

Preparation and characterization of multi walled carbon nanotubes /Ag nanoparticles hybrid materials

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Abstract

In this paper, multiwalled carbon nanotubes (MWCNTs) have been functionalized by concentrated acid treatment. Then Ag nanoparticles are attached onto the functionalized F-MWCNTs using a chemical reduction process as an example of direct formation of AgNPs/ MWCNTs hybrid materials between the functionalized F-MWCNTs and the Ag ions. Finally, chemical composition and crystallographic structure of F-MWCNTs and Ag/MWCNTs results have been confirmed by X-ray diffraction (XRD) and Raman measurements. Zeta potential analysis has been shown the change of the surface properties of F-MWCNTs and AgNPs/ MWCNTs hybrid materials, while transmission electron microscopy (TEM) has been used for characterization of the morphology of results as well as the distribution of nanocrystals on the MWCNTs surfaces. These observations point to the potential use of MWCNTs decorated with silver nanoparticles as building blocks for antimicrobial applications, optoelectronic devices, solar energy conversion, and photocatalysis.

Keywords: Nanomaterials, silver nanoparticles decorated Carbon nanotubes (Ag/MWCNTs), AgNPs/ MWCNTs hybrid materials, Functionalization Carbon nanotubes

1 INTRODUCTION

Since multi walled Carbon nanotubes (MWCNTs) have become the one of the mostly researched materials in the last decades because of their promising applications in any aspect of nanotechnology [1]. Unlike other carbon materials, such as graphite and diamond, CNTs are one dimensional carbon material. The graphene layer is rolled up cylindrically with diameter on a nanometer scale. The structure and morphology of CNTs enable them to serve as a specific template for preparing metal nanoparticle/CNT hybrids [2,3]. Since, AgNPs /multi walled Carbon nanotube hybrid materials have attracted more interest and they are believed to be useful as building blocks for solar energy conversion,

photocatalysis and sensors, result mainly from their high surface area, mechanical strength, chemical and thermal stability [4,5].

The combination of these two materials (i.e. MWCNTs and Ag nanoparticles) is particularly useful to integrate the properties of the two components in hybrid materials for use in catalysis, energy storage and nanotechnology [6].

However, the effective preparation of this type of hybrid using wet chemical methods is difficult since the MWCNTs are insoluble in common solvents. Furthermore, the surfaces of CNTs are generally inert and have almost no functional groups. Therefore, in order to attach the nanoparticles firmly onto the nanotube, a strong interaction force needs to be introduced between CNTs and the nanoparticles. Consequently the chemical functionalization method is required, whereby the use of strong acids such as HNO₃ or H₂SO₄ helps in the formation of hydroxyl and carboxylic groups on the surface of the CNTs and this technique provides for the nucleation of the metals [6]. Direct formation

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of nanoparticles onto CNTs has two important advantages: it is highly effective method as well as the inherent properties of the nanocrystals and nanotubes are preserved [7]. Among them, Ag nanoparticles (Ag-NPs) attached onto MWCNTs gained significant attention due to their potential applications. Those properties are closely related to their size and shape [8-10].

In presented work we report results of synthesis of carbon nanotubes decorated with Ag nanoparticles by reduction process as an example of direct formation of nanoparticles onto MWCNTs. Furthermore, the structures and the surface morphology of the treated MWCNTs and hybrids have been analyzed using transmission electron microscopy (TEM), X-Ray diffraction and Raman measurements. The change of the surface properties of MWCNTs after functionalization can be clearly seen by inspecting their zeta potential analysis.

2 Experimental work

2.1 Functionalized of MWCNT-COOH

Raw-MWCNTs (0.1 g) with Purity ($> 95\text{wt}\%$, outside diameter: 5-15 nm, Inside diameter: 3-5 nm and Length: $\sim 30\mu\text{m}$ /USA) were dispersed in mixture of concentrated sulfuric acid $95\% \text{H}_2\text{SO}_4$ and nitric acid $65\% \text{HNO}_3$ (3:1) under ultrasonication technique for 30 min to produce oxidized carbon nanotubes (MWCNT-COOH). The samples were washed with deionized water (D.I) and dried at 70°C for 24 h.

2.2 Preparation of MWCNT-COOAg

0.1g of F-MWCNT was dispersed in 40 mL of distilled water through ultrasonication for 30 min. To this solution, (100ml, 0.2M AgNO_3) solution was prepared with constant stirring at temperature greater than 60°C via magnetic stirring for approximately 2h to generate Ag^+ ions. Then 20 mL of Ag^+ ions solution was added to F-MWCNT solution and stirred for a further 2 hours to achieve the decoration of carbon nanotubes (MWCNT-COOAg). After the completion of reaction, solid products were collected by centrifuging and

dried under vacuum at 50°C . Then Ag ions grafted onto carbon nanotubes were reduced at 200°C for 2h and leave it in under vacuum for 24h to generate Ag nanoparticles on the carbon nanotube surface as shown in Fig (3.3) which represented Schematic diagram of Preparation of hybrid material (Ag+/MWNT). nanotubes were reduced at 200°C for 2h to generate Ag nanoparticles on the carbon.

