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Electroless plating of carbon nanotubes with silver

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The primary function of electrical contact materials is to carry current and to break it [1, 2]. Silver-graphite composites are typical electrical contact materials. Graphite has its deficiencies including brittleness, low strength, and current-carrying capacity [3]. Carbon nanotubes with many excellent properties, such as high tensile strength, excellent toughness, good electrical conductivity, low friction, are considered to be the ideal type of fiber-like reinforcements [4–6]. It is supposed that silver reinforced with carbon nanotubes would be better than graphite or carbon fiber. As with carbon fiber-reinforced metal matrix composites, the performance of the carbon nanotubes-reinforced metal matrix composites is largely controlled by the interface between the nanotubes and the metal matrix. The metal matrix poorly wets carbon nanotubes so that the interface of carbon-nanotubes–silver is extremely weak. To enable maximum loading of the carbon nanotubes, an adequate interface strength between the nanotubes and matrix is essential. Our previous work shows that surface treatment is an effective way to improve interfacial adhesion of composites [7, 8]. In this paper electroless plating is used as it can deposit many metals on almost any substrates regardless of size and shape. On the other hand, the selection of silver coating is based on the fact that carbon nanotubes are used as reinforcements for silver matrix electrical contact composites.

The multiwalled carbon nanotubes used in this work were provided by Shenzhen Nanotech Port Co. Ltd. The diameter of the nanotube is 30–50 nm, the length is 0.5–500 μm, and the purity is 95%. Before electroless plating, pretreatments including oxidation, hydrophilic treatment, sensitizing treatment, and activating treatment were performed on the carbon nanotubes. Oxidation: carbon nanotubes were immersed in the mixture of H_2SO_4 and HNO_3 (1:3) at 120 °C for 10 h. The carbon nanotubes were washed with distilled water and separated the medium by centrifugation. Sensitization and activation: like graphite, the surface of carbon nanotubes has low chemical reactivity and does not act as a catalyst for the deposition of the silver and no metal coating takes place. As a consequence, a preactivation (surface catalyst) was needed and this was accomplished by immersion of the carbon nanotubes for 30 min in aqueous solution (previously aged for 72 h at room temperature) of 0.1M$SnCl_2$–0.1MHCl, followed by rinsing in distilled water and immersion for a further 30 min in an aqueous solution of 0.0014M$PdCl_2$-0.25MHCl. The soaking time in both solutions was longer than usual for other materials in order to add activated sites. The activated carbon nanotubes were washed with distilled water and separated the solution by centrifugation and then introduced in the electroless bath. The composition of the electroless bath and the reaction conditions are given in Table I.

The chemicals used in this experiment were all analyzed reagent products. During sensitization, activation, and electroless plating, the reaction mixture was agitated using ultrasonic method and carbon nanotubes were separated from the solution by centrifugation. The surface morphology of the carbon nanotubes after electroless plating was observed and analyzed by the transmission electron microscope (TEM) and the energy-dispersive X-ray analytical system (EDX).

The procedure of the electroless plating of carbon nanotubes with silver is shown in Fig. 1.

The carbon nanotubes have low chemical reactivity, large surface curvature, small diameter, and large aspect ratio, so it is difficult to make a continuous electroless plating layer for carbon nanotubes. A series of ways are used to increase the number of activated sites and improve the silver coating. To modify the surface chemistry and improve dispersion in the electroless bath, carbon nanotubes were first subjected to an oxidation treatment in the mixture of nitric acid and vitriolic acid. Fig. 2 shows the TEM image of carbon nanotubes before oxidation treatment. From the TEM image, we can see that the nanotubes twisted as a result of high chemical activity and large ratio of length to diameter of the nanotubes. Fig. 3 shows that the oxidation made carbon nanotubes short and improved their dispersion in solution. Some previous studies show that nitric acid could create various functional groups (such as $-$COOH, $-$OH, and $-$C$=$O) on the surface of carbon nanotubes (Fig. 1a), which can remarkably modify wettability and further increase the absorption velocity of Sn^{2+} in the sensitizing solution to the surface. H_2SO_4 can absorb the water produced by HNO_3 and carbon nanotubes and makes the reaction continuous [9]. The oxidation of carbon nanotubes by a solution of

