

Coating of Carbon Nanotube with Nickel by Electroless Plating Method

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A method to fabricate one dimensional nanoscale composite based on coating of carbon nanotube with metal is proposed and demonstrated in this letter. Carbon nanotubes have been coated with a layer of nickel by electroless plating. It was found that the nickel coating had a tendency to form as nanoparticles on the surface of carbon nanotube and on the net of carbon nanotubes. High density active sites and low deposition rate were found to be critical for getting better coating.

KEYWORDS: carbon nanotube, electroless plating, nickel, coating, nanoparticle

1. Introduction

The discovery¹⁾ of carbon nanotube has led to an extensive study of this novel carbon form. Carbon nanotube is only a few nanometers in diameter and a few microns in length. This hollow structure can be used as a template to produce new one dimensional nanoscale materials. Carbon nanotubes have been filled with various materials through capillarity and electric arc method.²⁻⁵⁾ They have also been used to react with metal-oxide to produce metal-carbide nanoscale rods.^{6,7)} It may be speculated that one dimensional nanoscale composite structures can also be prepared by coating of carbon nanotubes with other materials.

In this letter, carbon nanotube is coated with a layer of nickel by electroless plating method. To our knowledge, this is the first experiment to make one dimensional nanocomposite based on coating of carbon nanotube. Electroless plating method is used as it can deposit many metals on almost any substrates regardless of size and shape,^{8,9)} also the carbon nanotubes can be ultrasonically dispersed in plating solution, so each nanotube may has probability to be coated. The purpose of choosing nickel as a coating material is to prepare one dimensional nanocomposite with ferromagnetic property which may be of interest to nanoscale magnetic research and high density record.

2. Experiments

The electroless plating procedure is shown schematically in Fig. 1, which is similar to that described by Caturla *et al.*¹⁰⁾ Preactivation (surface catalysts) of carbon nanotube was accomplished by ultrasonically dispersing the carbon nanotubes in a solution of 0.1M SnCl_2 /0.1M HCl for 30 minutes. The Sn^{2+} -sensitized carbon nanotube was further activated in a aqueous solution of 0.0014M PdCl_2 /0.25M HCl for another 30 minutes. The activated carbon nanotubes were then introduced into an electroless plating bath. The composition of the plating solution and the reaction conditions are given in Table I. The whole procedure was carried out at 25°C and the carbon nanotubes were washed with distilled water after each step. The morphology of the nickel coated nanotube was analyzed by transmission electron microscopy (TEM, Philips-CM200).

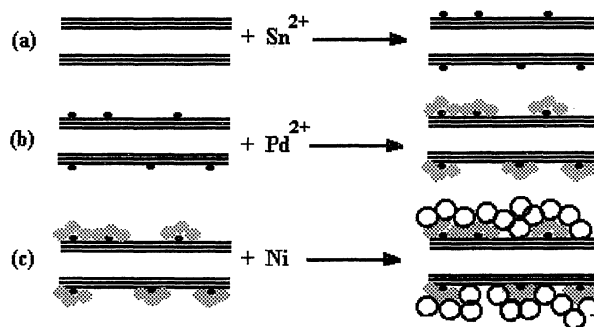


Fig. 1. Schematic diagram of the electroless plating procedure used to deposit nickel on the outer surface of carbon nanotube

Table I. Bath composition and operating conditions of electroless nickel coating.

Chemical	Concentration (mol/l)
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.25
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.09
$\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7 \cdot 1.5\text{H}_2\text{O}$	0.054
$\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$	0.84
NH_4Cl	1.87
$\text{Pb}(\text{NO}_3)_2$	7.5×10^{-3}
pH at 25°C (adjusted by NH_4OH)	8.75
Bath temperature	25°C

The multishell carbon nanotube used in this work were produced from catalytic decomposition of ethylene. The reaction gas ethylene and hydrogen flowed through a horizontal quartz tube heated at the temperature of 700°C. The yielded carbon nanotubes with the typical diameter around 15 nm are relatively pure and without any amorphous carbon coated on the outer surface of the tubes (Fig. 2(a)).

3. Results and discussion

Figure 2(b) shows the TEM image of carbon nanotubes after being immersed in the solution of Sn and Pd. It can be seen that the Pd/Sn appears as aggregates on the outer surface of the nanotubes, indicating the activated sites were formed.