2.3 Characterization of MWCNTs before and decorated with silver nanoparticles.

The surface morphology and structure of treated MWCNTs and hybrid material (Ag-MWCNTs) were studied with TEM analysis (EM208, Philips), X-Ray diffraction (XRD-6000, Shimadzu) and Raman (Renishaw Invia) measurements. Zeta potential analysis (Malvern ZS-Zetasizer) has been used to study the change of the surface properties of F-MWCNTs and AgNPs/ MWCNTs hybrid materials.

3 Results and discussion

3.1 Characterization studies of treated MWCNTs

X-ray diffraction (XRD) study is performed to characterize the dimensions and structure of MWCNTs. Fig (1 a, b, c) shows the XRD patterns of raw, functionalized F-MWCNTs and Ag+/MWCNTs, respectively. Fig (1, a) shows two peaks at 25.9° and 44.1° correspond to the (0 0 2) and (1 1 0) of raw-MWCNTs and the peaks at 25.8° and 44.1° for treated F-MWCNTs Fig (1,b) which are corresponding to (002) and (110) reflections of graphite from the MWCNTs. The shifting of characteristic peak position in the XRD pattern of F-MWCNTs shows the perfect modification of raw-MWCNTs. Besides, there is no drastic change in the position of characteristic peaks of raw-MWCNTs and F-MWCNTs was observed, which suggest that MWCNTs are well retained their original structure after functionalization. The diffraction peaks in Fig (1, c), except the peak at $2\theta = 25.8^\circ$, which is corresponding to the (0 0 2) reflection of the MWNTs, and all the other peaks are due to MWNTs-

COOAg. These results indicate that Ag-NPs were strongly attached to the F-MWCNTs surface due to the carboxylic groups' functionalization of the MWNTs after chemical treatment in our experiment, which enhanced the reactivity with Ag. The peaks at 38.1°, 44.3°, 64.7° and 77.4° degrees corresponding to main crystallographic planes, namely, Ag(111), Ag(200), Ag(220), and Ag(311), respectively as shown in Fig (1, c). The average particle size of the sample(111) reflection in our study have been estimated by using the Scherer's equation and was found to be ~11 nm for the strongest peak which is in good agreement with the result obtained by the TEM image Fig (4). As shown from Fig (1, c) the characteristic diffraction peak of (002) MWCNTs decreases in MWCNTs/Ag sample due to high intense peaks generated from strongly attached Ag NPs to the surface of functionalized MWCNTs (F-MWCNTs) as compared to raw-MWCNTs. Besides, the intensity of diffraction peak at (002) in treated acid F-MWCNTs was increased as compared to the raw- MWCNTs as shown in Fig (1, b). This is an indication of the ordered F-MWCNTs floss in the acid functionalized MWCNTs.

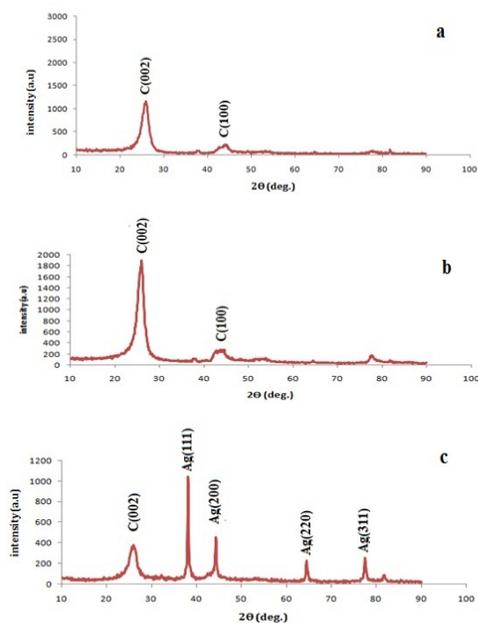


Fig (1): XRD patterns for a) raw, b) functionalized MWCNTs using chemical treatment b) and MWCNTs/Ag

spectrum with an excitation laser length of 633nm is used to analyze the presence of amorphous in crystalline phases corresponding to differences in graphitizations. Raman spectra of raw, acid treated (F-MWCNTs) and Ag/MWCNTs, which can be used to evaluate the degree of disorders/defects of MWCNTs after the acid treatment process, are appeared in Fig (2, a, b, c) respectively.