TABLE I Bath composition and operating condition for electroless plating

Chemical	Concentration
$AgNO_3$	10 kg/m^3
$NH_3{\cdot}H_2O$	1.5 (vol%)
HCHO (added later)	3.0 (vol%)
pH: 8.5 ± 0.5; Temperature: 20 °C	

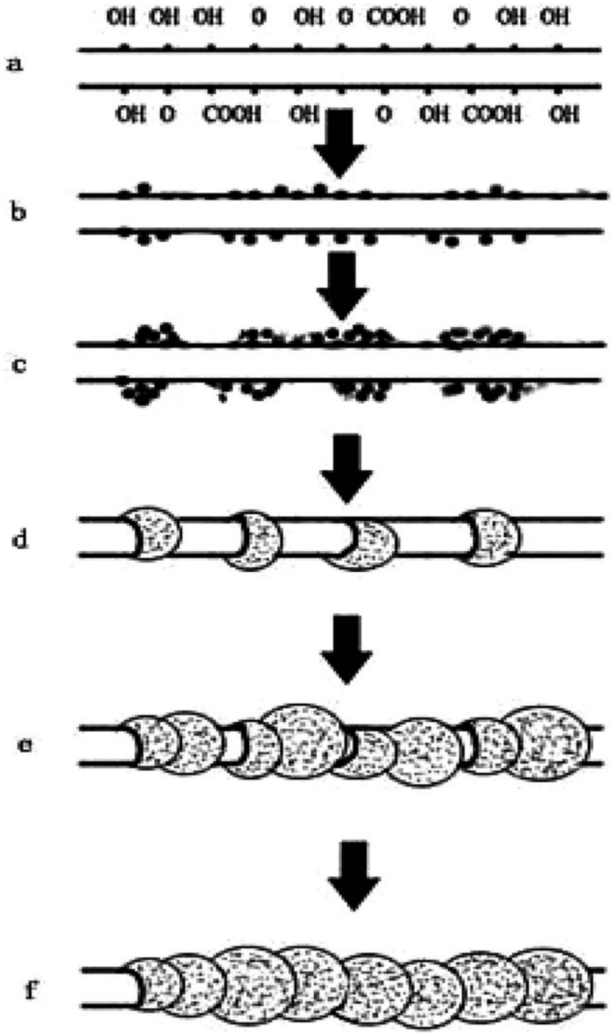

Figure 1 The procedure of the electroless plating of carbon nanotubes with silver: (a) oxidization, (b) sensitization, (c) activation, (d) silver particles depositing, (e) silver particles growing, and (f) silver particles filming.

H_2SO_4–HNO_3 not only improves their dispersion in the solution but also enhances the wetting efficiency by the colloidal polymeric sensitizer, and increased activated sites on the surface of the carbon nanotubes.

During the sensitization process, Sn^{2+} ions were deposited on the surface of the carbon nanotubes (Fig. 1b).

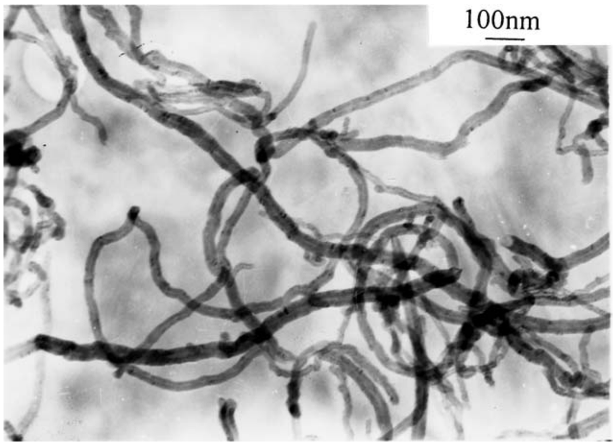

Figure 2 TEM image of original carbon nanotubes.

