

# SILVER NANOPARTICLES GRAFTED CARBON NANOTUBE CAPSULES: SYNTHESIS AND CHARACTERIZATION

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## 1 General Introduction

Carbon nanotubes have attracted great interest in the field of anode materials due to its unique properties as superior mechanical strength and good electrical conductivity [1-4]. Carbonaceous capsules, especially hollow carbonaceous capsules, posses unique physicochemical properties and have great potential applications in many fields such as catalyst supports, adsorbants, biomedical and electrochemical devices [5-6]. Using of carbon nanotubes in synthesizing carbon capsules combines the characteristics of carbon nanotubes and carbon capsules in a synergistic way. The capsules based on carbon nanotube having hollow interior and compact structure is more favorable for the preparation of metal or metal oxides encapsulated inside the nanostructures.

In the present study, we have grafted silver nanoparticles on the surface of carbon nanotube capsules via impregnation method and posterior microwave reduction. Microwave reduction technique is employed as a versatile tool to control the size of the nanoparticles grafted into the carbon nanotube capsules structure. Analytical approaches such as X-ray diffraction (XRD), transmission electron microscopy (TEM), Field emission scanning electron microscopy/energy dispersive X-ray analysis (FE-SEM/EDX) were used to characterize the synthesized materials.

## 2 Experimental

### 2.1 Synthesis of silver nanoparticle grafted carbon nanotube based capsules

Carbon nanotube capsules (CNCs) were prepared via self-assembly of acid modified carbon nanotubes in a water-in-oil emulsion system [6]. In brief, carbon nanotubes were treated with the mixture of sulfuric and nitric acid for 1 hr. This step was followed by the dispersion of the ammonia/water mixture using a high power ultrasonicator. Then, known quantity of olive oil was added and the sonication was continued for 150 min that lead to the formation of oil-in-water emulsion. After ultrasonication for 1 hr, the mixture containing CNCs and oil was cooled to room temperature and separated by centrifugation. The desired CNCs were obtained by washing with petroleum ether, separation and dryness. The synthesis of the silver nanoparticle grafted carbon nanotube capsules were prepared by impregnating the capsules into 0.25 molL<sup>-1</sup> silver nitrate/water for 48 h at 25°C, where the Ag<sup>+</sup> was adsorbed onto the surface of modified CNTs. The CNC capsules were then filtered, dried and subjected to microwave reduction reaction to generate silver nanoparticle grafted carbon nanocapsules.

### 2.2 Characterization studies of silver nanoparticle grafted carbon nanotube capsules

The morphology, microstructure and composition of the silver nanoparticle grafted CNC's were investigated by field-emission

scanning electron microscopy (FE-SEM, LEO SUPRA 55), transmission electron microscopy (TEM, JEOL 100C), X-ray diffraction (XRD) measurements. XRD was conducted using Bruker with Cu K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ). X-ray photoelectron spectroscopy (XPS, high resolution ESCA 2000) was used to check the surface composition of silver nanoparticle grafted CNC structures. The functional groups present in the samples were analyzed by Fourier Transform Infra Red spectroscopy, with a Perkin Elmer Spectrum 100 FT-IR spectrometer using KBr salt for solid pellet analysis.

