

## Microwave-assisted Electroless Deposition of Silver Nanoparticles onto Multiwalled Carbon Nanotubes

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In this study, an efficient microwave-assisted self-organization of silver nanoparticles onto multiwalled carbon nanotubes (MWCNTs) is proposed. Silver nanoparticles anchor onto the surface of MWCNTs through self-assembly at the reaction condition of 160 °C. We mixed the MWCNTs with saturated silver nitrate/nitric acid solution, without adding a reductant or stabilizer, and then heated them in the closed microwave heating system. The oxidizing conditions create active sites on the surface of MWCNTs and the silver nanoparticles spontaneously align at these sites through electroless deposition. The growing nanoparticles have fcc structures and their density increases upon increasing the reaction time.

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**Keywords:** Carbon Nanotubes, Electroless Deposition, Electron Microscopy, Silver Nanoparticles, Microwave.

### 1. INTRODUCTION

Metals shrinkage to nanostructures, especially noble metal nanoparticles (NPs) including gold, silver platinum and palladium, are of considerable interest for their applications in catalysis, batteries, fuel cells, capacitors and sensors. NPs, i.e. particles with structures approximately 1-100 nm in size, have significant impact in many scientific fields, including chemistry, material sciences, biology, medicine, and electronics. The physical, material, and chemical properties of NPs are directly related

to their intrinsic compositions, apparent sizes, and extrinsic surface structures; therefore, the design, synthesis, characterization, and applications of nanostructures are critical aspects for the emerging field of nanomaterials [1]. A variety of NPs on various substrates, such as platinum NPs on multiwalled carbon nanotubes (MWCNTs), lead dioxide NPs on lead electrode, and gold-rhodium NPs on glassy carbon electrode, has been reported from the deposition by electrochemical method [2-4]. Electroless deposition of nanomaterials is also an attractive method owing to the easy set-up of instrumentation system. Compton group develops a facile electroless method to obtain platinum NPs on glassy carbon support [5].

Carbon nanotubes, which have many potential industrial applications, have attracted a considerable degree of fundamental interest [6]. The applications of nanotube-integrated devices include single-electron transistors, molecular diodes, memory elements and logic gates [7-9]. There is great deal of interest in devising strategies to address each molecular unit individually and to interconnect them without affecting their local electronic structure adversely [10-11]. Two distinct research approaches have been investigated using carbon nanotubes as templates for forming nano-scale materials, namely those prepared within the carbon nanotubes (tube-in) and those prepared externally to the nanotubes (tube-out). For the tube-in modification (which is also called “filling”), the introduction of metals or metal carbides and oxides into multiwalled carbon nanotubes (MWCNTs) may significantly alter their conducting, electronic, and mechanical properties that arise from the internal framework within these structures [12-13]. In the tube-out modification, attaching metal or semiconductor nanoclusters to the nanotubes by chemical or physical means is very attractive. This approach is an interesting one for creating molecular-level hybrid units (e.g., quantum dots attached to molecular wires); it allows the new properties and effects that arise from the interactions between the constituent molecular units at the level of their electronic structures—as well as their applications (e.g., active nanodevices and heterogeneous nanocatalysts)—to be explored.

Several articles have appeared so far that have been devoted to studies of different methods for binding nanoparticles onto the side-walls of carbon nanotubes, including covalent bonding [14-15], electrostatic attraction [16–20], and spontaneous reduction [21-22]. In the covalent bonding method, amino functional groups on the surfaces of nanoparticles are reacted with carboxylic acid units (COOH) of the nanotubes to form amide (RCONH) or ether (C–O–C) bonds between the two systems. Electrostatic forces are also very useful for attaching nanoparticles to nanotubes. In addition, many papers have described how single-walled carbon nanotubes can be used as templates for condensing metal nanoparticles, such as gold [22] and platinum [21-22], by spontaneous reduction. The spontaneous electron transfer from single-walled nanotubes to gold or platinum ions occurs because the reduction potential of single-walled carbon nanotubes is well above the reduction potentials of  $\text{AuCl}_4^-$  and  $\text{PtCl}_4^{2-}$  ions. It is not possible, however, to attach Ag nanoparticles to nanotubes using this method; to the best of our knowledge, until now no other reduction processes to template the Ag nanoparticles on MWCNTs by microwave-assisted preparation, and their mechanisms, have not been reported.

