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Improved electroless plating method through ultrasonic spray atomization for depositing silver nanoparticles on multi-walled carbon nanotubes

Qi Zhao [a], Ming Xie [b], Yichun Liu [a,*], Jianhong Yi [a]

[a] School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b] Kunming Institute of Precious Metals, Kunming 650106, China

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ABSTRACT

A novel method was developed to deposit nanosized silver particles on multi-walled carbon nanotubes (MWCNTs). The electroless plating of silver on MWCNTs accomplished in small solution drops generated by ultrasonic spray atomization, which inhibited excessive growth of silver particles and led to much more uniform nanometer grain-sized coatings. The results showed that pretreatment was essential for silver particles to deposit on the MWCNTs, and the electrolyte concentration and reaction temperature were important parameters which had a great influence on the morphology and structure of the silver coatings. Possible mechanisms of this method are also discussed in the paper.

1. Introduction

With the properties of high tensile strength and toughness, good thermal and electrical conductivity, etc., MWCNTs have attracted much interesting in both research and application fields, such as microelectronics, energy storage, and composite materials [1]. One method for the further improvement of the properties is the deposition of metals on the MWCNTs surfaces [2,3], and the metal silver is a prior selection due to its high thermal and electrical conductivity [4,5].

The deposition of silver on MWCNTs permits combined or enhanced properties and attracts wide interest in the applications such as field emission [6], reinforcing fillers in polymers [7] and composite materials [4,8]. The approaches for silver deposition on MWCNTs include physical evaporation, magnetron sputtering, plasma deposition and electroless plating, etc., among which electroless plating is particularly appealing because it's low cost, inherent selectivity and significantly simpler than other method [9]. In common electroless plating progress, the mixing of reducing solution and metal salt solution is usually by drop wise addition or by direct solutions mixture, and homogenization of components in solution through diffusion needs a certain amount of time, implying concentration gradient and non-uniformity of reaction and deposition during that time [10]. For that reason, nonuniform coatings on MWCNTs associated with over-grown silver particles are usually the results as reported in literatures [11–14].

In this paper, an improved electroless plating method has been developed, the process of which is realized within micrometer scale droplets generated by ultrasonic spray atomization, for the purpose to get higher uniformity of silver deposits/coatings on MWCNTs.

2. Experimental

As-received MWCNT powders (with inner diameter of 5–12 nm, outer diameter of 30–50 nm, length of 10–20 μm and purity larger than 95 wt.%) fabricated by CVD method were acquired from Time Nano Co. Ltd of China. Before electroless plating, pretreatments including oxidation, sensitization and activation were performed as described in Ref. [15]. For the electroless plating, silver ammonia solution (composed of 0.004–0.01 M $AgNO_3$ and 0.1–0.13 M $NH_3{\cdot}H_2O$) and reducing solution (0.10 M hydrazine hydrate, HHA) were prepared separately, and 0.1 g MWCNTs were dispersed in 200 ml HHA solution by mechanical and ultrasound agitation to gain the suspension solution. The silver ammonia solution and suspension solution were heated to the expected temperatures and then atomized to droplets respectively with ultrasonic atomizers, which were delivered to a three-mouth flask for the later mixture and electroless plating progress for 10 min. The three-mouth flask was placed in a water bath for temperature compensation. The schematic diagram is shown in Fig. 1. The resultant suspension

* Corresponding author.
E-mail address: liuyichun@kmust.edu.cn (Y. Liu).

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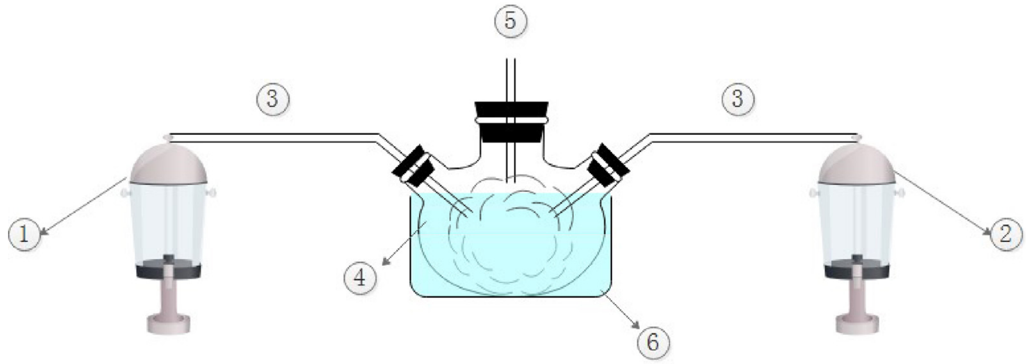

Fig. 1. Electroless plating device through ultrasonic spray atomization schematic diagram. (1) and (2) Ultrasonic atomizers. (3) Corrugated pipes. (4) Three-mouth flask. (5) Recycle path. (6) Homoeothermic water bath.

solution after reaction was washed many times by centrifugation with deionized water, and finally, the precipitates were dried at 323 K in vacuum drying oven to get the Ag/MWCNTs powders. Microstructures of the samples were characterized using transmission electron microscopy (TEM, JEM-2100) operated at a gun voltage of 200 kV. The Ag/MWCNTs powders were suspended on alcohol and in ultrasonic bath for several minutes to improve the suspension, and then the samples for TEM observation were prepared by dropping the suspension on a Cu grid and letting the solvent evaporate at room temperature. Raman spectroscopy data were recorded using a LabRam HR Evolution produced in France, with the laser probe wavelength of 532 nm, and the sample was exposed to the laser for 3 s during the spectrum acquisition.

