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Effect of highly dispersed sputtered silver nanoparticles on structural properties of multiwalled carbon nanotubes

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ABSTRACT

A simple method to decorate mutliwalled carbon nanotubes (MWCNTs) with silver nanoparticles (Ag NPs) to enhance the structural properties is reported in the present study. The Ag NPs of average size 9 nm were deposited uniformly on MWCNTs network by RF sputtering technique. X-ray diffraction (XRD), Raman spectroscopy and Scanning electron microscopy (SEM) are used to compare the structural properties of Ag NPs sputtered nanotubes with those containing functionalized tubes. In addition, effect of these Ag NPs on the surface of nanotubes and optimization of the experimental parameter for uniform deposition of Ag NPs are also discussed.

1. Introduction

Since their discovery, carbon nanotubes (CNTs) have been attracting extensive interests in many areas of science and research due to their high aspect ratio, unique electrical, excellent chemical and mechanical properties [1,2]. Metal decoration on CNTs has opened a new opportunity for researchers with significant applications in various branches [3,4]. A good interfacial interaction between metal nanoparticles and CNTs can be achieved by making various components compatible at the molecular level through chemical functionalization of nanotubes [5]. Functionalization via acids introduces various functional groups on the surface of nanotubes, which helps in nucleation of metal nanoparticles. In addition, the metal nanoparticles provide a continuous pathway for moving charge carriers between nanotubes, which improves the charge transfer process [6].

Silver (Ag) nanoparticles decorated CNTs have shown specific interest as hybrid materials due to their potential applications such as catalysts, broad-band optical limiters, electrodes and antimicrobial agents [7–11]. However, the decoration of a majority of metal nanoparticles on the nanotubes is very difficult [11]. Haider et al. [12] decorated the silver nanoparticles on the CNTs via chemical route for biological application. However, the distribution of the particles on the nanotubes was non-uniform. Various methods of Ag decoration on nanotubes have been reported such as solid-state reaction, vaporizing deposition, surface chemical reduction, electrochemical deposition and γ-irradiation to attach silver nanoparticles on the functionalized nanotubes [12–17]. The main drawback of these methods is agglomeration of Ag NPs causing difficulties in uniform decoration of nanotubes surface. To obtain an efficient fabrication of MWCNTs/Ag nanostructure, a simple and cost-effective route is required.

In the present work, we have attached carboxylic and hydroxyl groups to multiwalled carbon nanotubes (MWCNTs) by covalent functionalization. Then, Ag metal was sputtered to the network of nanotubes. Various characterization methods such as XRD, Raman spectroscopy and SEM have been used to identify structural and morphological changes in the nanotubes after Ag metal sputtering. To the best of our knowledge, such high electrical current of Ag sputtered nanotubes is reported for the first time by drop-casting only 2% by wt. F-MWCNTs on fabricated interdigitized electrodes (IDEs). Further, the influence of bombardment of energetic particles on the surface of nanotubes and its role in the deposition of Ag NPs on tubes is also reported.

2. Experimental procedure

Functionalized MWCNTs (F-MWCNTs) were used for the preparation of nanostructure. The details of functionalization procedure for pristine nanotubes have been reported in our previous work [18]. A network of these nanotubes was drop-casted on the silicon (Si) surface. RF sputtering process was used for Ag metal

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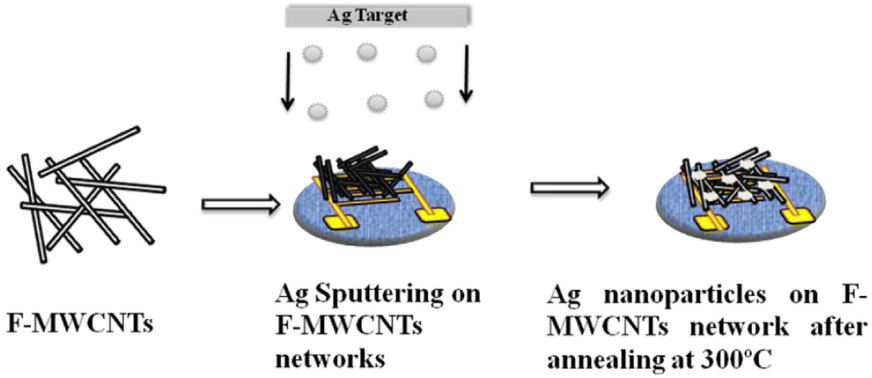

Fig. 1. Schematic diagram of Ag NPs sputtering process on nanotubes network.