In this paper, we describe a self-organization and electroless deposition process for agglomerating silver nanoparticles onto MWCNTs by microwave heating at 160 °C under strongly oxidizing conditions. We have used the Infrared spectroscopy and X-ray spectroscopy to evaluate the

surface bonding properties of MWCNTs and the crystal structure of the aligned silver nanoparticles, respectively. The morphology of MWCNTs and silver nanoparticles is observed by the transmission electron microscopy (TEM).

## 2. EXPERIMENTAL

### 2.1 Purification and electroless deposition of AgNPs in microwave oven

Pristine MWCNTs were purchased from the Chinese Academy of Sciences (China) and having a highly oriented morphologies and uniform outer diameters (ca. 40 – 70 nm) and lengths (ca. 50 – 60  $\mu\text{m}$ ). Prior to use MWCNTs for self-organization the AgNPs, we needed to purify the materials by following our previous publication method [23]. These purified materials were suitable for further studies. A mixture of the MWCNTs (0.1 mg) and an  $\text{AgNO}_3$  solution [5 mL; prepared by dissolving  $\text{AgNO}_3$  (3 mg) into concentrated  $\text{HNO}_3$  in a closed Teflon vessel] was placed into a closed Teflon vessel. We used temperature (maximum: 200  $^\circ\text{C}$ ) and pressure (maximum: 350 psi) sensors to monitor the reaction in situ within a microwave heating oven (MARS-5, CEM); after sensor feedback, the control units of the microwave system were used to control the temperature and pressure. The self-assembly processes that occurred between the nanoparticles and nanotubes took place without the addition of capping or stabilizing agents for templating the formation of the nanoparticles. We expected that it would be possible to modulate the amount and density of nanoparticle agglomeration on the nanotubes by changing the heating time. Such composites may have useful applications in molecular electronics and photocatalysis, and as probes for scanning force microscopy.

### 2.2 Characterization of AgNPs

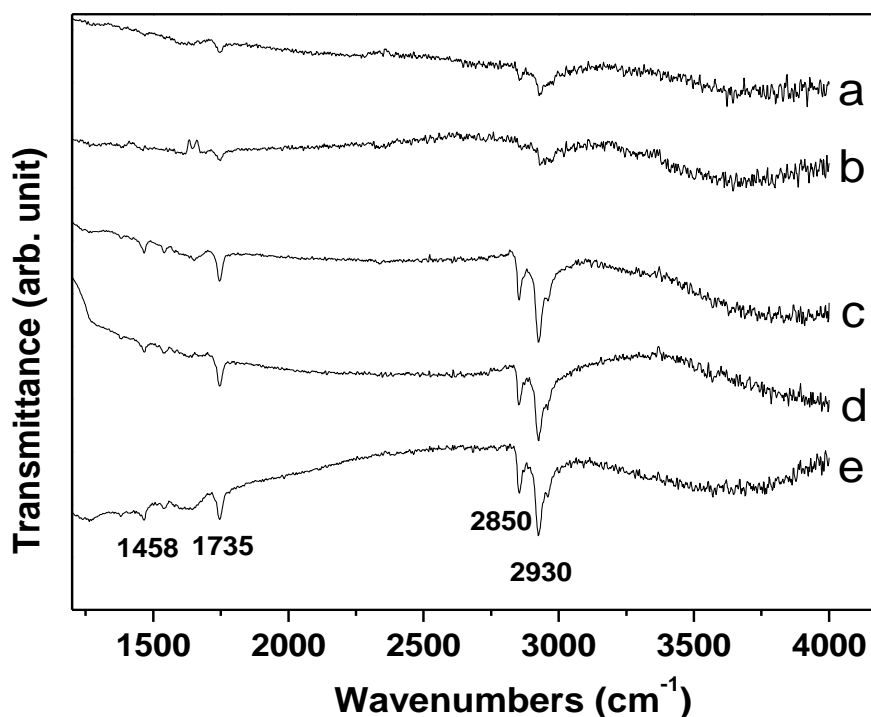
The MWCNT sample obtained after microwave-assisted template-directed synthesis was dried on a hotplate and then the product was collected. A portion of the sample was dispersed in ethanol under mild sonication. The sample solution was dipped onto a 300-mesh Cu grid. The morphology of this sample was characterized by TEM (JEM-2010F, JEOL) using an accelerating voltage of 200 keV. The TEM was equipped with an energy dispersive X-ray (EDX) elemental analysis tool. The sample was also analyzed by Fourier Transform Infrared (FTIR) Spectroscopy (ASTeX PDS-17 System) and X-ray diffraction spectroscopy (X'Pert Pro, Philips).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of reaction temperature from Fourier Transform Infrared Spectroscopy

