

INTERNATIONAL JOURNAL OF INSTITUTIONAL PHARMACY AND LIFE SCIENCES

Pharmaceutical Sciences

Research Article.....!!!

Received: 31-10-2012; Revised; Accepted: 26-10-2013

PURIFICATION AND FUNCTIONALIZATION OF MULTI WALLED CARBON NANOTUBE AND SILVER NANOPARTICLES

Manikandan D², Antony Bertie Morais¹, Arunodhaya N¹, Jayakumar C¹, Muniraj S² and Nagendra Gandhi N^{1*}

1. Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai-600025, Tamil Nadu, India.
2. Department of Chemistry, Ramakrishna Mission, Vivekananda College, (Autonomous), Chennai-600 004, India.

Keywords:

Multi-walled carbon
nanotubes, Carbon
nanotubes(MWCNT), *p*-
Phenylenediamine(PANI),
AgNO₃, Trifluoroacetic
acid

For Correspondence:

Nagendra Gandhi N

Department of Chemical
Engineering, A.C. College of
Technology, Anna University,
Chennai-600025, Tamil Nadu,
India

E-mail:

n_nagendra2002@yahoo.com

ABSTRACT

In the present investigation, silver (Ag) nanoparticles were allowed to deposit on multi-walled carbon nano tubes (MWNTs) by chemical reduction resulting in Ag-decorated MWNTs (Ag-MWNTs) / polyaniline composites were prepared. Effect of silver (Ag) being incorporated into the interface of the composites on the electrochemical performance of MWNTs / PANI was investigated. It was found that highly dispersed Ag nanoparticles have been deposited on to the MWNTs, and the Ag-MWNTs being successfully coated by PANI. Silver (Ag) nanoparticles which were deposited on MWNT's results a increase of charge transfer between MWNT's & PANI due to their high electric conductivity, which in the causes an enhancement in the electrochemical performance.

INTRODUCTION

Nanotechnology deals with the study of manipulating matter at the atomic, molecular or macromolecular level to create and control objects on the nanometer scale, with the goal of fabricating novel materials, devices and systems that have new properties and functions because of their small size. The term nanotechnology embraces many different fields and specialties, including engineering, chemistry, electronics, and medicine, among others, but all are concerned with bringing existing technologies down to a very small scale. The development of nanotechnology holds out great promise of improvements in the quality of life, including new treatments for disease and greater efficiency in computer data storage and processing. For example, tiny autonomous robots or nanobot may be sent into human bodies to repair cells and cure cancers, and even extending the human life span by many years. Nanotechnology may be able to create many new materials and devices with a vast range of applications such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterial. The Horst stormier told about “Nanotechnology has given us the tools to play with the ultimate toy box of nature atoms and materials. Everything is made from it. The possibilities to create new things appear limitless”.

Carbon nano tubes are recognized as reinforcements for high performance and multifunctional composites because of their extraordinary mechanical strength and excellent electrical / thermal conductivity. Considerable achievements have been made in CNT-PANI composites and a remarkable enhancement in electrical and mechanical properties compared to those of PANI and AgNO₃ has been observed¹⁻⁴. Among numerous conductive, polyaniline (PANI) is considerably attractive because of easy synthesis, environmental stability, high and controllable conductivity, and its various applications, such as light weight battery electrodes, energy storage devices, electromagnetic shielding devices, anti corrosion coatings, sensors, etc.

Recently, CNTs/PANI composites have attracted much attention in studies to enhance electrical and mechanical properties over pure PANI⁵⁻⁹. Although CNTs / PANI, a real so widely studied as electrode materials for super capacitors, the use of these individual materials in electrodes is limited by their drawbacks, such as the high cost of CNTs and weak mechanical properties and poor life of PANI. Therefore, PANI composites combined with CNTs will provide synergistic performance on the electronic and mechanical properties by the interaction of the two