Once the active sites are formed, the nickel would be reduced on them at proper pH value and temperature. Figures 3(a) and 3(b) show the coating results carried out at pH = 8.25 and at the temperature of 25°C. It can

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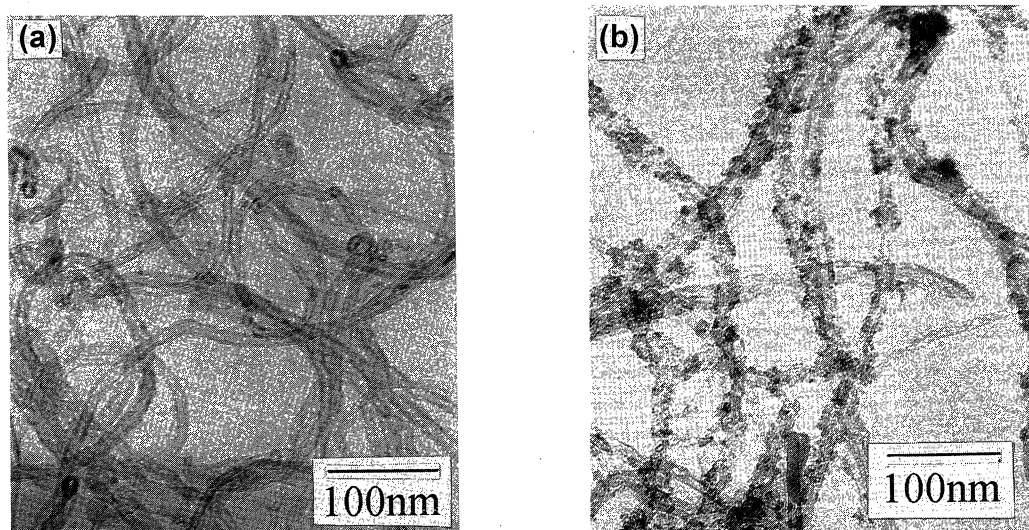


Fig. 2. TEM micrographs of catalytic grown carbon nanotube (a) before preactivation (b) after preactivation, note Sn and Pd aggregated on the outer surface of carbon nanotube as the active sites.