In our previous report [23], we have found that the MWCNTs can be effectively purified by closed vessel for 30 min at 160  $^\circ\text{C}$  in microwave oven. The heating by microwave method possesses the advantage of time-saving than conventional methods [24-25]. The heating temperature and time are

two important factors that determine the results of chemical reactions conducted in closed Teflon vessels. Figure 1 presents the transmission mode FTIR spectra of nanotubes treated with  $\text{AgNO}_3$  and  $\text{HNO}_3$  for 1 h at different oven temperatures (120–200 °C). The characteristic absorption peaks at 2850 and 2930  $\text{cm}^{-1}$  appeared to a significant extent after heating at 160 °C; these signals correspond to the unhindered symmetric and asymmetric stretchings, respectively, of the terminal  $\text{CH}_3$  groups on the nanotubes' surfaces. In addition, small peaks appear at 1735 and 1458  $\text{cm}^{-1}$ , which we identify as representing carbonyl ( $>\text{C}=\text{O}$ ) and nitrosyl ( $\text{N}-\text{O}$ ) groups, respectively. These observations indicate that the surface  $\text{sp}^2$ -hybridized carbon atoms of the nanotubes gradually decompose and form new active sites at temperatures  $> 160$  °C. In contrast, lower reaction temperatures (120–140 °C) have no significant effect on creating such active sites in the presence of nitric acid. These observations suggest that nitric acid plays an important role in the oxidation of MWCNTs at 160 °C and above: it leads to the oxidation of aliphatic or aromatic groups on the surfaces of the MWCNTs to the form carboxylic acid and/or nitrosyl groups. These processes seem to be thermodynamically driven because of their variations with temperature.

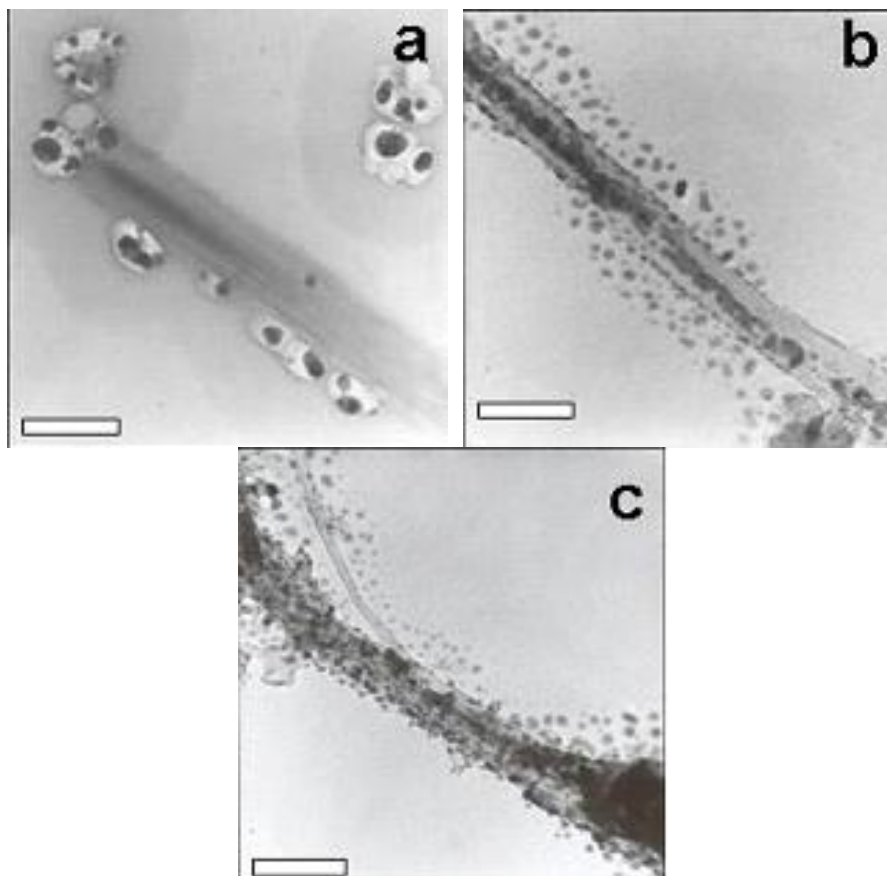


**Figure 1.** FTIR spectra of MWCNTs treated with silver nitrate at different microwave oven temperatures: (a) 120, (b) 140, (c) 160, (d) 180, and (e) 200 °C.

