-encapsulated metal nanoparticles with small size.

In the present work, CNTs decorated by graphitic shells encapsulated Cu nanoparticles have been fabricated through the low-energy hydrocarbon ion deposition using Cu as hold substrate at 900°C, the full surface of the CNTs is coated by graphitic shells encapsulated Cu nanoparticles with 7–10 graphitic shells and 1–2 nm of Cu core size.

2 Experiment

Multi-walled carbon nanotubes (MWCNTs), synthesized by chemical vapor deposition (CVD), were dispersed in alcohol by ultrasonic waves, dropped onto Cu substrates and formed thin film as the samples. The samples were placed in the chamber of Kaufman low-energy gas ion source. At first, the temperature of the substrate was heated to 900°C and kept for half an hour, then a mixture of methane and hydrogen was introduced into the ion source as the working gas at 2×10^{-1} Pa. The gas volume ratio of hydrogen to methane (H_2/CH_4) was 5/1 and the samples were irradiated by ion beam for 1.5 h with energy of 80 eV and current intensity of 60 μA/cm^2. In the process of ion treatment, the substrate temperature was maintained at 900°C. The morphology evolution of samples before and after the low-energy ion treatment was observed through scanning electron microscopy (SEM, LEO 1530VP). The characteristic of structural changing of CNTs was investigated by transmission electron microscope (TEM, JEOL 2010F) operated at 200 kV. In order to investigate the present of Cu, the CNTs by ion treatment were dispersed on the Ni grid as TEM samples.

3 Results and discussion

Figure 1 shows SEM images of as-grown CNTs and CNTs treated by hydrocarbon ions for 1.5 h at 900°C. The diameters of CNTs by CVD were 18–35 nm and the surfaces were very smooth. After hydrocarbon ion irradiation, the surfaces of CNTs were coarse, ripple and coated by some nanoparticles. The diameters of CNTs were 40–50 nm.

The typical TEM and high resolution TEM (HRTEM) images of as-grown CNTs and CNTs irradiated by hydrocarbon ions at 900°C are shown in Fig. 2. The as-grown CNTs are well structured and typically consisting of 20–30 concentric shells of carbon sheets. After hydrocarbon ion treatment, the inner hollow structure of the CNTs is intact and the surface is very coarse. The full surfaces of CNTs are coated by nanoparticles with uniform size of 5–10 nm and there are some smaller particles appearing as "dust" cluster was in the cores of these dense nanoparticles (as shown in Fig. 2b).

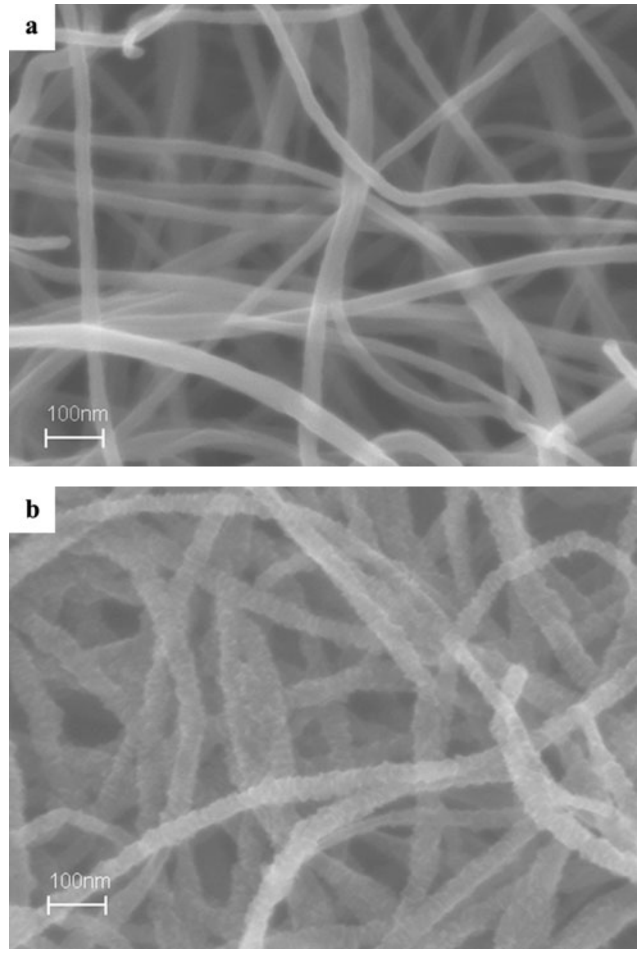

Fig. 1 Morphologies of the as-grown CNTs and CNTs by hydrocarbon ion irradiation at 900°C using Cu as hold substrate: (**a**) as-grown CNTs; (**b**) CNTs treated by hydrocarbon ions

