

## Decoration of activated carbon nanotubes by assembling nano-silver

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**Abstract:** A facile solution processed strategy of synthesizing nano silver assembled on carbon nanotubes (CNTs) at room temperature was put forward. Activated carbon nanotubes were used as precursors for preparing silver-decorated nanotubes. The nature of the decorated nanotubes was studied using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The inert surfaces of carbon nanotubes were activated by introducing catalytic nuclei *via* an oxidation-sensitization-activation approach. Activated carbon nanotubes catalyzed the metal deposition specifically onto their surfaces upon immersion in electroless plating baths. The method produced nanotubes decorated with silver. The extent of silver decoration was found to be dependent on fabrication conditions. Dense nano silver assembled on nanotube surfaces could be obtained by keeping a low reaction rate in the solution phase. The results here show that this method is an efficient and simple means of achieving carbon nanotubes being assembled by nano metal.

**Key words:** carbon nanotubes; nano silver; assembly; surface activation

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### 1. Introduction

Both carbon nanotubes (CNTs) [1] and metal nanocrystals have aroused international interest in the academic and industrial communities because of their unusual structures, unique properties, and great potential applications [2-4]. It is desirable to create novel CNT/nano-metal nanohybrids, so that the unique properties of each material can be integrated, and novel properties due to the interactions between the two components can be discovered. Many researchers have thus attempted to deposit metals or metal compounds onto nanotube surfaces. The most straightforward route for achieving this would be to melt the element on the nanotube surfaces. However, research efforts by Ebbesen *et al.* [5] have shown that only liquids with low surface tensions will wet the surfaces of nanotubes, the cut-off surface tension lying between 100-200 mN/m [6].

There have also been theoretical studies in the area of wetting of carbon nanotubes. For example, Miyamoto *et al.* [7] studied the adsorption of kalium atoms

on the outside and inside of carbon nanotubes. Interestingly, they showed that this phenomenon was energetically favorable at small nanotube diameters, implying that the picture of classical wetting and Ebbesen's findings may not apply below a critical nanotube diameter. However, if one uses the findings of Ebbesen as a rough gauge, most metals and other elements in the periodic table would not be able to wet the surfaces of nanotubes. This has led many to apply a decoration method in which nanotube surfaces are modified by oxidation in order to obtain the nucleation of metals or metal compounds of interest specifically, on the carbon nanotube surfaces [8-11]. Carboxylic, carbonyl, and hydroxyl groups on the oxidized nanotube surface [12] have thus been harnessed to nucleate metal and metal compounds onto the surfaces of nanotubes. Using the above chemical method to deposit metals onto oxidized nanotube surfaces results in a rather even distribution of the metals on the surfaces, but the density of decoration is low in many cases. Even when the elements/compounds with low surface tensions are melted onto the nanotube surfaces, the

wetting of the surfaces is incomplete. Nanotube surfaces in all these cases do not catalyze the deposition of the metal/metal compound. This results in random deposition throughout the solution, and not only on the surfaces of nanotubes.

In this paper, the electroless plating of activated carbon nanotubes with catalytic surfaces was explored, as a better platform to obtain densely decorated nanotubes, by assembly of nano metals. An oxidation-sensitization-activation method, which involves the introduction of catalytic nuclei onto noncatalytic surfaces, was studied. These nuclei then initiate the redox reaction specifically on the activated surfaces. Using this method, the authors have successfully realized nano silver being assembled on nanotube surfaces.

## 2. Experimental procedure

### 2.1. Preparation of CNTs

Carbon nanotubes were produced catalytically with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles before use. A micrograph of carbon nanotubes by transmission electron microscopy (TEM) after such a preparation is shown in Fig. 1. The multiwalled carbon nanotubes have a diameter of 30 to 40 nm and a length of several microns to several tens of microns.

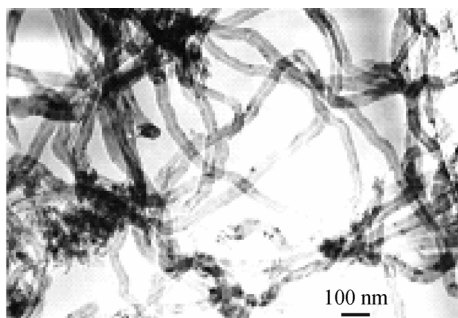


Fig. 1. TEM micrograph of the as-produced CNTs.

