

DIFFERENT METHODS TO FUNCTIONALIZATION OF MULTIWALLED CARBON NANOTUBES FOR HYBRID NANOARCHITECTURES

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Abstract - Multiwalled carbon nanotubes (MWCNTs) were functionalized with various functional groups in order to obtain new hybrid materials with better properties used for many applications. Four methods of functionalization were used in this paper to obtain functionalized multiwalled carbon nanotubes: MWCNT-COOH, MWCNT-COOAg, MWCNT-COOCu and MWCNT-NH₂. The morphology of these materials was analyzed with transmission electron microscopy (TEM) and the chemical bonds were put in evidence using infrared spectroscopy (FTIR) analysis.

Keywords: carbon nanotubes, functionalization, dispersion, TEM, FTIR.

1. INTRODUCTION

Since their discovery in 1991 by Iijima [1], carbon nanotubes (CNTs) have attracted great interest in most areas of science and engineering due to their unique physical and chemical properties, which enable them to be applied for a wide range of applications [2–5].

A common technique to improve dispersion and realize such a great capability of CNTs is through chemical functionalization, which enables chemical covalent or non-covalent bonding between the CNTs and material of interest. The covalent side-wall modifications of nanotubes have been well described in several review papers [6, 7].

Taking into account that nanotubes are heterogeneous materials and their dimensions, functionalization surface charge, and agglomeration have impact on reactivity we have to understand how we can improve the dispersion of these materials. The functional groups which can be attached to the CNTs surface range from small molecules to macromolecules can be used in different applications, especially in the nanocomposites field. Applications in compound materials, electronic devices, nanosensors or gas storage material and solar cells are intensively explored. All these potential applications require an extended functionalization of the nanotubes to make them processable and to tune their properties.

The present study proposes a modality of increasing the degree of dispersion in different solvents using four modalities of functionalization.

The nanotubes functionalization is performed according a chemical procedure introducing -COOH groups, -COOAg, -COOCu and -CONH₂.

Regarding silver nanoparticles there are several elaboration methods including biogenic production [8, 9]. Our method involves 100 mL of aqueous solution of silver nitrate with a concentration of 0.25 M, and 85 mL 0.25 M trisodium citrate. While stirring vigorously, 0.6 mL of 10 mM NaBH₄ was added to the solution. Following this the silver nanoparticles were deposited onto carbon nanotubes.

Multiwalled carbon nanotubes of curled shape have about 20-40 nm in diameter and 0.1-10 μm length are provided by Sigma Aldrich with a purity of 90%.

It has been shown in the literature that functionalized CNTs has several applications in different fields, which makes this area of research very attractive indeed for many researchers. The present study presents a detailed methodology for functionalizing MWCNTs with different functional groups of value for a variety of different purposes.

2. METHODOLOGY FOR FUNCTIONALIZING MWCNTs

2.1. Functionalization of MWCNTs

Multiwalled carbon nanotubes were covalently functionalized by the oxidation procedure. As shown literature [10], this oxidation treatment disrupts the π bonding symmetry of sp² hybridize carbon atoms and produces a high density of functional groups along the entire length of CNTs, such as carboxyl, carbonyl, and phenolic groups.

MWCNTs (3.0 g) were dispersed in 98% concentrated sulphuric acid under ultrasonication at 50°C for 6 h to produce oxidized carbon nanotubes (MWCNT-COOH) [11]. The samples were washed with ultrapure water and dried at 50 °C for 12 h.

The final products were nanotube fragments whose ends and sidewalls were decorated with various oxygen-containing groups (mainly carboxyl groups) (Fig. 1). Moreover, the percentage of carboxylic functional groups on the oxidized MWCNTs surface does not exceed 4% in the best cases which corresponds to the percentage of MWCNTs structural defects [12].

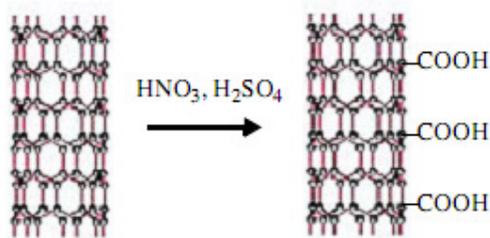


Fig. 1. Chemical modification of carbon nanotubes (CNTs) through thermal oxidation

With these groups present, carbon nanotubes show a very good dispersibility in aqueous solvents, where they remain stable for months.

The larger surface area of MWNTs can be used as templates to prepare nanoparticulate hybrid systems consisting of Ag and Cu nanoparticles.