with standard deposition rate of 30 nm/min at 100 W. With this standard rate, we found that a thick film was deposited on the network of nanotubes. Therefore, to deposit the Ag NPs instead of thin film, we have optimized deposition parameters by changing deposition power and time. During Ag deposition, initial pressure $\sim 2.7^{*}10^{-3}$ bar was maintained in the system. Afterwards, the base pressure $\sim 1.3^{*}10^{-5}$ bar was maintained in Ar atmosphere. In this work, the deposition of Ag metal was done at 20 W for 1 min. The sputtered sample was annealed in Ar atmosphere at 300 °C using rapid thermal processing (RTP) unit. The rate of rise in temperature was kept at 30 °C/s and average cooling rate at 16.2 °C/s. All aforesaid steps are shown in Fig. 1. The Ag NPs decorated nanotubes were named as F-MWCNTs/Ag. For electrical measurements same process was adopted on nanotubes network casted on IDEs. The schematic representation of adopted method is shown in Fig. 1.

The structural properties of the samples were studied by using X-ray diffraction (XRD) and Raman techniques. The XRD spectrum of the Ag sputtered sample was recorded on PANalytical X'Pert Pro diffractometer, utilizing Cu Kα- X-ray with wavelength 1.54 Å. The Raman spectra of the samples were recorded on Renishaw spectrometer at room temperature using the excitation wavelength 514.5 nm of Ar^{+} laser. The morphology of the samples was confirmed by scanning electron microscope (SEM, Raith 150 Two). The current–voltage characteristics of both the samples were recorded using Proxima probe station (Model-PM8-PS) in two probes configuration.

3. Results and discussion

3.1. Structural analysis

The XRD spectra of F-MWCNTs before and after Ag deposition are shown in Fig. 2(a) and (b). XRD spectra of nanotubes show a broad diffraction peak at $2\theta = 25°$, which is characteristic peak for MWCNTs and related to spacing between graphene sheets of the tubes. Also, three different peaks corresponding to the planes (100), (102) and (110) corresponds to crystalline graphite-like structures [10]. For Ag deposited nanotubes, prominent carbon peak (002) appears at higher diffraction angle ($2\theta = 25.3°$) as shown in Fig. 2(a). In addition, the F-MWCNTs/Ag (Fig. 2(a)) showed four main crystallographic planes for Ag NPs; such as (111), (200), (220) and (311), which confirmed the face centered cubic (fcc) phase of Ag NPs (JCPDS card no. 40783). The average crystallite size of Ag NPs (~8 nm) from these four planes was calculated using the Scherrer formula.

From Fig. 2b, the graphitic peak (002) of F-MWCNTs/Ag nanostructure shifts to higher diffraction angle as compared to F-MWCNTs. This indicates that an interplanar spacing (d) decreases after attachment of Ag NPs on the tubes. This shift is mainly originated from strong interaction between nanotubes and Ag NPs. Moreover, this interaction may result in compressive stress, giving rise to decrease in interplanar distance [19].

The various parameters obtained from XRD spectra of both samples are shown in Table 1. The parameters to estimate the line shape broadening of nanotubes scattering are; domain size broadening (ΔQ) and strain broadening (ΔQ_s). The domain broadening (ΔQ) was calculated from following formula [20]:

$$\Delta Q = (2\pi \ln 2)^{\frac{1}{2}} \frac{1}{Nd}$$

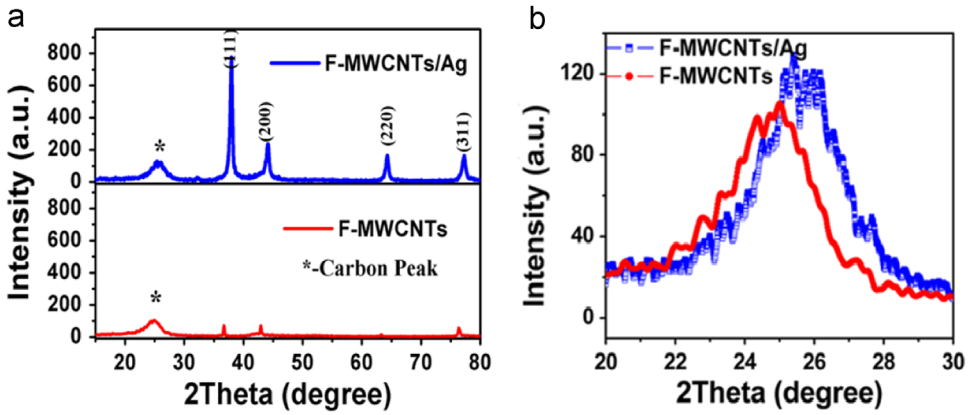

Fig. 2. XRD spectra of (a) functionalized and AgNPs deposited nanotubes network (b) the shifting in (002) plane in functionalized and AgNPs deposited nanotubes.