### 2.2. Decorating CNTs by electroless plating silver

To modify the surface character, carbon nanotubes were first subjected to an oxidation treatment before surface sensitization. They were annealed in air at 600°C for 20 min [13]. Then sensitization was accomplished by dispersing them in a solution of 0.1 M SnCl<sub>2</sub>/0.1 M HCl and agitating with a magnetic agitator for about 60 min, followed by rinsing in distilled water. The 1.5 g Sn<sup>2+</sup>-sensitized carbon nanotubes were further activated in a 100-mL aqueous solution of 0.0014 M PdCl<sub>2</sub>/0.25 M HCl for 60 min, which was first sonicated for 30 min and then agitated for another 30 min. The activated carbon nanotubes were washed with distilled water and dried at 80°C.

The employed electroless plating included two parts as follows. Solution A was prepared by dissolving 7 g AgNO<sub>3</sub> in 200 mL distilled water, then mixing with 45 mL aqua ammonia. The mixture was agitated until the precipitate disappeared. Solution B was prepared by dissolving 2.2 g HCHO in 8 mL distilled water, and then mixing with 190 mL ethanol.

Three samples of silver-decorated carbon nanotubes were obtained by different fabrication processes. CNT/Ag (A): 0.5 g carbon nanotubes were put into the mixture of solution A and solution B. The reaction solution was agitated by a magnetic agitator for about 60 min. The deposit was filtered, rinsed with distilled water, dried at 80°C and then ground, to disperse. CNT/Ag (B): 0.5 g CNT/Ag (A) was putted into solution A. With agitating, solution B was titrated drop by drop within 30 min. Then the reaction solution was continuously agitated for another 30 min. The deposit was filtered, rinsed, dried and then ground, to disperse. CNT/Ag (C): 0.5 g carbon nanotubes were first treated by the electroless plating process which was the same as that of preparing CNT/Ag (B). Then the product was treated by the second electroless plating process which was the same as that of preparing CNT/Ag (A). The temperature of electroless plating at which the three samples were fabricated was 25°C, and the pH value was about 9.0.

### 2.3. Apparatus

The samples were characterized by TEM (JEOL-200CX), field emission scanning electron microscopy (FE-SEM, AMRAY-1910), fitted with an energy dispersive X-ray (EDX) analytical system for composition analysis, and X-ray diffraction (XRD, Rigaku D<sub>max</sub> γ A X-ray diffractometer with Cu K<sub>α</sub> radiation, λ=0.154178 nm).

## 3. Results and discussion

Sensitizing and activating the surfaces of carbon nanotubes with a solution of tin and palladium formed the Pd/Sn particles as activated sites to initiate the deposition of silver. However, owing to the low chemical reactivity, smooth surface, and high curvature of carbon nanotubes, to increase the number of activated sites, oxidation is necessary to enhance the wettability of the surfaces before surface sensitization and activation. For this approach, carbon nanotubes were annealed in air at 600°C for a short time. Oxygen attacked the cylindrical walls of carbon nanotubes. Some outer graphitic layers were etched away, giving a rough CNT-surface [10]. The rough surfaces increased the effective area and afforded the graphitic layer edges with a higher wettability for forming acti-

vated sites.

The electroless solution contained not only a metal salt and reducing agent but also some other compounds, such as a complexing agent which maintained the level of metal ions in the solution, and buffers which maintained a given pH. There were, in addition, other additives, at very low concentrations, to stabilize the solution or to improve the morphology of the metal deposition. In solution A,  $[\text{Ag}(\text{NH}_3)_2]$  molecules were generated *via* a complex reaction between  $\text{Ag}^+$  and  $\text{NH}_3$ . In the mixture of solution A and solution B, the silver could be reduced by HCHO on the activated sites of CNT surfaces to form activated centers of silver. The sequentially reduced silver atoms would deposit around the activated centers, resulting in silver phase coatings on CNT surfaces.

Based on the principles of electroless plating, the reducing ability of HCHO is dependent on the pH value of the plating solution, temperature, concentration of HCHO, and so on, which are concerned with the speed and extent of reduction in the electroless plating procedure. In order to control the silver particle size and the homogeneous distribution on carbon nanotube surfaces, the above-mentioned parameters that control the electroless plating process are very important besides the pretreatment of carbon nanotubes.