Three characteristic peaks of MWCNTs are observed for raw MWCNTs namely D-band at 1325cm⁻¹, G-band at 1576cm⁻¹ and G'- band at 2647 cm⁻¹, for F-MWCNTs D-band at 1329 cm⁻¹, G-band at 1591 cm⁻¹ and G'- band at 2649 cm⁻¹. Finally, for Ag/MWCNTs D-band at 1331 cm⁻¹, G-band at 1597cm⁻¹ and G'- band at 2645 cm⁻¹ as shown in Fig (4.1,a,b,c),respectively .The D line indicates disordered or amorphous carbons, while the G line indicates graphite or ordered carbons in the MWCNTs, and the G' line indicates a second harmonic of the D line .

As shown from the results after oxidation and decoration with Ag+NPs, these characteristic peaks are still present, proving that the acid treatment does not damage the structure of MWCNTs. Moreover, the degree of crystallinity in carbon samples was evaluated using the D to G band intensity (I_D/I_G) ratio as shown in table (1) which is the intensity of the disorder mode at D band divided by the intensity of graphite mode at G band. The ratio of I_D/I_G is increased for functionalized (F- MWCNTs) as compared to raw MWCNTs as shown in Fig (2,a,b). It means that the oxidation of MWCNTs breaks some bonds and inserts functional groups that can be considered as defects on the structure like the carboxyl and hydroxyl groups caused in the treatment process and these results are consistent with those reported earlier [48,107].

In contrast, the intensity (I_D/I_G) ratio shows no increase after deposition of Ag/NPs on treated MWCNTs indicating that no significant sidewall damage is caused and also suggests a charge-transfer process and chemical interaction between the Ag NPs and the MWCNTs surface after the deposition process as shown in Fig (2,c).

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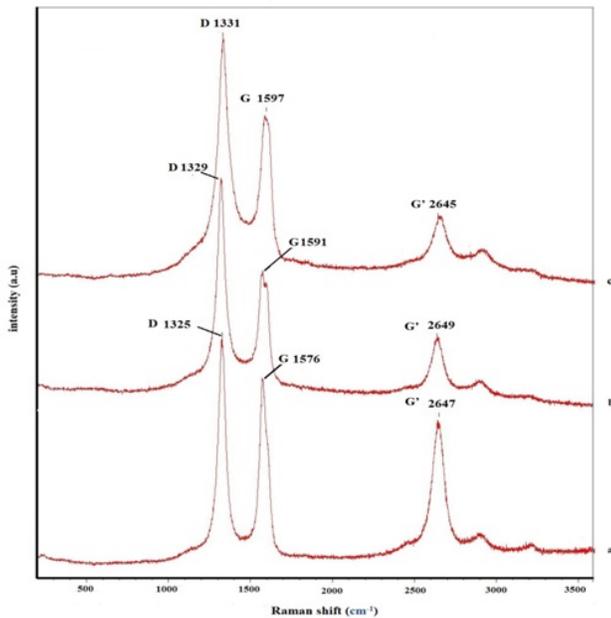


Fig (2): Raman spectra of a) raw MWCNTs, b) acid-treated F-MWCNTs and c) Ag/MWCNTs.

Table (1): list of ratio intensity of D and G band, (I_D/I_G) of three different structural nanotubes

The material	I_D/I_G ratio
Raw-MWCNTs	1.16
F-MWCNTs	1.58
Ag/MWCNTs	1.41

The change of the surface properties of MWCNTs after acid treated F-MWCNTs and deposition of AgNPs onto the surface of MW CNTs Ag/MWCNTs can be clearly seen by inspecting their zeta potential, which is shown in table (2).

Table (2): list of zeta potential data of MWCNTs before and after AgNPs decorations

The sample	zeta potential (mV)	The state
Raw-MWCNTs	-18	Aggregation(not stable)
F-MWCNTs	-38	Not Aggregation (stable)
Ag/MWCNTs	-36	Not Aggregation (stable)

According to the results above, it's found that raw-MWCNTs sample showed low stability (aggregation state) as compared with F-MWCNTs and Ag/MWCNTs samples. According to *ASTM Standard (D 4187-82)*, colloids with zeta potential from $\pm 30\text{mV}$ to $\pm 40\text{mV}$ have moderate stability solvents (like ethanol, water...). When the potential value is lower than this standard, attraction exceeds repulsion and the dispersion will break down and tend to aggregate as shown in Raw-MWCNTs. So, colloids with zeta potential (negative or positive) beyond the standard value are electrically stabilized. As shown in table (4.2), F-MWCNTs in ethanol decreased from -18 mV to -38mV after acid treatment. This change can be explained by the introduction of negatively charged groups on the MWCNTs by the acid treatment [122,123]. In addition, Ag NPs that deposited onto the MWCNT surface through chemical reduction approaching the zeta potential of hybrid materials from positive value than the raw-MWCNT and F-MWCNTs in solvents. However, the original negative charge on the raw-MWCNTs surface could be decreased by the deposition of various metals.

