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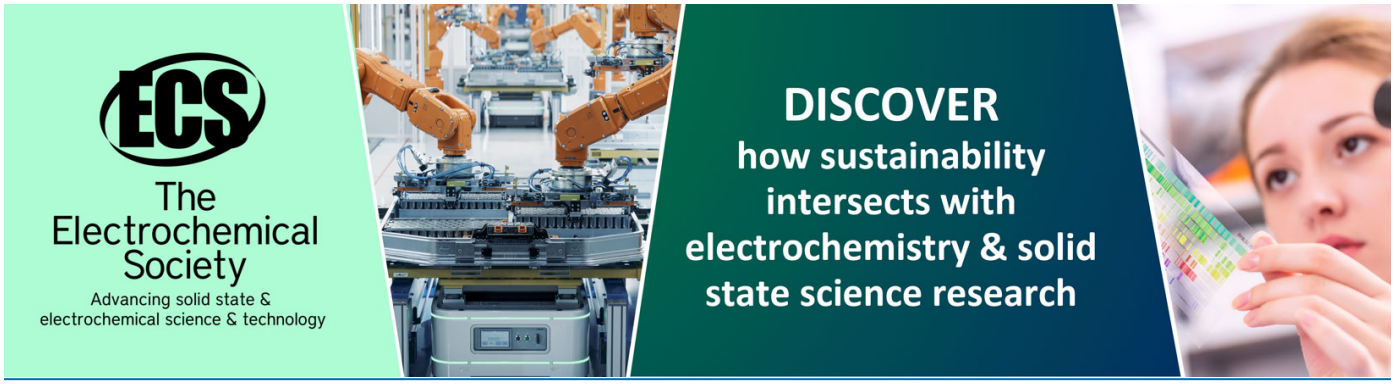

Effect of pretreatment on the microstructure of multiwalled carbon nanotubes

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Abstract. Four kinds of multi-walled carbon nanotubes pretreated by different methods were studied. Chemically functionalized (hydroxylation and carboxylation) CNTs were prepared by oxidizing original CNTs in H_2SO_4 solutions of different temperatures and concentrations by $KMnO_4$. Graphitized CNTs were prepared by heat-treating original CNTs in an inert gas at 2800°C for 20 hours. CNTs Nickel plating on the surface was obtained by electroless plating. The effect of pretreatment on the surface state and microstructure of carbon nanotubes was also studied. The results showed that Chemical functionalization could form some functional groups on the surface of CNTs, which could not only improve the compatibility of CNTs with some solvents, but also purified CNTs, which had a positive effect on the preparation of composite materials. High-temperature graphitization treatment could significantly increase the degree of crystallization of carbon nanotubes and reduce structural defects. After electroless nickel plating, evenly distributed nano-sized metal particles were formed on the surface of the CNTs, and the interface between the two was well bonded.

1. Introduction

Carbon nanotubes have excellent mechanical properties and super physical properties (such as bending strength up to 14.2GPa, thermal expansion coefficient almost zero, and thermal conductivity at room temperature up to 3000W/mK, etc.), which are ideal reinforcements for metal matrix composite materials [1–5]. Raw carbon nanotubes usually contain many structural defects and impurities, including amorphous carbon, fullerenes, metal catalyst particles and carbon nanoparticles. In addition, because carbon nanotubes have a large aspect ratio and specific surface area, their high surface energy makes the carbon nanotubes often adsorb together with van der Waals force, and the van der Waals binding energy between the carbon nanotubes in contact with each other is about 500eV/um. Due to the lack of active groups on the surface of carbon nanotubes, the solubility in various solvents is very low, which brings great difficulties to dispersion. In addition, the preparation of carbon nanotube-reinforced metal matrix composites often undergoes a high-temperature process, and in a high-temperature environment, various carbon-containing impurities in carbon nanotubes are likely to interact with the metal matrix to form brittle intermetallic compounds. At the same time, the coiled shape of carbon nanotubes also causes their surface to be inert. During the preparation of composite materials, the interface between them and the matrix is weak. These factors would reduce the performance of composite materials. To solve these problems, carbon nanotubes need to be pretreated, including purification, high-temperature graphitization and surface modification.