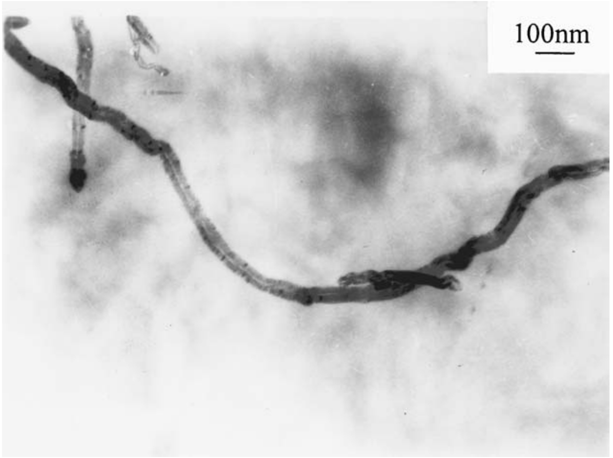

Figure 3 TEM image of oxidized carbon nanotubes.

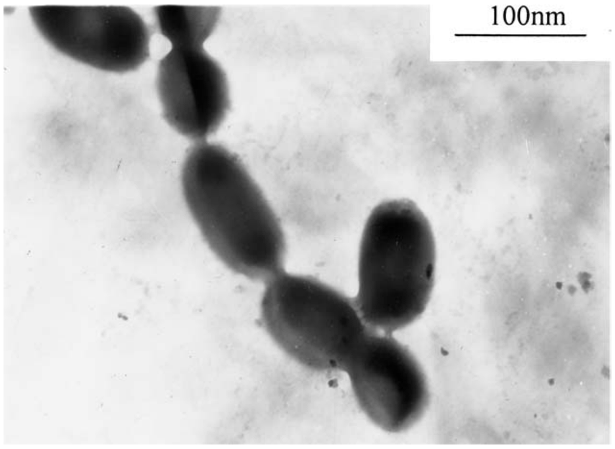

Figure 4 TEM image of carbon nanotube coated with a discontinuous silver layer.

When introduced in the activation solution, Pd^{2+} ions were reduced to Pd by Sn^{2+} and these Pd particles were distributed on the surface of the nanotubes and acted as catalytic centers (Fig. 1c). During electroless plating, the above individual Pd catalytic center would reduce silver ions to neutral silver atoms (Fig. 1d), silver particles grew laterally and vertically (Fig. 1e) and formed a continuous coating layer (Fig. 1f).

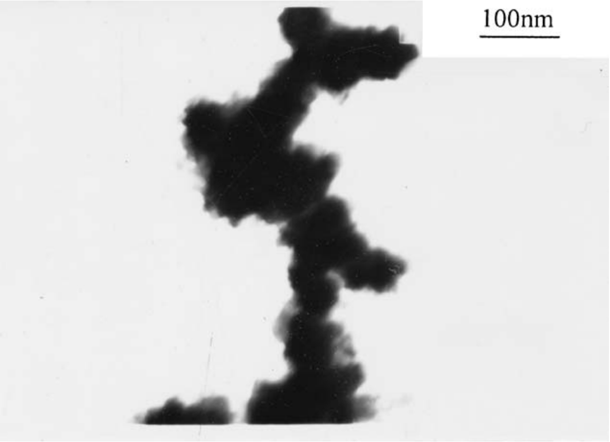

Figure 5 TEM image of carbon nanotube coated with a continuous silver layer.