### 3. Results and discussion

Fig. 1 shows the FT-IR results of pristine MWCNT, oxidized MWCNT, CNC and Ag-CNC. In pristine MWCNTs, the appearance of vibration band at  $1570 \text{ cm}^{-1}$  alongwith the peaks at  $1622$  and  $1385 \text{ cm}^{-1}$  are corroborated to the CNT skeletal in-plane vibration, conjugated C=C stretching vibrations and C-C interaction. Appearance of small peak at  $1716 \text{ cm}^{-1}$  is attributed to the incorporation of acidic groups at the surface of the MWCNTs during the refining process. However, peak intensity corresponding to the peak at  $1716 \text{ cm}^{-1}$  significantly increases corroborating the fact that new -COOH groups are introduced on the MWCNT surface due to acid oxidation. Appearance of vibration band at  $1220 \text{ cm}^{-1}$  and at  $1425 \text{ cm}^{-1}$  that are corresponds to C-O functionality and -OH bending vibrations further supports the above fact. Besides these, acid treatment with nitric acid results in the appearance of a new stretching vibration at  $1364 \text{ cm}^{-1}$ , which can be correlated to NO<sub>2</sub> groups introduced on the surface during the oxidation reaction. The peak corresponding to  $1716 \text{ cm}^{-1}$  slightly shift to lower wave number ( $1712 \text{ cm}^{-1}$ ), which implies that many hydrogen bonding formed between -COOH group and -OH between the oxidized carbon nanotubes during the self assembly process (Fig.1c). These

interactions make the texture of CNCs compact and stable.

The peak ( $1622 \text{ cm}^{-1}$ ) corresponds to the  $-\text{COO}^-$  stretching vibration is intensified in Ag/CNC composites besides the peak shift at  $1712 \text{ cm}^{-1}$  due to hydrogen bonding corroborates the existence of interaction between  $-\text{COO}^-$  and unreduced Ag<sup>+</sup> ions in the system [Fig. 4d].

X-ray diffraction (XRD) study is performed to characterize the dimensions and structure of the Ag/CNCs nanocomposites. XRD patterns of Ag/CNCs nanocomposites are shown in Figure 2. It can be seen that all Ag/CNCs profiles at different concentrations exhibit strong diffraction peaks at  $2\theta = 38.1^\circ, 44.3^\circ, 64.5^\circ$  and  $77.5^\circ$  assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections, respectively, of Ag metal crystals with face centered cubic symmetry (JCPDS 04-0783). The crystalline size of Ag nanoparticles, determined using Scherrer's equation, reveals that the particle sizes are 18.4, 23.2, 26.1 and 47.5 nm for 0.25M, 0.5M, 1.0 M and 1.5 M Ag/CNCs composites, respectively. There is a clear trend of increasing of particle size at higher metal loadings, indicating the formation of a larger sized aggregate in the case of a higher silver impregnation.

The Ag atomic states are investigated using the Ag XPS spectra. Fig. 3 shows the Ag 3d spectrum of Ag/MWCNTs. Two peaks, with binding energies of 368.4 and 374.4 eV corresponding to Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, reveal the presence of Ag nanoparticles grafted on the CNCs walls. Fig. 4 shows the high resolution C 1s spectrum of 0.25 M Ag/CNC. Non-linear Gaussian fitting of this spectra results in three peaks: 289.2, 286.7 and 284.8 eV, which can be assigned to carboxyl carbon (O=C-O) on the nanotube surface, hydroxyl carbon (C-OH) and extensively delocalized sp<sup>2</sup>- hybridized carbon, respectively [7]. Both O 1s and C 1s spectrum results indicates that the functional groups are

successfully introduced during the oxidation of the MWCNTs, which as we mentioned before and these are key anchoring sites for the deposition of metal species into the support. These results also confirm the fact that, even with the hard oxidizing pretreatment that MWCNTs are subjected, the intrinsic structure of the nanotubes remained basically intact. Besides from the peak areas, of 0.25 M Ag/CNC C1s spectrum (Fig. 4b) and CNC C1s spectrum (Fig. 4a), it can be seen that the proportion of O=C-O to C-OH groups ( $[O=C-O]/[C-OH]$ ) decrease for the 0.25 M Ag/CNC ( $[O=C-O]/[C-OH]=0.67$ ) comparing with the CNCs ( $[O=C-O]/[C-OH]=0.72$ ). The above result indicates that Ag particles were successfully anchored in the carboxylic groups (COOH) of the oxidized surface of CNCs.