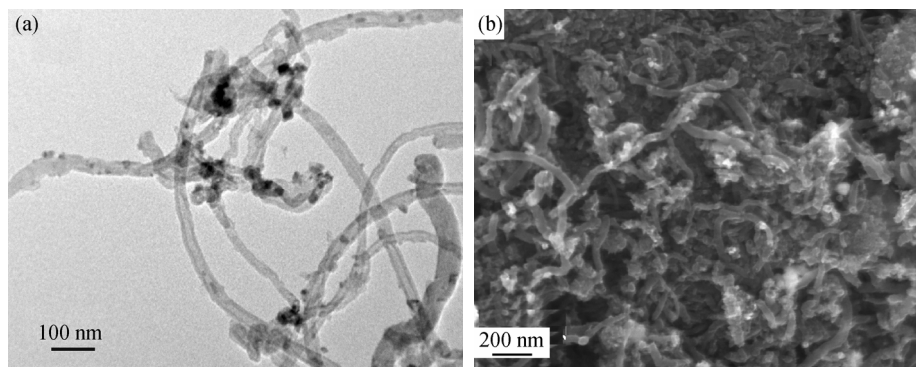


Fig. 2. TEM (a) and SEM (b) photographs of the prepared CNT/Ag (A).

Fig. 3, the TEM and SEM photographs of a sample thus obtained, CNT/Ag (B), shows that carbon nanotubes are still not effectively coated by silver particles, they carry sparse silver particles with diameters being much larger than nanotubes. The reason should be that most  $\text{Ag}^+$  were reduced in the solution phase, and seldom activated centers of silver were formed on CNT surfaces during the electroless plating process of preparing CNT/Ag (A). Although the reaction rate was controlled by the slowly titrating HCHO solution in the second electroless plating process, the generated silver atoms could only deposit on the former formed sparse silver particles on CNT surfaces, resulting in sparse, large-sized silver particles being formed on

It was observed that reduction could be effectively achieved when the pH value of the solution was larger than 8.0. With the increase of pH, the reduction of silver increased, and the suitable pH value for the electroless plating silver on carbon nanotubes was about 9.0. Temperature was thought to be the critical factor that affected the reduction speed in the electroless plating process. It was observed that when the temperature was raised to  $60^\circ\text{C}$ , the change in plating solution color occurred within 10 min after HCHO was added. After a series of tests, it was found that at  $25^\circ\text{C}$ , the reduction speed was suitable to obtain the best distribution of the silver particle size.

The concentration of HCHO also influenced the reduction speed. If the HCHO solution (solution B) was added directly into the plating solution (solution A), it would lead to a fast reduction of  $\text{Ag}^+$  around them, which resulted in a majority of the silver being generated in the solution phase and carbon nanotubes not being effectively coated by silver particles, as shown in Fig. 2, the TEM and SEM photographs of sample CNT/Ag (A). Hence, dilution of the HCHO solution is necessary. CNT/Ag (A) was decorated again by electroless plating in the fabrication condition that the HCHO solution was slowly added by titrating drop by drop into the plating solution, which was equal to the effect of the diluted HCHO solution.

CNT surfaces. If the former electroless plating was processed at a low reaction rate by slow titrating the HCHO solution, large quantities of activated centers could be gradually formed on CNT surfaces. Although HCHO solution was added directly into the plating solution in the second process, the dense activated centers on CNT surfaces catalyzed the reduction of  $\text{Ag}^+$  and generated silver atoms to continuously deposit on them, resulting in many nanosized silver particles densely assembling on CNT surfaces.

As shown in Fig. 4(a), the TEM photograph of a sample thus obtained, CNT/Ag (C), shows that the diameters of silver particles, which were densely assembled on the CNT surfaces, are below 10 nm. Fig.

4(b), the SEM image of CNT/Ag (C), shows that most carbon nanotubes of sample CNT/Ag (C) are homo-

geneously and densely decorated by silver nanoparticles.

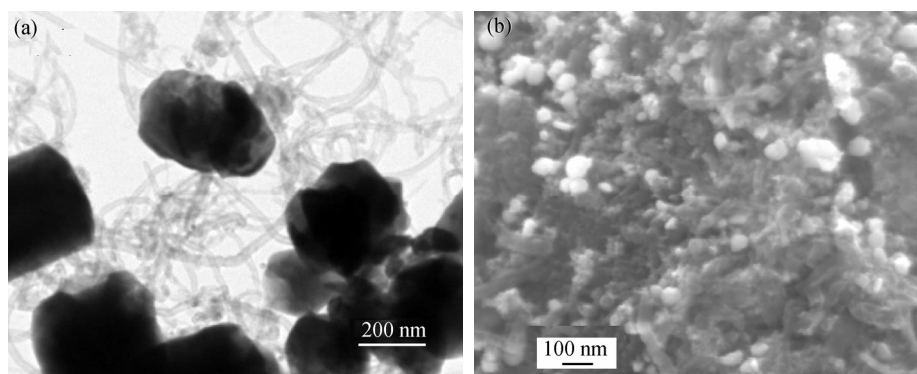


Fig. 3. TEM (a) and SEM (b) photographs of the prepared CNT/Ag (B).

