

In Situ Synthesis of Highly Dispersed Silver Nanoparticles on Multiwalled Carbon

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Since their discovery,¹ carbon nanotubes (CNTs) have been continuously attracting extensive interests in many areas of science and technology and have been the focus of current research for many years due to their unique structure-dependent optical, electrical, and mechanical properties. Recently, silver decorated CNT hybrids are increasingly attracting extensive attention due to their potential applications as catalyst,² broad-band optical limiters,³ electrodes,⁴ and advanced materials.⁵ Hybrid systems of nanomaterials may have collective properties that are drastically different from a simple combination of individual components. Therefore, many approaches and strategies, including the solid-state reaction,² vaporizing deposition,³ surface chemical reduction,⁴ electrochemical deposition,⁶ γ -irradiation,⁷ and other synthesis routes,⁸⁻¹⁴ have been attempted to attach silver nanoparticles (NPs) or nanoclusters on the functionalized CNTs. To prepare well-constructed silver NP-decorated CNTs, however, a simple and effective route is still more desired.

Here we report on a novel and facile wet-chemical method for the synthesis of silver NP-CNT assemblies, that is based on traditional coordination chemistry and can be generally applied to common metal elements. Key to the synthesis lies in the 3-aminopropyltriethoxysilane (APS)-mediated loading of silver precursors on the functionalized CNTs. The full procedure for preparing silver NP-CNT composites is shown in Figure 1.

MWCNTs were obtained from NTP (Shenzhen, China). Lithium aluminum hydride (LiAlH_4 , 95%) and APS (99%) were purchased from Aldrich. Other chemicals used were all analytical pure and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

Surface treatment of MWCNTs followed a standard route. In brief, MWCNTs were refluxed in mixture acids made of nitric acid and sulfuric acid for 2 h to give carboxyl groups modified MWCNT (MWCNT-COOH),¹⁵ followed by reac-

tion with LiAlH_4 in dry tetrahydrofuran (THF) at room temperature for 12 h, resulting in hydroxyl group functionalized MWCNT (MWCNT-OH). The $(\text{MWCNT-O})_3\text{-Si}(\text{CH}_2)_3\text{NH}_2$ intermediate was realized *via* covalent coupling of MWCNT-OH and an excess of APS in anhydrous toluene at 120 °C for 24 h under the protection of argon (Ar). The $(\text{MWCNT-O})_3\text{-Si}(\text{CH}_2)_3\text{NH}_2\text{-Ag}^+$ complex was obtained by reaction between $(\text{MWCNT-O})_3\text{-Si}(\text{CH}_2)_3\text{NH}_2$ and 1.0 mol/L AgNO_3 solution at room temperature for 2 h. The final silver NP loaded MWCNT ($(\text{MWCNT-O})_3\text{-Si}(\text{CH}_2)_3\text{-NH}_2\text{Ag}$) hybrids were fabricated *via in situ* reduction with sodium borohydride (NaBH_4). The as-prepared mixtures were fully washed with distilled water and absolute ethanol for several times. Finally, the products were collected by centrifugation and the precipitate was dried at 60 °C in vacuum for 10 h.

The morphology and dimension of the product were observed by transmission electron microscopy (TEM), which was taken on a Hitachi Model H-600 electron microscopy using an accelerating voltage of 100 kV. The crystalline structure of the sample was characterized by X-ray diffractometer equipped with a monochromated $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The powder X-ray diffraction (XRD) pattern is recorded from 15 to 90° in 2θ with a scanning rate of 0.017°/s. The products were also analyzed by X-ray photoelectron spectroscopy (XPS), which was carried out on a PHI5702 multi-functional X-ray photoelectron spectrometer (Physical Electronics, USA), using $\text{Al K}\alpha$ X-ray as the excitation source.

A representative TEM image of silver NP modified MWCNTs is shown in Figure 2. It can be clearly seen that silver NPs are generated after a round of ion coordination and reduction. The surface-deposited silver NPs are highly dispersed along MWCNTs with average sizes of 10-12 nm. The silver NPs show no tendency to aggregate at defects of the MWCNT surfaces.

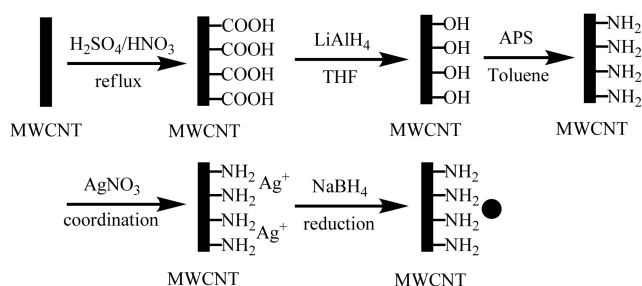


Figure 1. Schematic procedure for the attachment of silver NPs on the functionalized MWCNTs.