2.2. Preparation of MWCNT-COOAg

One gram of MWCNT-COOH was dispersed in 100 mL of distilled water through ultrasonication.

To this solution, 100 mL of 0.2 M Ag nitrate solution was added with constant stirring at 60°C to generate Ag ions grafted carbon nanotubes (MWCNT-COOAg). After the completion of reaction, solid products were collected by centrifuging and dried under vacuum at 50°C. Ag ions grafted onto carbon nanotubes were reduced at 200°C to generate Ag nanoparticles on the carbon nanotube surface.

The complete scheme for the modification of the nanotube surface and the attachment process of the gold nanoparticle on the nanotube surfaces is shown in Fig. 2.

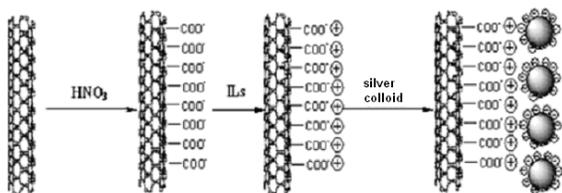


Fig. 2. Schematic process for anchoring silver nanoparticles to nanotubes

2.3. Preparation of MWCNT-COOCu

One gram of MWCNT-COOH was dispersed in 100 mL of distilled water through ultrasonication.

To this solution, 100 mL of 0.2 M CuCl₂ solution was added with constant stirring at 80°C to generate Cu ions grafted carbon nanotubes (MWCNT-COOCu).

After the completion of reaction, solid products were collected by centrifuging and dried under vacuum at 50°C. It is expected that during drying process, Cu ions developed on the carbon nanotube surface get reduced to

Cu nanoparticles and adhered on the surface by Van der Waals force of interaction.

The schematic representation of the obtaining processes of MWCNT-COOCu is show in Fig. 3.

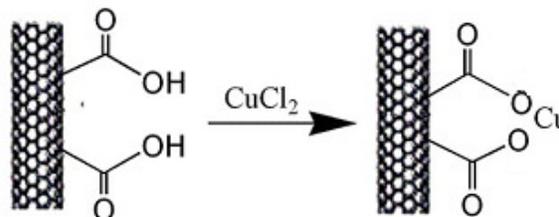


Fig. 3. Schematic process for anchoring copper nanoparticles to nanotubes

2.4. Synthesis of MWCNT-NH₂

Dried MWCNT-COOH (0.1 mg) was reacted with excess SOCl₂ (25 mL) at room temperature for 30 minutes. The residual SOCl₂ was removed by washing with tetrahydrofuran THF and filtered with ultrapure water. The MWCNTs were dried for 20 minutes at the room temperature.

The new functionalized nanotubes MWCNT-SOCl₂ (10 mg) are added in etilendiamine in excess for 10 hours at the room temperature. The mixture was washed with THF and filtered. The nanotubes were dried at 80°C for 10 hours.

2.5. Synthesis of nanoarchitectures based on MWCNTs and hydroxyapatite (HA)

Another type of nanoarchitecture with nanoparticles was biomimetic coating with HA (hydroxyapatite) on MWCNTs surface. Such coating was elaborated via immersion in a solution of 0.042M Ca(NO₃)₂·4H₂O and 0.025M NH₄H₂PO₄ at a pH of 4.8.

Functionalized MWCNTs material was dispersed in a dispersive material and ultrasonically prepared for 10 min.

It was studied the synthesis of HA from a Ca/P solution and to obtain the growth of the crystals were used carbon nanotubes. The temperature was kept at 37°C, the temperature of human body. This factor leads to the formation of cubical HA.

The morphology was tested with transmission electron microscopy.

3. RESULTS

3.1. TEM ANALYSYS

Nanosized particles are investigated using Transmission Electron Microscopy analysis (TEM) with an EM-410 Philips, 60kV microscope. Acid treatment removes the impurities as amorphous carbon particles and also introduces the -COOH groups on the surface of MWCNTs.

The formation of Ag and Cu nanoparticles (nAg and nCu) on the MWCNTs surface is confirmed by TEM. TEM analysis shows in Figs. 4 MWCNTs having 20-40 nm in diameter MWCNTs functionalized with Ag ions and MWCNTs functionalized with Cu ions grafted onto carbon nanotubes that were reduced at 200° C. Regarding distribution of silver and copper nanoparticles ImageJ soft were used. Particle sizes of Cu solutions were determined and the average diameter is between 10.8-39.9 nm meanwhile particle size of Ag solutions were determined and the average diameter is between 11.8-17.9 nm as is shows in Figs. 5.