The energy dispersive X-ray spectra (EDX) demonstrate the presence of carbon and copper. It can be speculated that these "dust" clusters are the activity of Cu. The investigation of HRTEM indicates that the products consist of Cu–C core-shell structure nanoparticles with typical shell size of 5–10 nm and core size of 1–2 nm, as shown in Fig. 2d. The carbon shells tightly surround the core nanoparticles, no obvious voids can be observed between the core and shell. The shells are uniform in thickness and usually consist of 7–10 layers. The spacing of the lattice fringes is about 0.34 nm, which is equal to the lattice spacing of graphite (002) planes. Therefore, the investigation of SEM and TEM indicates that CNTs decorated by graphitic shells encapsulated Cu nanoparticles have been fabricated by low-energy hydrocarbon ion deposition by using Cu as hold substrate at 900°C. The particles of graphitic shells encapsulated Cu nanoparticles were uniform and consist of 7–10 graphitic shells with the Cu nanoparticle size of 1–2 nm.

It is known that various techniques have been developed to synthesize carbon-encapsulated metal nanoparticles, such

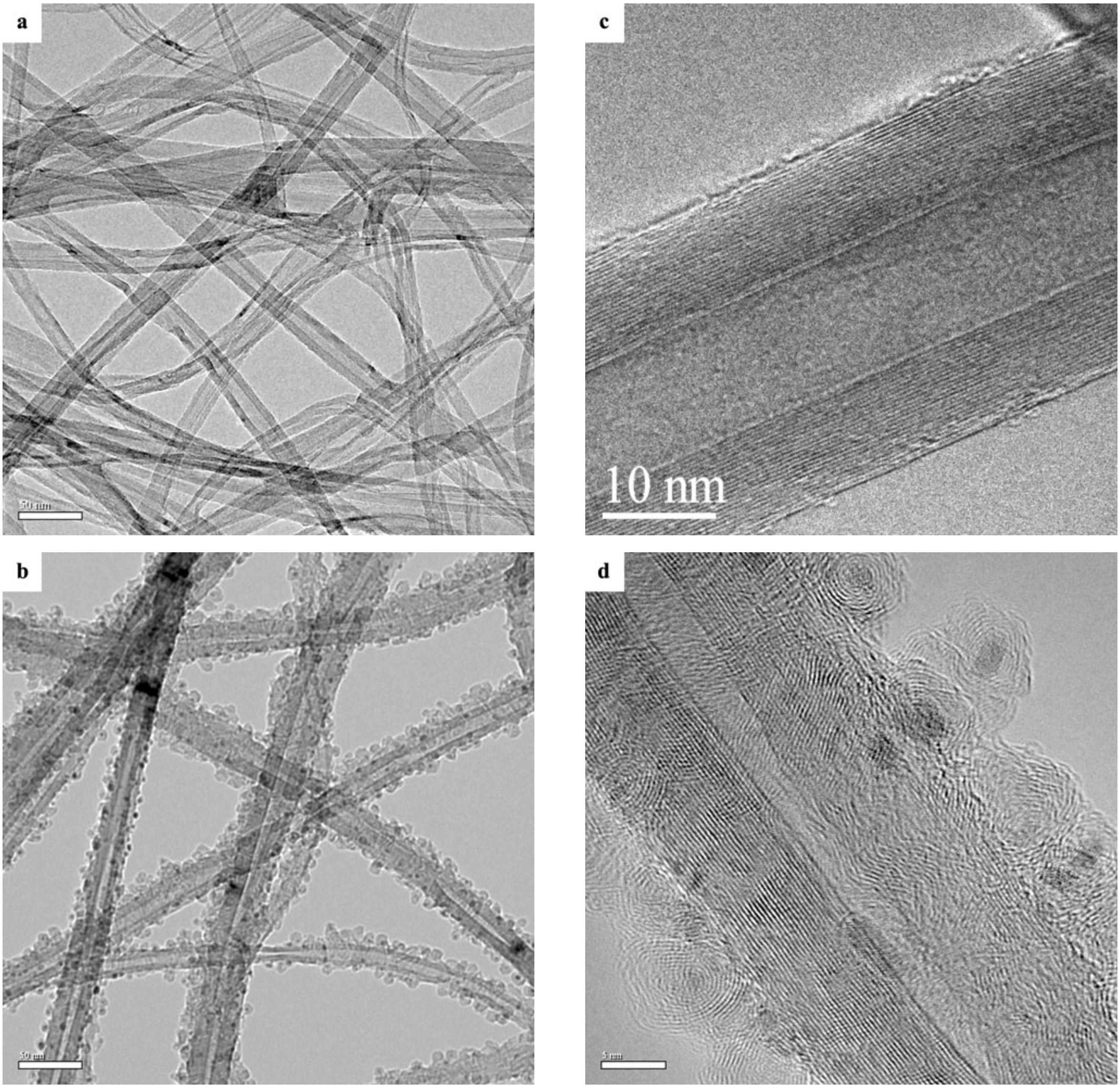

Fig. 2 The microtextures of as-grown CNTs and CNTs by hydrocarbon ion irradiation at 900°C using Cu as hold substrate. (**a**) and (**c**) Typical TEM and HRTEM images of as-grown CNTs; (**b**) and (**d**) typical TEM and HRTEM images of CNTs treated by hydrocarbon ions

as carbon arc techniques, tungsten arc technique, magnetron and ion-beam co-sputtering, catalytic chemical vapor deposition and pyrolysis of organometallic compound [7–13]. Meanwhile, the investigation shows that the growth mechanism of carbon-encapsulated metal nanoparticles is almost similar. At first, the small carbon and metal species are produced induced by various techniques. Then, these species condense into solid materials when they are cooled and the simultaneous condensation of metal cluster and small carbon species leads to the formation of metal and carbon alloy. When the carbon dissolution in the metal nanoparticles reaches saturation, pure carbon materials around the nanoparticles would start to precipitate. The precipitation of carbon is endothermic (some 40.5 kJ mol^{-1} of graphite [19]) and would cause a decrease of local temperature. The cooling of the alloy prevails and