In this paper, four kinds of multi-walled carbon nanotubes pretreated by different methods were studied. Chemically functionalized (hydroxylation and carboxylation) CNTs were prepared by oxidizing original CNTs in H_2SO_4 solutions of different temperatures and concentrations by KMnO4. Graphitized CNTs were prepared by heat-treating original CNTs in an inert gas at 2800°C for 20 hours. CNTS Nickel plating on the surface was obtained by electroless plating. The effect of pretreatment on the surface state and microstructure of carbon nanotubes was studied, which laid the foundation for the preparation of high-performance metal matrix composites with better carbon nanotube dispersion and better CNT and metal matrix interface bonding.

2. Experimental details

2.1 Materials

Multiwalled carbon nanotubes were purchased from Shenzhen Nanotech Port Co., with length of 5-15 μm, diameter of 40-60 nm, and purity more than 97 wt.%.

2.2 Analysis and characterization

The microstructure of CNTs was observed by scanning electron microscope (Nova Nano SEM 450) and transmission electron microscope (JEOL 2100). The changes of polar groups on the carbon tube surface after pretreatment were detected by infrared spectrum scanning on Nicolet IS10 Fourier Infrared Transformer.The crystallization degree and structural integrity of the original CNTs, as well as the damage degree and structural changes of the CNTs during ball milling was studied by Raman spectrometer (Jobin YvonHR800) with the laser wavelength of 532 nm and the power of 0.1 mW.

3. Results and discussion

3.1 Pretreatment of carbon nanotubes

Four kinds of multi-walled carbon nanotubes pretreated by different methods were studied as shown in Table 1. Chemically functionalized (hydroxylation and carboxylation) CNTs were prepared by oxidizing original CNTs in H_2SO_4 solutions of different temperatures and concentrations by $KMnO_4$. Graphitized CNTs were prepared by heat-treating original CNTs in an inert gas at 2800°C for 20 hours. CNTs Nickel plating on the surface was obtained by electroless plating.

Table 1 Multi-walled carbon nanotubes pretreated by different methods

Sample	Outer diameter /nm	Length/μm	Purity /wt.%	-OH wt.%	-COOH wt.%	Ni wt.%
Original state	~50.0	10.0-20.0	98.0	-	-	-
Hydroxylation	~50.0	10.0-20.0	98.0	0.7	-	-
Carboxylation	~50.0	10.0-20.0	98.0	-	0.5	-
Graphitization	~50.0	10.0-20.0	98.0	-	-	-
Nickel plated	~50.0	10.0-20.0	98.0	-	-	~60.0

3.2 Chemical functionalization of Carbon nanotubes

Figure 1 showed the microscopic morphology of CNTs in the original state and after hydroxylation and carboxylation treatment. As shown in Figure 1, the morphology of carbon nanotubes after chemical functionalization treatment had no significant change compared with that before treatment. Carbon nanotubes have a diameter of about tens of nanometers and a length of a few micrometers, and they were entangled to form a carbon nanotube bundle.