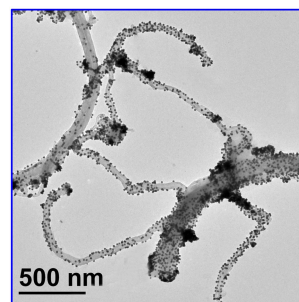


Figure 2. TEM image of silver NP-loaded MWCNT composites.

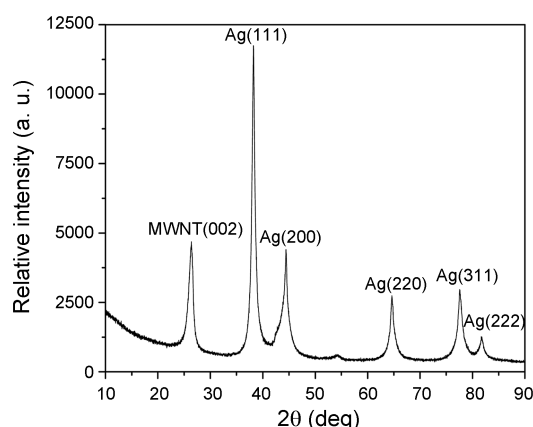


Figure 3. XRD pattern of silver NP coated MWCNT composites.

One of the reasons is that in the present work we protect the MWCNT surfaces through molecule level design. Covalent bonding of APS monolayer grafted on the MWCNT surfaces and subsequent coordination with Ag^+ provides a uniformly functionalized surface, so resulting silver NPs show no tendency to aggregate but exhibit uniform and orderly attachment to the modified MWCNTs.

Figure 3 shows a typical XRD pattern of as-prepared silver NP-loaded MWCNT composites. The major diffraction peaks can be readily indexed to face-centered cubic (fcc) phase silver based on the data of the JCPDS file (JCPDS 4-783). The MWCNTs showed a typical of(002) phase of CNT or graphite,¹⁶ and the peaks appeared at about 38.9° , 45.1° , 65.1° , 78.2° , and 82.1° can be assigned to (111), (200), (220), (311), and (222) crystalline plane diffraction peaks of silver, respectively. The broad peaks in the XRD pattern indicate that in situ synthesized silver NPs are small. The average crystallite size of silver NPs is 10.6 nm calculated using the Scherrer formula, which is in good agreement with the result from the TEM image.

XPS measurements were made to further confirm the chemical composition of the above-synthesized MWCNT/silver nanohybrid surface. The binding energies are corrected for specimen charging by referring to the C1s at 284.8 eV. As depicted in Figure 4(a), the XPS spectrum of silver NP coated MWCNT composites shows the Ag 3d5/2 and 3d3/2 doublet with the binding energies of 367.8 and 373.8 eV, respectively. These are typical values for Ag^0 ,¹⁷ indicating the formation of silver NPs on the surface of MWCNTs. In addition, two characteristic peaks, one at about 103.0 eV (Figure 4(b)), attributable to the Si-O species,¹⁸ and the other centered at about 399.8 eV (shown in Figure 4(c)), corre-

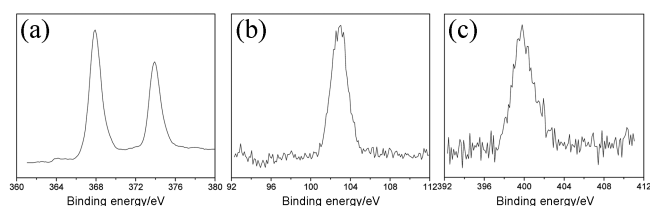


Figure 4. The XPS spectra of the as-prepared MWCNT/silver nanohybrids: (a) Ag region; (b) Si region; (c) N region.

sponding to N1s of the organic amino groups,¹⁹ are observed for the MWCNT/silver nanocomposites, which on one hand verifies successful attachment of APS and on the other hand provides the powerful evidence of the successful immobilization of silver NPs on the modified MWCNTs. The above data support the in situ formation of silver NPs on the APS-functionalized MWCNT surface.

In summary, we have reported a simple and novel in situ synthetic route for the preparation of silver NP coated MWCNT heterogeneous composites. A layer of APS was first grafted on the activated MWCNTs and then reacted with moderate concentration AgNO_3 , which introduced a large number of Ag^+ groups on the MWCNTs. Silver NPs with the size of ~ 10.6 nm were in situ deposited on the MWCNTs by the reaction between Ag^+ and NaBH_4 . This method brings forward a facile idea to direct favorable growth of silver NPs on the modified MWCNTs. It is a simple, effective, fast, and mild route, which avoids the complicated synthetic procedures and the use of rigorous reaction conditions. The above-prepared heterogeneous nanostructures may have potential applications in catalysis, sensor, and fuel cells. Using the similar strategy it is expected to prepare other CNT/metal nanomaterials with the analogous structures.

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