From the results of TEM analysis it was found that the main parameter affecting the disentanglement (debundling) of treated MWNTs is the chemical treatment and also leads to existence of physical defects on the surface of MWNTs as shown in Figs (4,a,b). Moreover, formation of functional groups on the surface of nanotubes generates repulsion force which leads to debundling of nanotubes and therefore causes surface increases. Also, the functional groups introduced by surface oxidation play an important role for the deposition of metal ions.

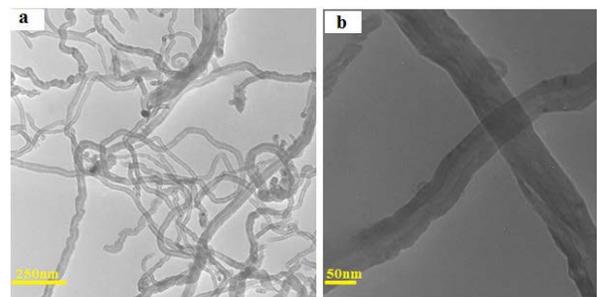


Fig (4): TEM image of treated MWCNT after 30 min of acid treatment (ultrasonication in mixture of concentrated

The morphology of attachment of silver nanoparticles on treated MWCNTs (Ag+/MWCNTs) were examined by TEM at different magnifications as shown in Figs (5,a,b) respectively. In Fig (5 a,b) the formation of Ag nanoparticles (Ag⁺) on the MWCNTs surface at different magnifications by using (AgNO₃, 0.2M) was confirmed by TEM results. TEM analysis shows dark spots (indicated by circles) correspond to Ag nanoparticles and light tubes correspond to MWCNTs. As shown in Fig (5) with scale bars = 50nm the side walls of MWCNTs are evenly decorated with Ag nanoparticles and there are AgNPs aggregates on the wall of MWNTs so densely and uniformly that it is hardly to see the hollow cavity of the tubes which may result from application of heat for long time. Since, observed silver particles appear to have a narrow size distribution, and no free particles are observed in the background of the TEM images, which confirms all formed Ag nanoparticles are durably attached to the nanotubes.

From the TEM images in Fig (5 a,b) it is possible to determine directly the diameter of one nanotube and bundle diameter were about a few nanometers (10 to 25 nm). Due to this information number of nanotubes in the bundle can be found out.

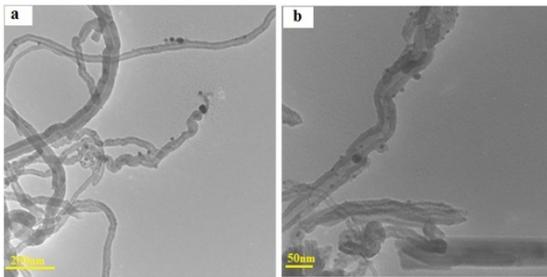


Fig (5): TEM images of Ag+ NPs decoration MWCNTs at different magnifications a) Scale bars = 500nm, b) Scale

4. Conclusions

Integrated analysis of functional group attached on the MWCNT surface has been conducted. Moreover, density of carboxyl groups strongly depends on the power of acid solution whereas carboxyl groups were dominantly introduced on the carbon nanotube surface. In our study, data from both XRD and Raman

measurements have proven functionalized multiwalled carbon nanotubes (F-MWCNTs) using chemical treatment and also found to be good supports for decorating Ag nanoparticles (Ag/MWCNTs). Since, the oxidation of MWCNTs breaks some bonds and inserts functional groups that can be considered as defects on the structure as shown in Raman analysis. Acid treatment in this method did not affect the crystallinity of MWCNTs as proved in XRD analysis.

Moreover, Zeta potential analysis shows that MWCNTs become obviously negatively charged after acid treatment and it's found that raw-MWCNTs sample showed low stability (aggregation state) as compared with F-MWCNTs and Ag/MWCNTs samples. Furthermore, the results obtained have been characterized by transmission electron microscopy (TEM) analysis which reveals the successful AgNPs decoration onto the MWCNTs surface after functionalization that result from application of heat and this combination can lead to the very promising hybrid materials (Ag/MWCNTs) which could be used for water purification and disinfection or for medical purposes.

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