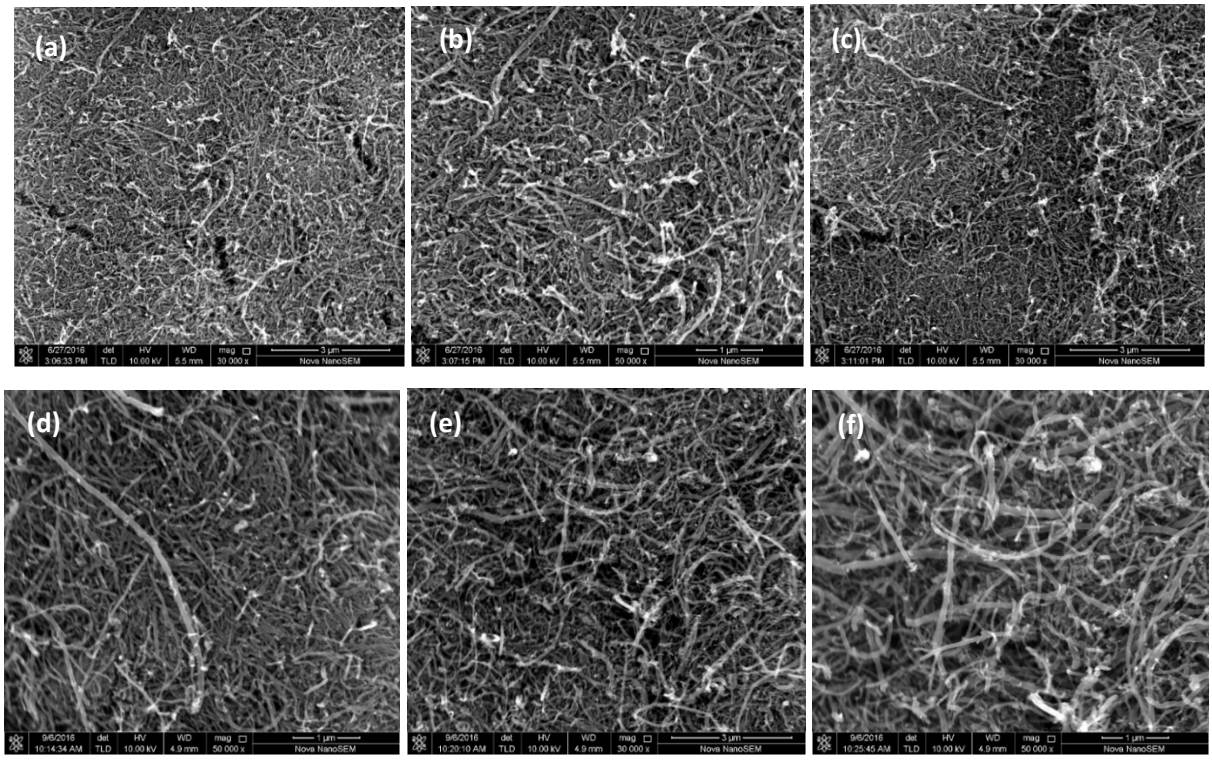

Figure 1 Microscopic morphology of CNTs after chemical functionalization

The infrared spectrum of carbon nanotubes after chemical functionalization was shown in Figure 2. It could be found that there was almost no absorption peak in the original CNTs, indicating that there were almost no functional groups on the surface. In contrast, CNTs after chemical functionalization produced many characteristic peaks, but the nominal hydroxylation or carboxylation treatment had little difference in functional groups. In other words, -OH (3450cm^{-1}, 3600cm^{-1}, 1050~1150cm^{-1}) and -COOH (1730cm^{-1}) existed on both surfaces. The reason for the formation of functional groups on the surface of CNTs was that strong oxidants could cause CNTs to be damaged or broken to a certain extent. There were carbon atoms with two unsaturated bonds in the cracks on CNTs and the defects of amorphous carbon, which could easily combine with free oxygen atoms decomposed by acid to form a carbonyl group, and then the carbonyl group continues to interact with H^+, OH^- in water to form hydroxyl and carboxyl groups [6].