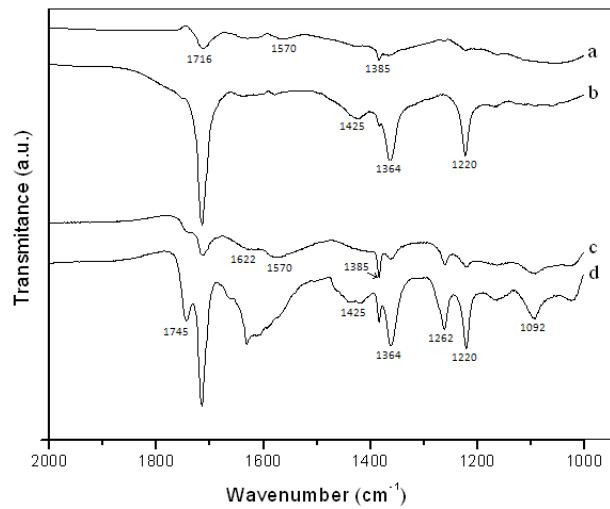
The O 1s spectrum of 0.25 M Ag/CNC (Fig. 5b) is resolved into three individual component peaks: O-C=O (533.4 eV), C-O group (532.1 eV) and O-H (531.7 eV) group. Figure 5a shows O1s spectrum of CNCs which presents the same peaks as the above mentioned. However it can be clearly seen a difference in the proportion of O=C-O to C-O groups between both samples (Fig. 5a and Fig. 5b). Specifically the 0.25 M Ag/CNC O 1s spectrum presents a ratio of  $[O=C-O]/[C-O]$  of 0.82, while the CNCs O1s spectrum presents a ratio of  $[O=C-O]/[C-OH]$  of 1.43. The decrease of the ratio above mentioned is attributed to the successfully anchoring of the Ag particles to the carboxylic groups (COOH) in the oxidize surfaces of the MWCNTs that forms the CNCs, fact that reduces the amount of O=C-O groups after the decoration of the support with the metal particles.

Morphological characterization of Ag/CNCs, at different silver wt % loadings, is done using TEM and FE-SEM/EDX analysis. EDX results evidence a moderate increasing trend of Ag wt%, according to the larger metal precursor loadings during preparation (Fig. 7). However it

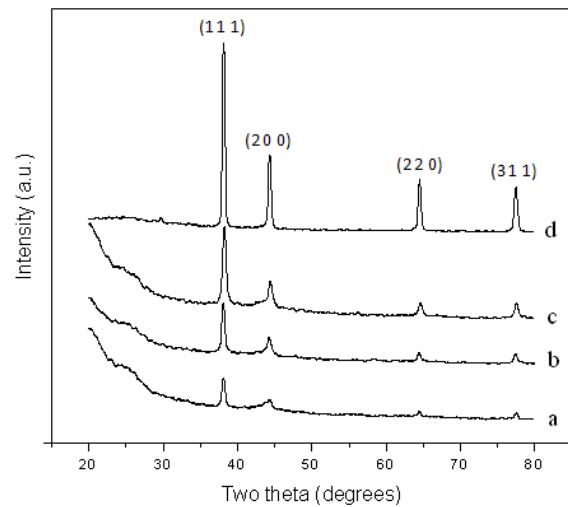
can be observed that the concentration of Ag remained almost constant from Ag/CNCs 0.25 M to Ag/CNC 0.5M, which can be attributed to the several factors as, efficiency of decoration method, sensitivity of EDX analysis. From the FE-SEM images (Fig. 6), it can be easily seen a substantial difference among the surface of the pristine CNCs and the surface of the Ag/CNCs composites. The surface of all the Ag/CNCs at different metal loadings show a rough texture compared with the smooth surface of the pristine CNCs, which reveal the success of the decoration of the metal on the CNCs. TEM micrograph of Ag nanoparticles on CNCs is showed in Figure 2. It corresponds to the 0.25 M Ag/CNCs, and it can bee seen from it that particles are distributed fairly evenly onto the surface of the CNCs.