### 3.2 Morphology, diameter, particle density and crystal face for AgNPs after electroless deposition

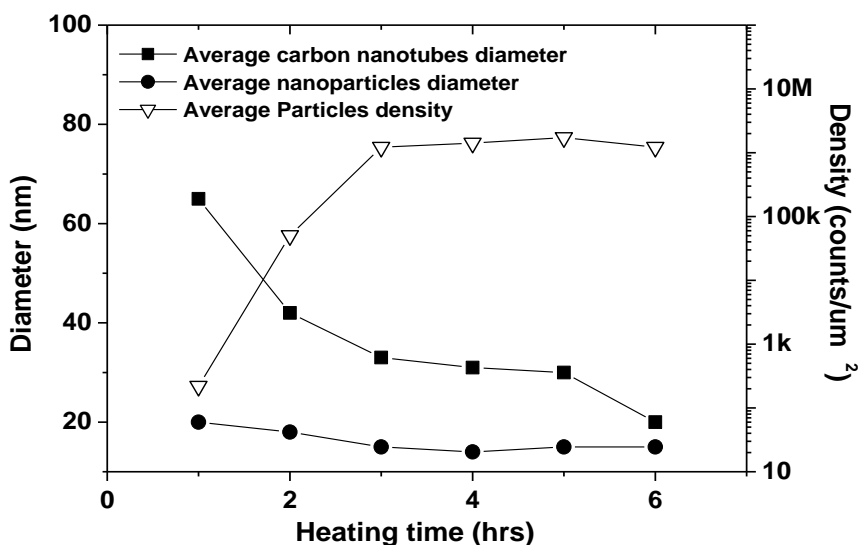
The morphology of the MWCNTs obtained after templating the formation of Ag nanoparticles for 1 h at 160 °C is present in Figure 2a. We observe that the end caps of the MWCNTs gradually open

and that the outer diameter of each nanotube is ca. 50 nm. Active sites were created on the tubes' surfaces and nanoparticles became embedded on these sites. In addition, we observe that silver ions have diffused into the tubes and fill them in the form of nanowires. This observation implies the nitric acid also creates active sites within the tubes. We estimate that the diameters of these nanowires are ca. 20 nm. It has been reported previously [26] that silver nanowires fill in the nanotubes by capillary effect, but this technique requires two steps and has a low filling efficiency (25%). To verify that nitric acid creates the active site for deposition of the nanoparticles, we repeated the reactions using a series of reaction times. It is interesting to note from Figure 2b that the outer shell of the MWCNTs oxidized and decomposed after a reaction time of 3 h, and that nanoparticles were aligned to a great extent across the surface of the MWCNTs. This finding suggests the following template sequence: creation of active sites on the MWCNTs, deposition of silver seeds at these active sites, formation of nanoparticles from the seeds, and then decomposition of the nanotubes' walls. When comparing Figures 2a and 2b, we observe that more than half of the wall of each MWCNT has decomposed completely. Figure 2c illustrates that when the reaction period is increased to 5 h, most of the organic wall decomposes and the nanoparticles are distributed across the entire MWNT. The images in Figures 2b and 2c suggest that the microwave-assisted reaction simultaneously templates the attachment of the nanoparticles and nanowires and decomposes the MWCNTs.



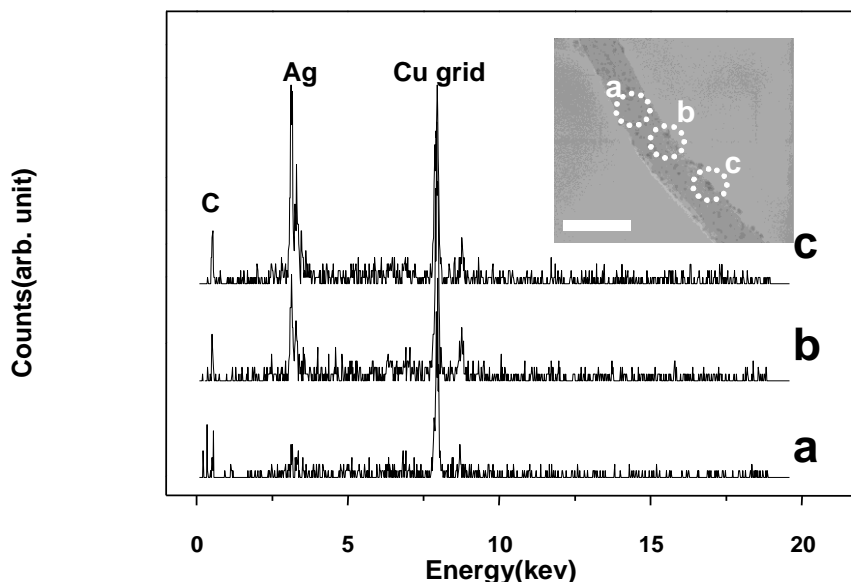
**Figure 2.** TEM images (scale bar: 55 nm) of MWCNTs subjected to treatment with  $\text{AgNO}_3/\text{HNO}_3$  at  $160\text{ }^\circ\text{C}$  in a microwave oven at different times: (a) 1, (b) 3, and (c) 5 h.