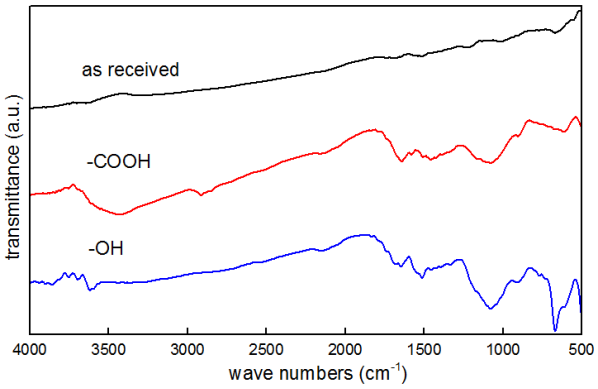

Figure 2 Infrared spectrum of CNTs after chemical functionalization

Figure 3 showed Raman spectra of CNTs after chemical functionalization. There were two distinct characteristic peaks on the Raman spectrum curve, G peak at about 1580 cm^{-1} and the D peak near 1350 cm^{-1}. G peak originated from the optical phonon mode of two unequal carbon atoms in the

graphite unit cell. It was related to the in-plane tangential vibration of the carbon atoms and was a characteristic peak of crystalline carbon. Peak D was generally considered to be caused by various disorder. The disordered structure in carbon nanotubes could be attributed to its own structural defects (vacancies, impurity atoms, five- to seven-membered rings), nano-scale graphite sheets and the existence of other carbon allotropes (such as sp^3 or incomplete sp^2 hybridized carbon atoms) [7-10]. In general, the smaller the ID/IG, the higher the degree of graphitization, and the more complete the structure of CNTs [11-14]. The ID/IG values of the original state, carboxylated and hydroxylated CNTs were 0.68, 0.65 and 0.56, respectively, indicating that the impurity content in the CNTs was reduced after functionalization. On the one hand, chemical functionalization could form some functional groups on the surface to improve the compatibility of CNTs with some solvents, and on the other hand, it could purify CNTs, which had a positive effect on the preparation process of composite materials.

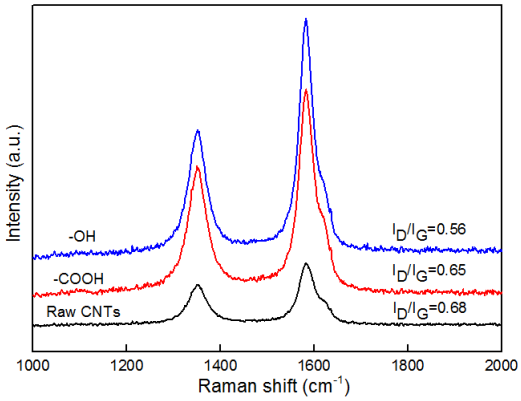

Figure 3 Raman spectra of CNTs after chemical functionalization

3.3 High-temperature graphitization of carbon nanotubes

Figure 4 showed the microscopic morphology of carbon nanotubes after high-temperature graphitization treatment, which still appeared to be coiled and entangled with each other. Figure 5 showed the Raman spectrum of the original state and the graphitized CNTs. The ID/IG value of the latter was only 0.19, which was significantly lower than 0.68 of the original state CNTs, which also proved that the carbon nanotubes are highly graphitized. In the process of high temperature graphitization, the energy required for graphitization of the discontinuous microcrystalline structure of the inner layer of carbon nanotubes was provided by heat. Crystal merger and growth. The outer layer of amorphous carbon mainly relied on the catalysis of simple metals (such as iron and titanium) to achieve graphitization by first forming carbides and then decomposing to form graphitizable carbon.