From the FE-SEM studies, it can be seen that the size of the CNCs is in the range 25  $\mu\text{m}$  – 160  $\mu\text{m}$ . Even though the size distribution is quite broad, the approximately spherical shape is maintained throughout the range size. It is important to mention that the capsule structure could withstand the metal decoration and the microwave reduction mechanism. The above fact allows us to conclude that both ion adsorption impregnation and microwave reduction are suitable mechanisms for the grafting of Ag particles on the surface of the CNCs. Besides it is important to recognize the resistant nature of the CNCs, that are able to withstand a broad range of metal loading concentration (0.25 M to 1.5 M) maintaining the main features, despite the variation of conditions they are subjected.

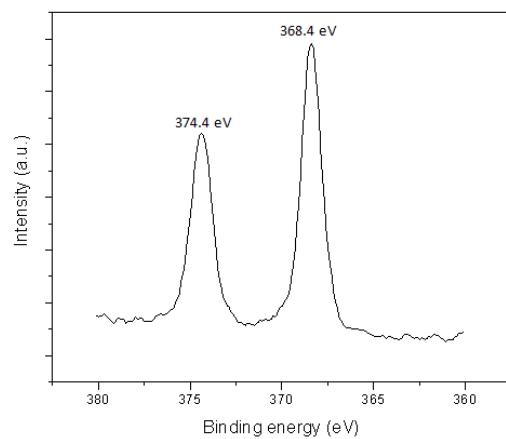
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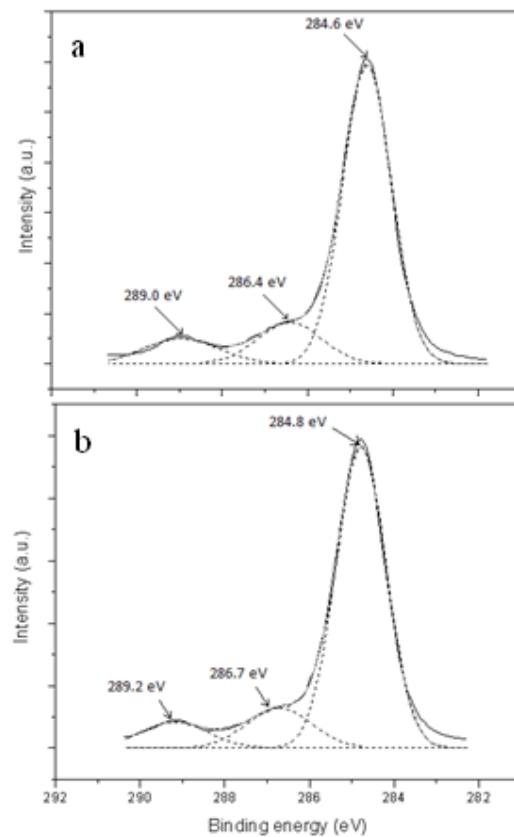
**Fig. 1** FTIR spectra of a) pristine MWCNT b)  
MWCNT-OOH c) CNCs and d) Ag/MWCNT 1.5  
M.