The effect of the reaction time on the diameter and density of the nanoparticles and on the diameters of the nanotubes is summarized in Figure 3. These results were obtained by averaging the data from TEM observations of 100 separate MWCNTs. The average diameter of the nanoparticles decreased from 20 to 15 nm upon increasing the heating time from 1 to 4 h, but after that time the average diameter remained constant. This finding suggests that, as the reaction time increases at a temperature 160 °C, the growing Ag nanoparticles become oxidized and then dissolve. This hypothesis raises the question of why the diameter of the nanoparticles does not decrease further as the reaction proceeds longer than 4 h. We infer that the dissolution of the nano-scale particles under highly oxidizing condition exhibits a nano-size effect. The density of nanoparticles increases up to a reaction time of 3 h and then it remains constant. In addition, the diameters of the MWCNTs decrease as the reaction time progresses. This observation indicates that the tubes' initial outer walls are replaced by Ag nanoparticles and their inner cavities become filled with Ag nanowires.



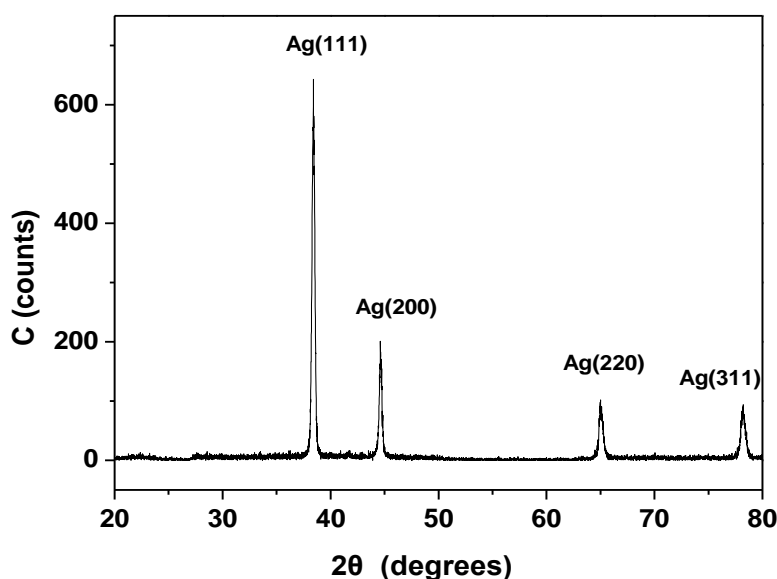
**Figure 3.** The relationships between the average nanotube diameter, average nanoparticle diameter, and the average particle density and the microwave heating time.

Figure 4 presents EDX spectra that allowed us to identify characteristics of the nanoparticles formed on the nanotubes. After sonication and filtration, the multilayer nanoparticles were gradually separated from the nanotubes that we had treated at 160 °C for 3 h. We scanned, by EDX analysis, different areas (a–c; see inset to Fig. 4) in which particles were distributed on a nanotube. Areas “a” and “c” are zones in which a small and a large number of nanoparticles had formed, respectively; area “b” has a particle density that is intermediate between those of the other two. These spectra illustrate the presence of peaks representing carbon, silver, and copper atoms at various energies. The carbon atom peak obviously reflects the presence of the multiwalled carbon nanotubes. The abundances of the peaks representing the Ag atoms in each area reflect the nanoparticles’ density.



**Figure 4.** (a–c) EDX spectra recorded in various regions of an MWCNT. The density of nanoparticles increases in the order zone “a” < zone “b” < zone “c”. The length of the scale bar in the inset is 30 nm.