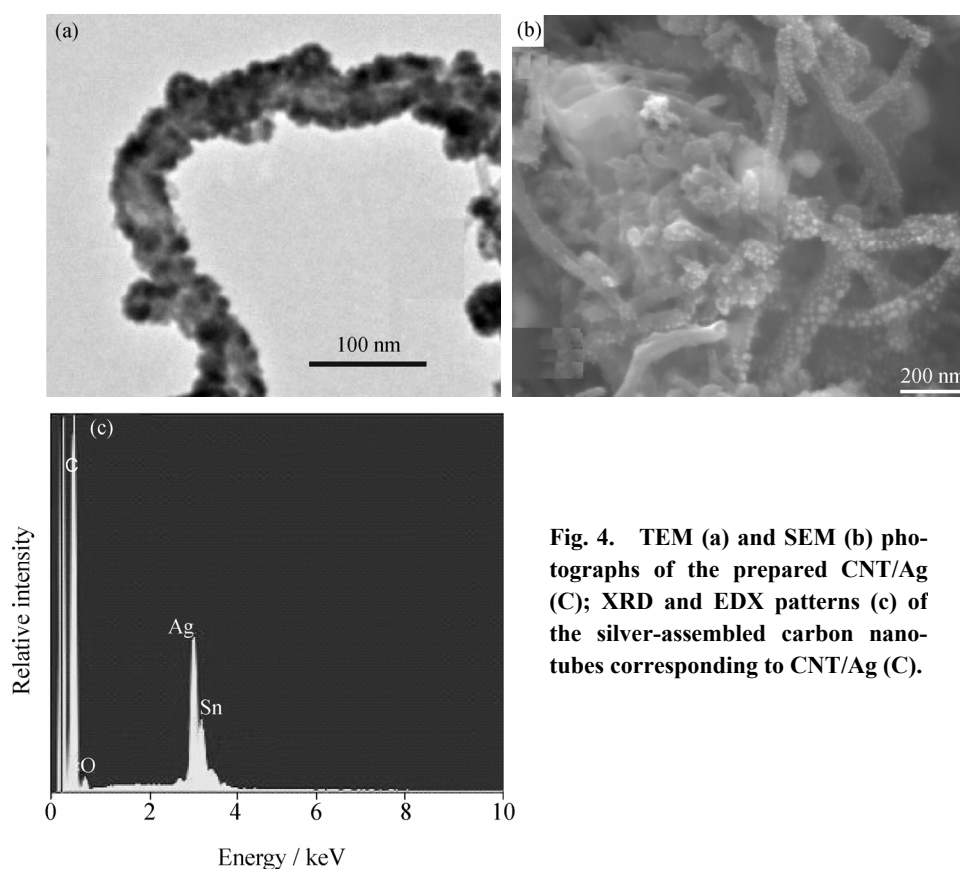


Fig. 4. TEM (a) and SEM (b) photographs of the prepared CNT/Ag (C); XRD and EDX patterns (c) of the silver-assembled carbon nanotubes corresponding to CNT/Ag (C).

Powder X-ray diffraction was used to further measure the phase structure of the obtained CNT/Ag nanocomposites. As shown in Fig. 4(c), the peak at  $2\theta=26.2^\circ$  is assigned to the graphite crystalline phase (CNTs), and the other four peaks are assigned to the diffractions from the (111), (200), (220), and (311) planes of face-centered cubic silver crystals, respectively.

The EDX result in Fig. 4(d) shows that the obtained silver decorated carbon nanotubes contain carbon, silver, a little oxygen, and microcontent tin. Here, residual tin was from pretreating by sensitization before the electroless plating, and the small amount oxygen

might be from air adsorbing. The analysis of the used EDX patterns indicated that silver contents of CNT/Ag (A), CNT/Ag (B), and CNT/Ag (C) were 8.18wt%, 28.14wt%, and 37.11wt%, respectively. This demonstrated that CNT/Ag (C), which had realized a dense assembling of nanosized silver on the carbon nanotube surfaces, also had the highest silver content.

#### 4. Conclusion

A new way to prepare nanosized silver particles assembling on carbon nanotubes by the electroless plating method was demonstrated. It is found that the pretreatment of carbon nanotubes is very important to

deposit silver nanoparticles onto their surfaces. In the experiment, an oxidization-sensitization-activation method was used. Meanwhile, in order to attain nanosized metal particles assembling on carbon nanotube surfaces, electroless plating conditions should be controlled carefully, suitable pH value, low temperature, and low reaction rate should be kept. The method is simple, inexpensive, highly reproducible, and might be used to prepare a wide variety of one-dimensional nanocomposites, by using carbon nanotubes as templates.

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