stimulates further carbon precipitation as a result of the decrease of the carbon solubility [20–22], and results in the formation of carbon-encapsulated metal nanoparticles. Therefore, it is believed that the mechanism of the graphitic shells encapsulated Cu nanoparticles in our experiment is accorded with that of graphitic shells encapsulated metal nanoparticles by other techniques, mentioned above. At first, some Cu atoms gained enough energy at high temperature and escaped from the surface of substrate and became Cu species. Then, the Cu and carbon alloys were formed under the interaction of Cu species and the carbon species provided by low-energy hydrocarbon ions. Subsequently, with the duration of hydrocarbon ions, the carbon dissolution in the Cu nanoparticles reaches saturation and a precipitation of pure carbon around the nanoparticles would start in the form of graphite, as a result of the formation of graphitic shells encapsulated Cu nanoparticles.

CNTs modified by high density and small size of graphitic shells of encapsulated Cu nanoparticles have been achieved by our simple technique. It can be expected that this novel material possesses other advantageous properties. These hybrid materials may open new avenues for application of biomedicines, radar-absorbing materials and the investigation of the dimensionally confined system. In the future, the physical and chemical properties of this hybrid materials and the controlled fabrication of CNTs modified by graphitic shells encapsulated Cu and other metal nanoparticles will be investigated.

4 Conclusions

The nanoscale hybrid material of carbon nanotubes (CNTs) decorated by graphitic shells encapsulated Cu nanoparticles has been fabricated by low-energy hydrocarbon ion deposition with using Cu as hold substrate at 900°C. Scanning electron microscopy shows that the surface of CNTs becomes very coarse and is rippled by hydrocarbon ion treatment. The investigation of transmission electron microscope shows that surfaces of CNTs are coated by graphitic shells encapsulated Cu nanoparticles. The shells are uniform in thickness, usually consisting of 7–10 layers, and the size of the Cu core is 1–2 nm. It is very simple to achieve a high density and small size of graphitic shells of encapsulated Cu nanoparticles in our experiment.

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