Figure 5 displays the grazing angle XRD spectrum (incidence angle:  $0.5^\circ$ ) of a sample treated at  $160^\circ\text{C}$  for 5 h, sonicated to remove the nanotubes, and then coated onto a wafer. The diffraction peaks found in the range  $20^\circ < 2\theta < 80^\circ$  can be indexed to Ag(111), (200), (220), and (311), which suggest that the nanoparticles have fcc structures.

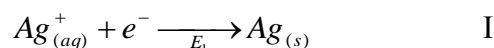


**Figure 5.** XRD pattern of the silver nanoparticles deposited on MWCNTs after treatment at  $160^\circ\text{C}$  for 5 h.

The lattice constant calculated from this XRD pattern is 4.092 Å, which is very close to the reported value ( $a = 4.0862$  Å; JCPDS file 04-783). Figure 5 also indicates the purity of the sample: no additional XRD peaks arising from impurities can be detected. This observation suggests the pure silver nanoparticles are successfully achieved by using the microwave-assisted reaction under strongly oxidizing conditions.

### 3.3 Mechanism for spontaneous self-organization of AgNPs in electroless microwave deposition system

Taking all of these results together, we have shown that a high density of silver nanoparticles can be condensed onto carbon nanotubes without the need to use any external linker on the surface of the nanotubes. After heating for at least 1 h, the surface functional groups behave as active sites at which the nanoparticles spontaneously form under the highly oxidizing conditions. Jia et al. [27] have reported similar results for the adsorbing of silver and gold ions onto activated carbon and have demonstrated that the metal adsorption capacity increases upon increasing the total pore volume of the activated carbon. Liu and coworkers [28] also assemble gold nanoparticles onto silicon surface by using simple spin-coating method. Similarity, we observed that the surfaces of the carbon nanotubes decomposed under the highly oxidizing conditions, or they became activated, by the action of nitric acid, which led to increased porosity of the surface shell. Once the metal ions adsorb onto the surface of the nanotubes, these surfaces play the role of reduction sites and reduce the silver ions to silver atoms by oxidation of carbon atoms near the surface. In addition, the reduced metal ions behave as seeds upon which silver ions in the solution condense. The half-reaction of Ag(I) reduction to Ag(0) is:

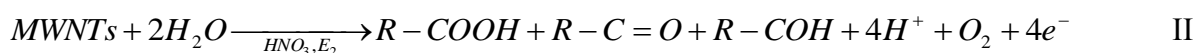


The redox potential of reaction I, according to the concentration of silver ions, is expressed by the Nernst equation:

$$E_1 = E_1^0 - \frac{RT}{0.434F} \log \left( \frac{1}{a_{\text{Ag}^{+}}} \right) \quad (1)$$

where R is the gas constant ( $8.314 \text{ Pa}\cdot\text{m}^3\cdot\text{K}^{-1}$ ), T is the absolute temperature, and F is the Faraday constant ( $96485.3 \text{ C}\cdot\text{mol}^{-1}$ ).

A plausible oxidation mechanism of the surface functional groups on the nanotubes is:



The redox potential of reaction II has the following relationship with respect to the acid concentration and the pressure of oxygen released in the reaction vessel:



$$E_{(2)} = E_{(2)}^0 - \frac{RT}{0.434F} (\log[H^+] + \log P_{O_2})^{-1} \quad (2)$$

The overall redox reaction, obtained by combining the two half-reactions of I and II, takes place only when the difference between reaction potentials (i.e., electromotive force) is positive; i.e., when

$$E = E_{(1)} - E_{(2)} = (E_{(1)}^0 - E_{(2)}^0) + \frac{RT}{0.434F} (\log a_{Ag^+} - \log[H^+] - \log P_{O_2}) > 0 \quad (3)$$

The reduction reaction is favorable at higher  $Ag^+(aq)$  activity and temperature. At reaction temperatures above the normal boiling point of the solution, the nitric acid will not only oxidize the surface of the nanotubes but also increase the redox reaction rate between the nanotubes and silver ions in the same manner as a spontaneous reaction between a metal/metal-ion pair.

#### 4. CONCLUSIONS

We have developed a method for depositing metal nanoparticles onto multiwalled carbon nanotubes; this self-assembly process occurs at high temperature under oxidizing conditions. The nanotubes behave as robust reducing agents, even under such strongly oxidizing conditions, to form silver nanoparticles having diameters of ca. 18 nm. The growing nanoparticles that condense onto the surfaces of the MWCNTs have fcc structures. Our findings suggest that there are simple methods for the efficient fabrication of nanoparticle/nanotube heterostructures that do not require any additional surface chemical reagents.

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