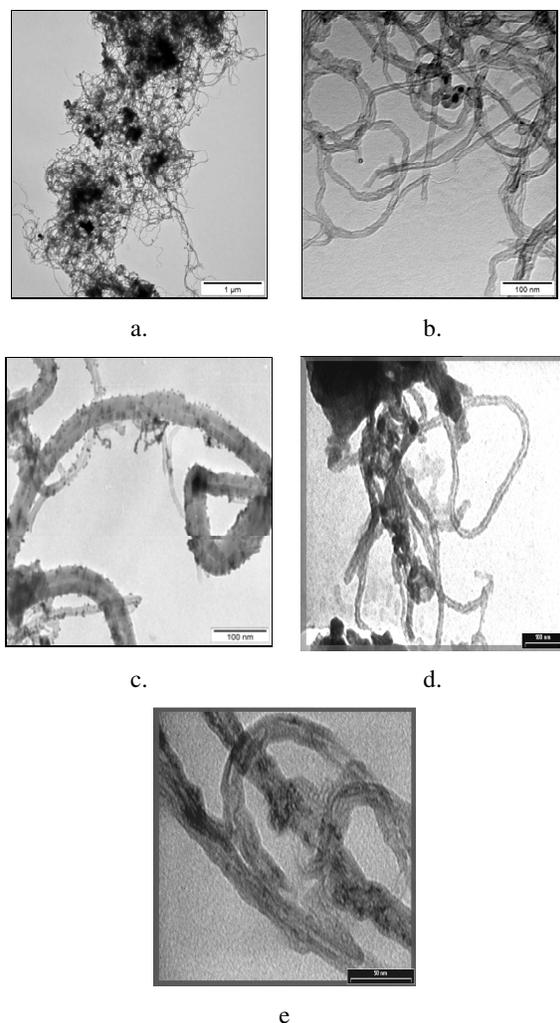


Fig. 4. TEM images for a. MWCNTs; b. MWCNT-COOH and c. MWCNT-COOAg d. MWCNT-COOCu and e. MWCNT-NH₂

It can be seen that the silver and copper particles preferentially adhere to the surfaces of MWCNTs rather than to other regions without MWCNTs. Dark spots correspond to Ag and Cu nanoparticles and the tubes correspond to MWCNTs. The side walls of MWCNTs are evenly decorated with Ag or Cu nanoparticles. The densities of attached nanocrystals are

high. Observed nanoparticles 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 or Cu nanoparticles are durably attached to the nanotubes. These nanoparticle-decorated nanotube heterostructures could be used in catalytic, electronic, optical, medical and magnetic applications.

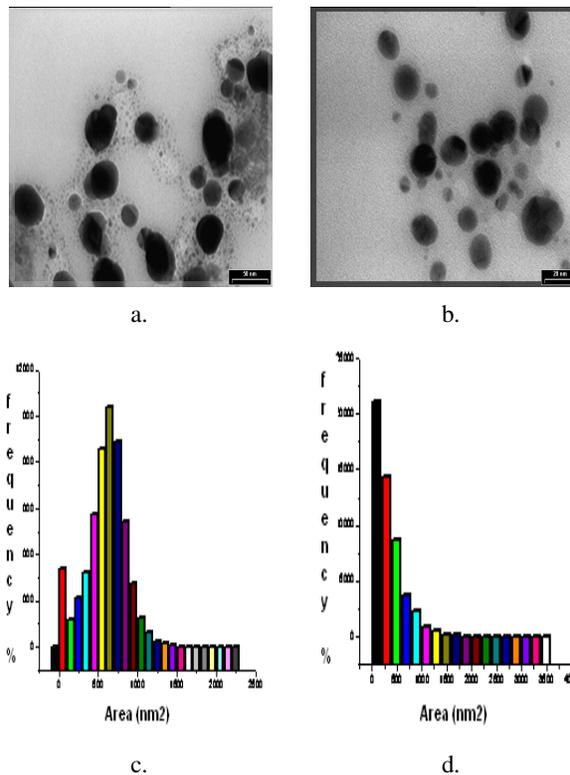


Fig. 5. TEM images for a. nCu; b. nAg and c. size distribution histogram for nCu d. size distribution histogram for nAg