3. Result and discussion

To reveal the reliability of MWCNTs transmission and silver deposition reaction in droplets through ultrasonic spray atomization, a pre-experiment with raw MWCNTs underwent the electroless plating progress and the TEM observation results are shown in Fig. 2. Silver nanoparticles are dispersed around MWCNTs rather than deposited on them, as shown in Fig. 2(a), and according to size distribution analysis in Fig. 2(b), the average diameter of the silver particles is about 4.9 nm. It can be deduced that MWCNTs can be transferred in the atomized solution drops, and through the mutual collision, contact and mixing of the ultrasonic atomized solution drops, the corresponding chemical reaction occurred, and a large amount of uniform silver nanoparticles can be generated. On the other hand, the Ag nanoparticles did not deposit or combined with MWCNTs, but dispersed around them, which phenomenon implied that the raw MWCNTs surface was inert, and failed to become the silver nucleation substrate. It is worth mentioning this reported electroless plating through ultrasonic spray atomization is also a template-free and addictive-free method for nanoparticles preparation. While for the silver deposition on MWCNTs, the surface pretreatment such as sensitization and activation process is essential, the same as electroless deposition of other metals [16].

An ideal coated carbon nanotube can be approximately described as the cylinder model, the inner of which is the MWCNTs and the outer is the silver coating. As known from Fig. 2, the average diameters of silver particles and MWCNTs are respectively about 5 nm and 30 nm. Assuming that the cylinder diameter is 4/3 times of the inner MWCNTs diameter, and regarding the relative density ratio of Ag to MWCNT is about 5:1, the estimated minimum mass ratio of Ag/MWCNTs is about 4:1 for a complete coating on MWCNTs. Thus, in the sequent experiments, the ratios were set as about 4:1 (0.004 M $AgNO_3$), 6:1 (0.006 M $AgNO_3$) and 10:1 (0.01 M $AgNO_3$) by adjusting the silver ammonia solution concentration.

Fig. 3 shows the TEM observation of the pretreated MWCNTs after electroless plating through ultrasonic spray atomization with different silver ammonia solution concentrations (the reaction temperature: 293 K). The electron diffraction patterns indicate high crystallization of the silver nanoparticles generated from electroless plating through ultrasonic spray atomization. From Fig. 3(a)–(c), it is obvious that almost all of the silver nanoparticles were deposited on MWCNTs, rather than dispersed around them as in Fig. 2. The phenomenon could be resulted from the structure changes of MWCNTs before and after pretreatment, which was quite significant as deduced from the Raman spectra in Fig. 4. Two features in first-order Raman spectra are a G-band at 1570–1580 cm^{-1} revealing two-dimensional graphitic ordering of nested graphene layers of MWCNTs and a D-band at 1340–1350 cm^{-1} which is highly responsive to non-planar atomic

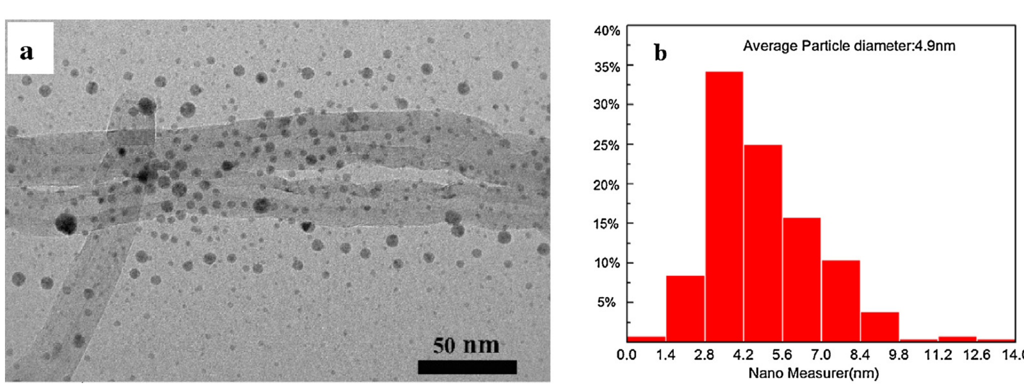

Fig. 2. (a) TEM micrographs of the un-pretreated MWCNTs sample after electroless plating through ultrasonic spray atomization. (b) Size distribution of the silver particles.