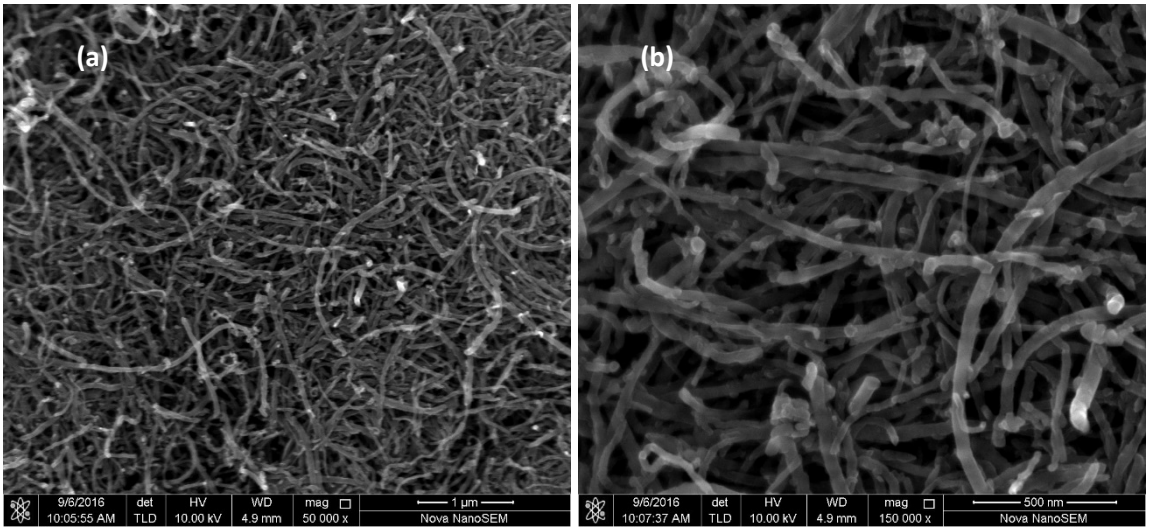

Figure 4 Microscopic morphology of CNTs after high-temperature graphitization treatment

(a)50000×; (b) 150000×

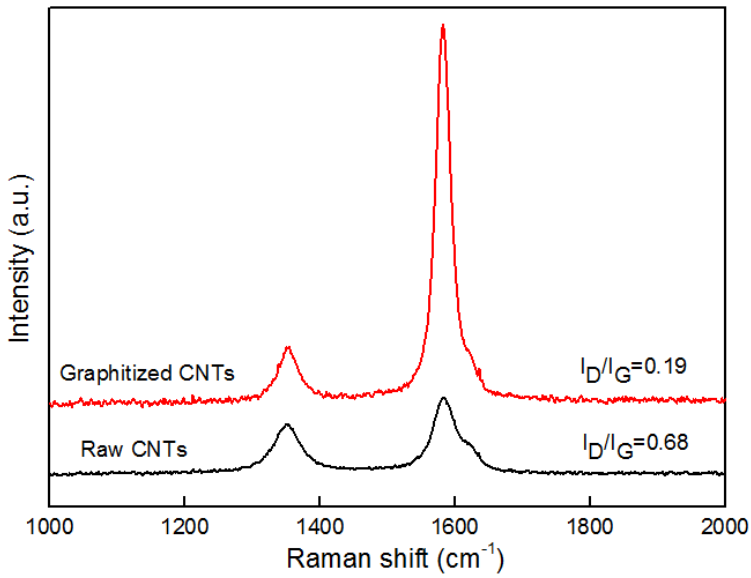

Figure 5 Raman spectrum of the original state and the graphitized CNT*s*.

3.4 Nickel plating on the surface of carbon nanotubes

Figure 6 showed the microscopic morphology of carbon nanotubes after electroless nickel plating. Nano-sized metal particles were uniformly coated on the surface of the carbon nanotubes, and the two were well bonded. Since carbon and aluminum were non-wetting, the bonding force at the interface was often weak. Obviously, the use of metallic nickel as the plating layer would improve the compatibility and make the interface form a good bonding state, so that the material played the role of effective load transfer during the load process.