**Fig. 2.** XRD pattern of a) 0.25 M Ag/CNCs b)  
0.5 M Ag/CNCs c) 1.0 M Ag/CNCs and d) 1.5  
M Ag/CNCs.

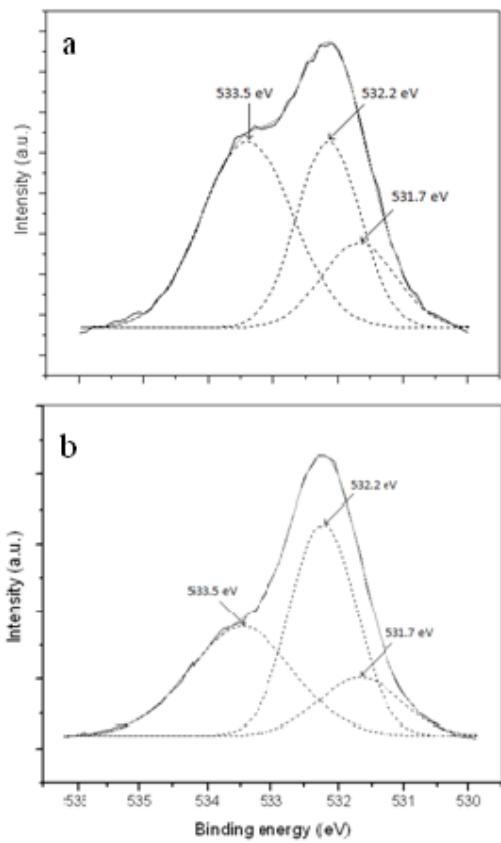


**Figure 3.** XPS Ag 3d spectra of Ag/CNCs.

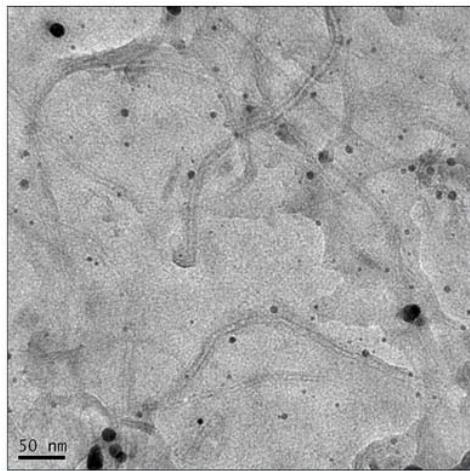


**Figure 4.** XPS C1s spectra of a) CNCs and b)  
AgCNCs 0.25M.

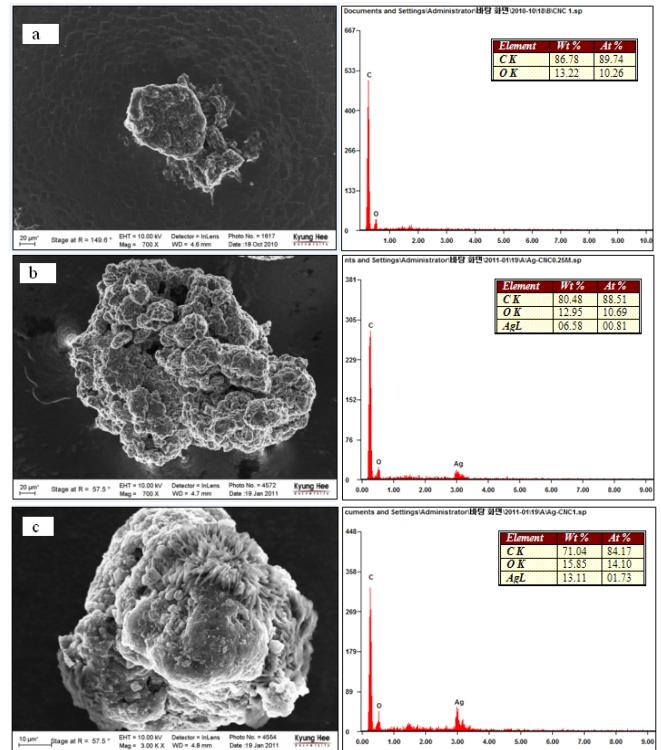
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**Fig. 5.** XPS O1s spectra of a) CNCs and b) Ag/CNCs 0.25M.



**Fig. 6.** TEM image of pristine CNCs.



**Fig. 7.** FE-SEM/EDX images of a) pristine CNCs, b) Ag/CNCs 0.25 M and c) Ag/CNCs 1.5 M.

## 4. Conclusion

The results of the study showed that silver particles are successfully grafted on the structure of CNCs. The particle size appeared to have a close dependence with the metal loading content, ranging from 18.4 to 47.5 nm with the variation of the silver concentration in the precursor solution (0.25 M to 1.5 M). Narrow metal particle size distribution, stiffness of the CNCs, outstanding properties of MWCNTs and simplicity of microwave reduction method, renders this kind of method and material is suitable for variety of applications.

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