Meanwhile, the -COOH and -NH₂ functionalization doesn't change the morphology of multiwalled carbon nanotubes but improve the degree of dispersion. Figs. 6 shows the TEM micrographies for the hybrid samples, functionalized with Ag and Cu nanoparticles, immersed in a solution with 0.042 M Ca(NO₃)₂·4H₂O and 0.025 M NH₄H₂PO₄. TEM images shows that the crystallites of 100 nm in width and 500 nm in length were grown radially originating from a common center to the intersection of two MWCNTs and perpendicularly to the longitudinal direction of MWCNTs. HA layers first starts to grow in zone with more agglomerations of MWCNTs as it is shows in Fig. 6. The MWCNTs maintained their typical tubular structure in the HA matrix, as shown in Fig. 6a, and would therefore be expected to act as an excellent reinforcement in the HA matrix. Potential and realized applications of the resulting functionalised MWCNTs/HA composite coatings are bioactive coatings.

Using immersion method of obtaining the hybrid material based on MWCNTs and HA, we observe the different morphologies depending of the functionalized groups of the MWCNTs. (Figs.6)

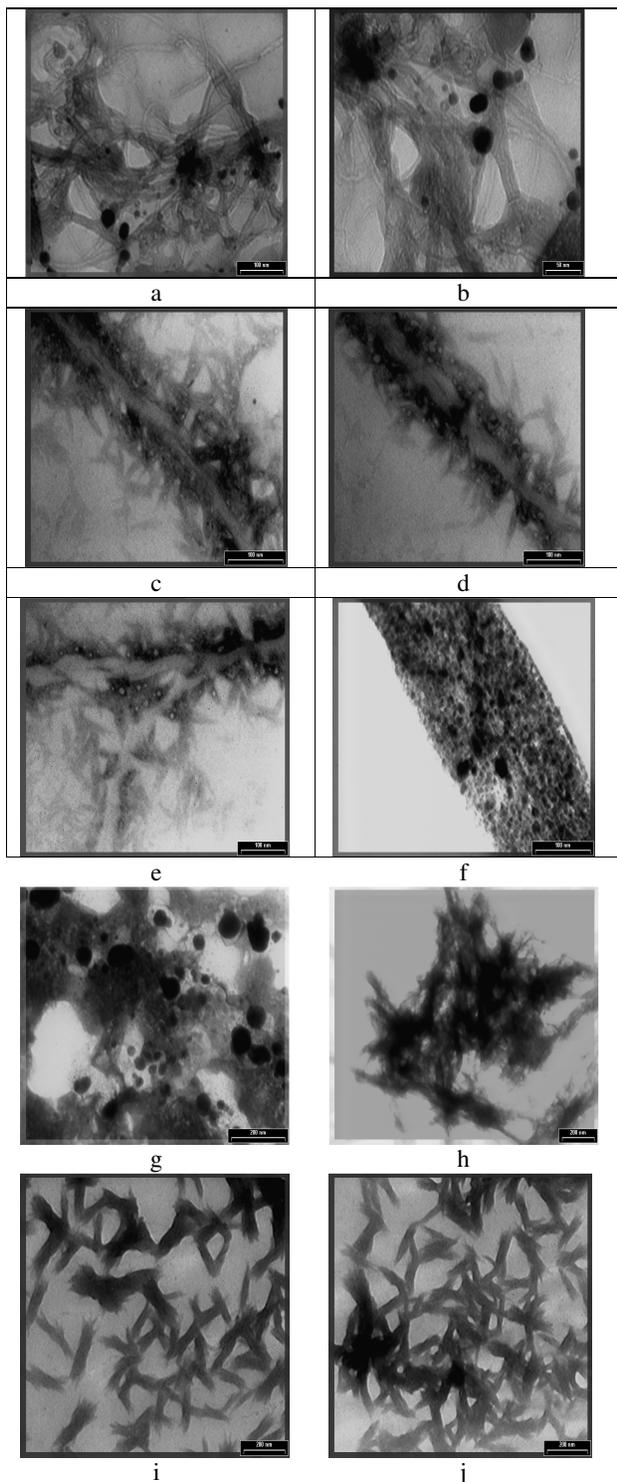


Fig. 6. TEM images for a,b,c,d,e) MWCNT-COOAg/HA and f,g,h,i,j) MWCNT-COOCu/HA

The EDS spectra, showing the constituent elements of the HA coatings with MWCNTs, are presented in Fig. 7.

The presence of the MWCNTs was confirmed by the peaks for carbon in the EDS spectrum of the MWCNTs/HA composite coating.