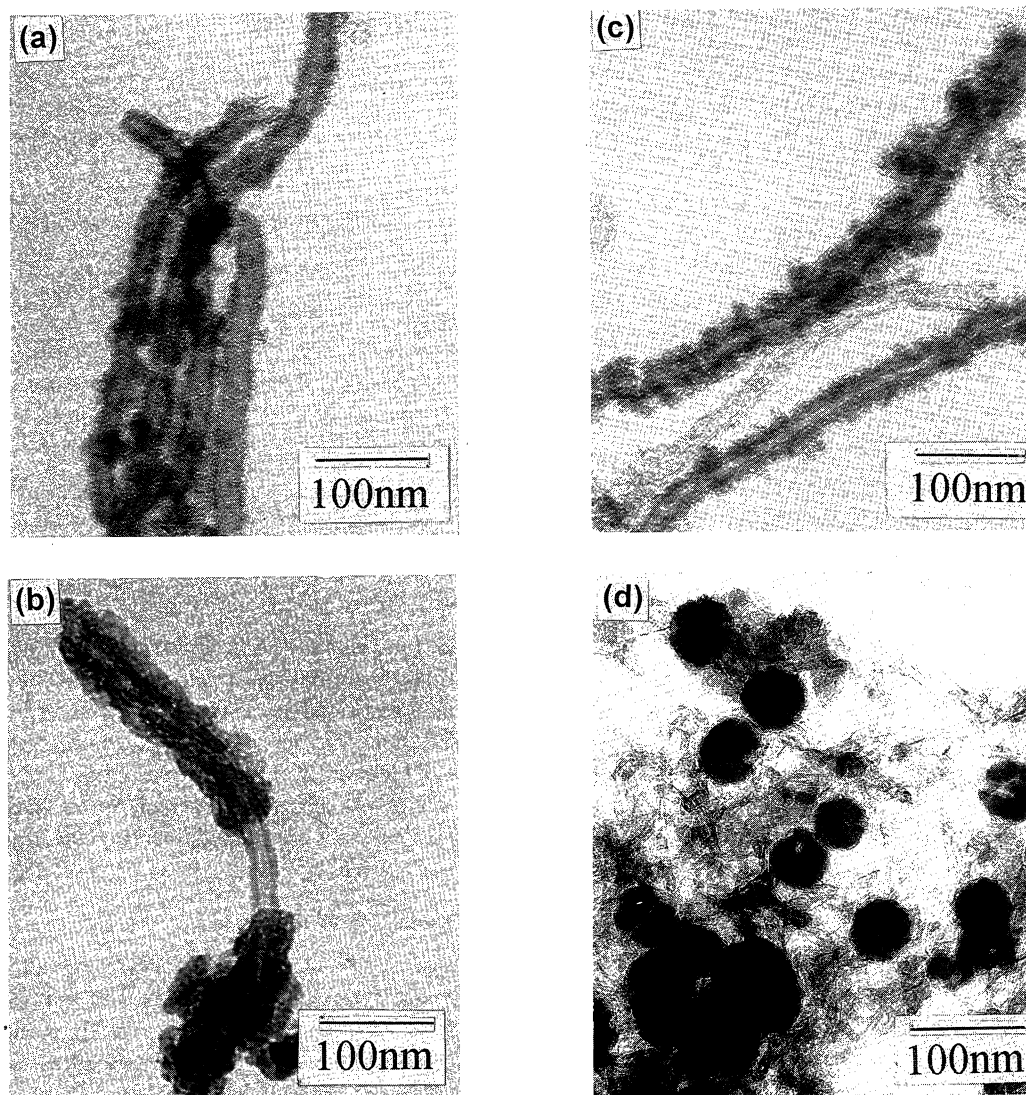


Fig. 3. TEM micrographs of the nickel coated carbon nanotubes by electroless plating at different pH values. (a) pH = 8.25, carbon nanotubes are coated with a layer of nickel. (b) pH = 8.25, a carbon nanotube was coated with a discontinuous layer of nickel. (c) pH = 8.5, nickel formed as balls on the outer surface of carbon nanotube. (d) pH = 8.75, nickel formed as balls on the net of carbon nanotubes.

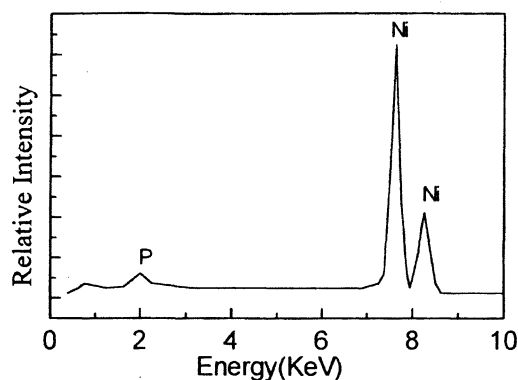


Fig. 4. EDAX pattern of the coatings on the surface of carbon nanotubes corresponding to Fig. 3(a).

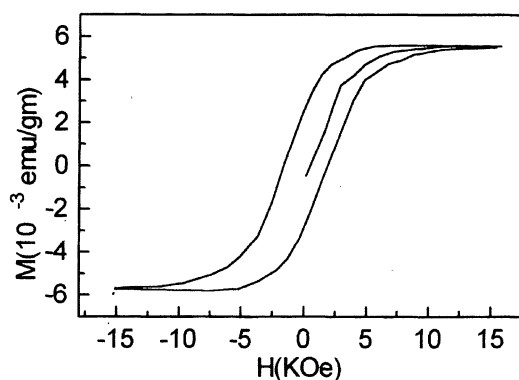


Fig. 5. M-H curves for the nickel coated carbon nanotubes treated at pH = 8.25.

be seen the carbon nanotubes are coated by a layer of material which appears as polycrystal. The EDAX result shows the coating material is nickel (Fig. 4). In Fig. 3 the nickel coating layer is discontinuous, which might due to nonuniformity of the active sites on the surface of the carbon nanotube. We noted that the reaction rate was very sensitive to pH value of the solution which could be adjusted by $\text{NH}_3 \cdot \text{H}_2\text{O}$. When we increase the reaction rate by increasing pH value of the solution, the nickel tended to aggregate as nanoparticles on the outer surface of nanotube and on the net of nanotubes (Figs. 3(c) and 3(d)). We have observed the nickel ball grew up to 500 nm in diameter at high deposition rate.

The nickel electroless plating on graphite surface has been done earlier and got a uniform coating layer.¹⁰⁾ The aggregation tendency of coating nickel on the outer surface of carbon nanotube might be because the coating was on the surface with a big curvature. On the curved surface, if the normal growth rate is higher than lateral growth rate, the coating layer tends to form as the discrete grains. Also, the aggregation tendency would be more serious if the density of the active sites is too low. Therefore, increasing the density of active sites and keeping a low deposition rate might be helpful to get better coating layer on the outer surface of carbon nanotube.

The magnetization measurement of the nickel coated carbon nanotubes were performed at room temperature with a vibrating sample magnetometer. The hysteresis curves is shown in Fig. 5. The coercive force for the nickel coated carbon nanotube is 1550 Oe, which is much higher than the values of a few tens for the bulk nickel. The magnetic coercivity enhancement might be because of that the sample is consisted of isolated nanoscale magnetic rods.¹¹⁾ Here, we limit the discussion to the case of the applied electric field.

4. Conclusion

In conclusion, one dimensional magnetic nanocompos-

ite of nickel coating carbon nanotubes were fabricated by electroless plating. The nickel tended to form as particles on the surface of carbon nanotubes and on the net of carbon nanotubes. High density of active sites and low deposition rate are critical for getting better coating. The magnetic coated carbon nanotubes might be useful for microscopic magnetism research and high density magnetic recording. Also, the method we presented in this paper might be used to fabricate a wide variety of one dimensional nanocomposites based on carbon nanotube.

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