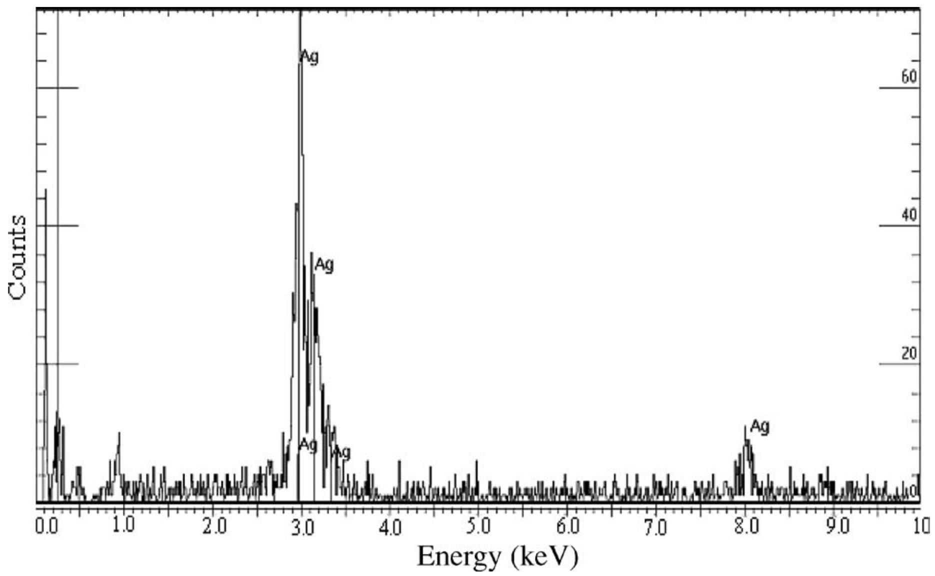

Figure 6 The EDX pattern of silver-coated carbon nanotubes.

When using electroless plating for general materials, the coating layer is generally about 10–100 μm thick [10]. So only a few activated sites are needed to initiate metal growth. The metal atoms have enough time to aggregate laterally and vertically to form a continuous layer. The coating layer on the carbon nanotubes is only about 10–20 nm thick. This thickness can be achieved within minutes of immersion of the carbon nanotubes in the plating bath and lateral growth of the silver nuclei would be small and cannot cover the whole surface of the nanotubes (Fig. 4). Only when the activated sites are very high in concentration and the distance between activated sites is short can continuous coating layers be obtained (Fig. 5).

For general substrates, the deposition rate is about 10–15 μm/h [11] and is too fast for carbon nanotubes. By adjustment of the traditional composition of the silver electroless plating bath, we can decrease the electroless plating rate from 10–15 μm/h to 0.8–1 μm/h and control the thickness of the coating.

Fig. 5 is the TEM image of a coated nanotube. In comparison with the clean surface of the uncoated carbon nanotubes, a coating layer apparently covers the whole surface of the nanotube and no void or gap can be found. The diameter of the coated carbon nanotube was about 70–100 nm, so we can calculate that the coating layer is about 10–20 nm thick. The chemical composition of the coating layer was determined by EDX and Fig. 6 indicated that only silver could be detected. From Fig. 5 we also found that the thickness of the silver coating layer on nanotubes was not uniform. This is due to the fact that the activated sites on the surface of the nanotubes are not uniformly distributed and the vertical growth of stacks of silver atoms on the surface of nanotubes is not simultaneous. But this does not lower the properties of carbon-nanotubes-reinforced metal matrix composites for the coating layer only enhancing the interface strength between the nanotubes and the metal matrix.

In this paper, a method based on deposition of silver onto carbon nanotubes by electroless plating was proposed to improve interfacial adhesion of composites. To obtain a continuous coating layer, a series of ways (oxidization, sensitization, activation, and the adjustment of composition of copper electroless plating bath) are used to improve dispersion, increase the activated sites, and lower the deposition rate. TEM images show that the surface of carbon nanotubes is successfully coated with a continuous layer of silver, which lays a good foundation for applying carbon nanotubes in composite materials.

Acknowledgments

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