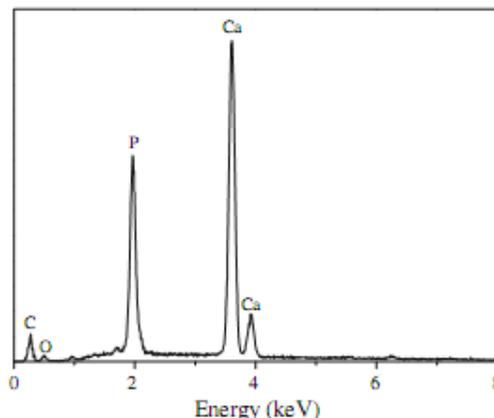
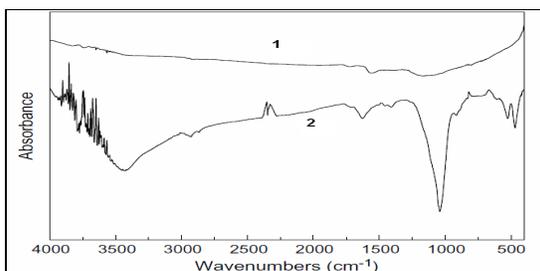


Fig. 7. EDS spectrum of hybrid material MWCNTs/HA

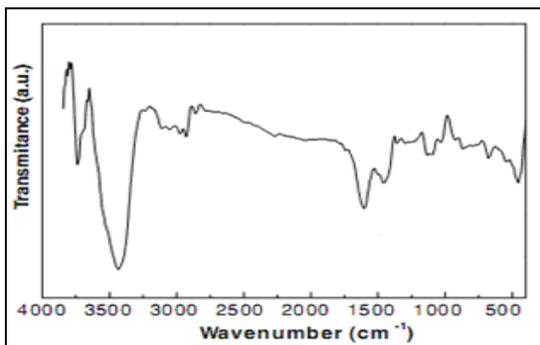
3.2. FTIR analysis

The $-COOH$ and $-NH_2$ functionalization is put in evidence by FTIR measurements.

FTIR has been used to map the chemical distribution of carbon nanotubes MWCNTs, acid treated MWCNT-COOH and MWCNT-NH₂. Infrared Microscopy Spectral data were recorded by an ATR Perkin- Elmer equipment. FTIR spectra from the MWCNTs show a broad peak at 3436 cm⁻¹, which refers to the O-H stretch of the hydroxyl group which can be ascribed to the oscillation of carboxyl groups. Carboxyl groups on the surfaces of as-received MWCNTs could be due to the partial oxidation of the surfaces of MWCNTs during purification by the manufacturer. This feature moves to 1726 cm⁻¹ and is associated with the stretch mode of carboxylic groups as observed in the IR spectrum of the acid-treated MWCNTs (Fig. 8a) indicating that carboxylic groups are formed due to the oxidation of some carbon atoms on the surfaces of the MWCNTs by sulphuric acid. The IR spectra of oxidized MWCNTs shows four major peaks, located at 3750, 3450, 2370, and 1562 cm⁻¹. The peak at 3750 cm⁻¹ is attributed to free hydroxyl groups. The peak at 3436 cm⁻¹ can be assigned to the O-H stretch from carboxyl groups (O=C-OH and C-OH), while the peak at 2364 cm⁻¹ can be associated with the O-H stretch from strongly hydrogen-bonded -COOH. The peak at 1565 cm⁻¹ is related to the carboxylate anion stretch mode. The peak at 1631 cm⁻¹ can be associated with the stretching of the carbon nanotube backbone. The peaks at around 2877 and 2933 cm⁻¹ correspond to the H-C stretch modes of H-C=O in the carboxyl group.



a.



b.

Fig. 8. FTIR spectra of: a) 1. MWCNTs, 2. MWCNT-COOH; b) MWCNT-NH₂

For MWCNT-NH₂ (Fig. 8b) the bands at 2918 and 2850 cm⁻¹ represent asymmetrical and symmetrical stretching of CH₂ groups. The C-N stretching vibration and the scissoring in-plane N-H distortion of free primary amine group are observed at 1040 cm⁻¹ and 1628 cm⁻¹, respectively. The broad band at 3410 cm⁻¹ is attributed to the NH₂ stretching.

4. CONCLUSIONS

The functionalized MWCNTs obtained using different functional groups were analyzed using Fourier Transform Infrared (FTIR) spectroscopy. The immersion in Ca/P solution was used with good results for obtaining HA coatings on carbon nanotubes surface. We obtained the HA on the MWCNTs surface with different size and morphology puts in evidence by TEM. Functionalized MWCNTs and HA formed some

systems appear like a booklet with unique morphology that can be used in a different applications.

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