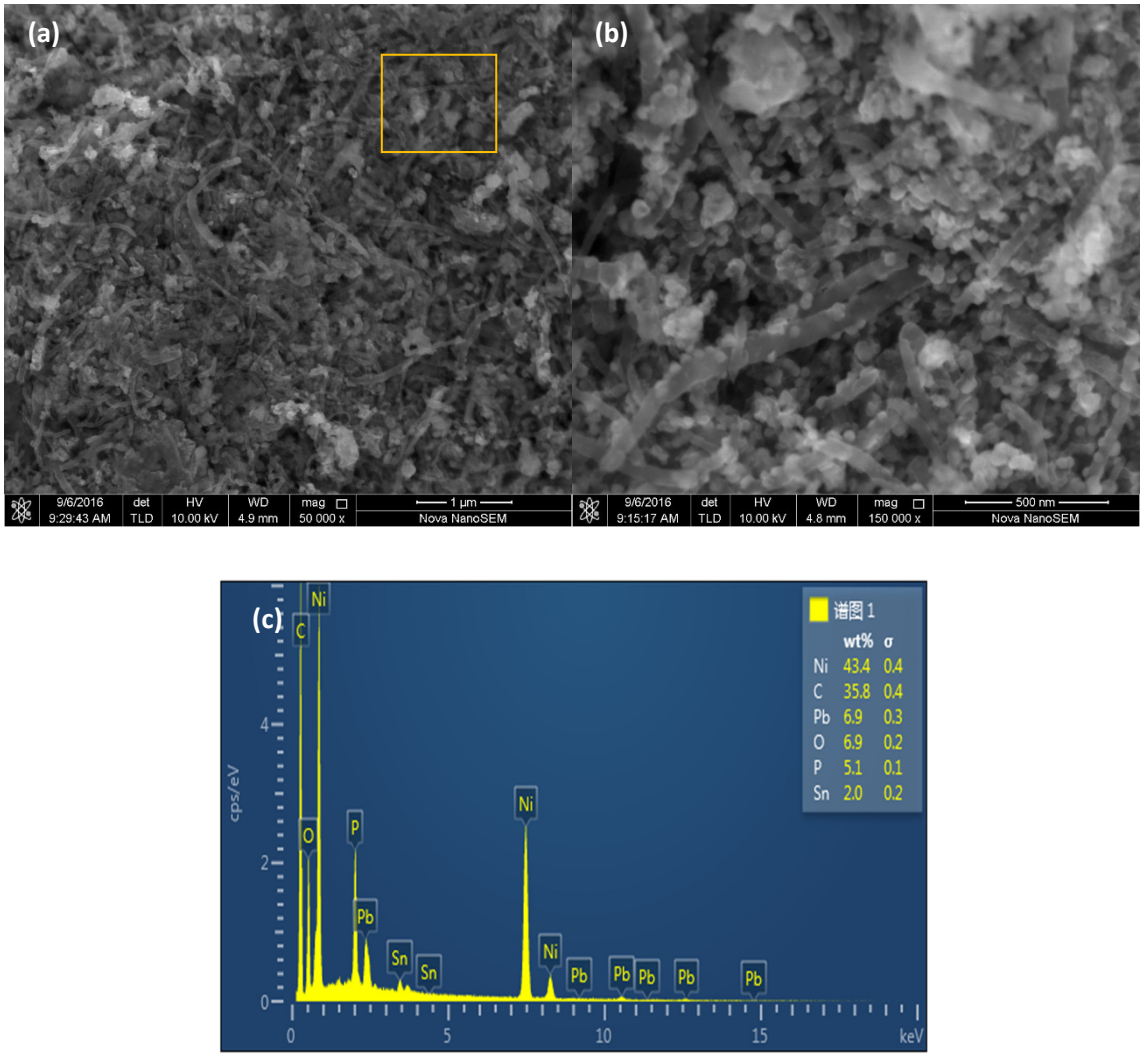

Figure 6 microscopic morphology of carbon nanotubes after electroless nickel plating

(a)50000× (b) 150000× (c) Energy spectrum analysis in the frame of (a)

4. Conclusions

Following conclusions were drawn from this work:

(1) Chemical functionalization could form some functional groups on the surface of CNTs, which could not only improve the compatibility of CNTs with some solvents, but also purified CNTs, which had a positive effect on the preparation of composite materials.

(2) High-temperature graphitization treatment could significantly increase the degree of crystallization of carbon nanotubes and reduce structural defects.

(3) After electroless nickel plating, evenly distributed nano-sized metal particles were formed on the surface of the CNTs, and the interface between the two was well bonded.

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