components¹⁰⁻¹¹. For application of CNT/PANI as electrode materials, the functionality and process ability of the composites are key points. These properties are related to the dispersion of the CNTs and the interfacial adhesion between the CNTs and the PANI matrix. Various methods have obtained CNTs / PANI composites, such as solution mixing, direct mechanical mixing and in situ or electro- chemical etc¹⁰⁻¹¹. Lately, metal doped PANI composites are also attractive materials as they combine the properties of low dimensional organic conductors and high surface area materials, and are currently of great research interest due to the numerous applications for PANI, as well as the unique optical and catalytic properties of metal nanoparticles. However, many studies have been performed on the effect of metal decoration on the electrochemical properties of MWNTs or MWNTs / PANI, where as there has been limited work on the effect of metal in corporation between MWNTs and PANI on the electrochemical properties of MWNTs / PANI⁰⁸⁻⁰⁹. In the present work, multi-walled carbon nano tubes (MWNTs) are decorated by silver nanoparticles, and the Ag-decorated MWNTs (Ag-MWNTs) / polyaniline (PANI) composites were prepared by oxidation polymerization of the corresponding aniline monomer in the presence of MWNTs in a solution. The effect of Ag incorporated between the components on the electrochemical properties of the MWNTs / PANI is discussed.

MATERIALS AND METHODS

Materials

Multi-walled carbon tubes (MWNTs) produced by chemical vapor deposition (CVD) process were obtained from nano solution 495 % (C:96 %), diameter 10–25nm and length 25–50 mm. Aniline, silver nitrate, Sulfuric acid nitric acid, and all other organic solvents used in this study were of analytical grade and used without further purification.

Purification of MWNTs

Approximately 1.5 g of CNTs was dispersed in a mixture of 50.0 ml of toluene and 5.0 mL of TFA. The dispersion was subsequently maintained under an ultra-sound bath (unique ,154 W37 kHz)for 2 h in an ice-bath (To avoid the TFA evaporation). The insoluble CNTs were then separated by centrifugation (3000 rpm for 5 min), washed three times with toluene, and three times with acetone, and dried at 50°C

Silver decoration on the MWNTs

One g of MWNTs was acid-treated with 100ml of a sulfuric acid and nitric acid mixture (3:1,v/v) under sonication for 2 h and was then reacted for 12 h at 90 °C with reflux under stirring. Acid-

treated MWNTs (A-MWNTs) were washed using water until pH 7.0 was attained, after which the washed samples were filtered and dried at 100 °C. Ag decorated MWNTs were prepared by the reducing reaction of silver ions using hydrazine. 0.1 g of A-MWNTs was suspended in 100 ml of, 0.1 M HNO₃ was added to adjust the pH for weak acidic solution (pH^{1/4} 6). Ten milliliter of silver nitrate solution (0.05, 0.1, and 0.15 mol/L) was added to the MWNT solution with in 30 min at 60 °C while the MWNT solution was stirred and then hydrazine was added to the mixture solution. This mixture was kept with stirring at room temperature for 24 h. Finally, Ag-MWNTs were obtained by filtration and washed with de-ionized water and acetone, and then dried in a vacuum oven for 24 h. The preparation procedure of Ag decorated MWNTs is presented in Figure 1 and named 0.05 Ag-MWNTs, 0.1 Ag-MWNTs, and 0.15 Ag-MWNTs

Preparation of Ag-MWNTs/PANI

0.1 g of A-MWNTs (Ag-MWNTs) was dispersed in 100 ml of 1 M HCl solution with the assistance of ultra sonication for 1 h. Five milliliter of the aniline monomer was added to the MWNTs solution with constant stirring. Finally, 100 ml of 0.1 M APS solution was dropped in the above solution for 30 min to initiate the polymerization. The action was continued for 24 h at 0–51 °C. Then, the final product was washed using water and acetone. The washed powder was dried in a vacuum oven at 80 °C for 24 h. The scheme for the preparation of Ag-MWNTs/PANI is presented in following diagram.

Measurements

Ag-MWNTs were confirmed using transmission electron microscopy (FTIR) and X-ray diffraction (XRD, and UV). The XRD patterns were obtained in 2 θ ranges between 5° and 70° at a scanning rate of 2°/min. Infrared spectra of A-MWNTs, Ag-MWNTs, and Ag-MWNTs/PANI were confirmed with Fourier transform infrared spectrophotometer (FT-IR 4000, Jasco). The thermal property of Ag-MWNTs, PANI, and Ag-MWNTs/PANI. The morphologies of Ag-MWNTs, PANI, -MWNTs/PANI were observed by scanning electron microscopy (SEM, S-4200, Hitachi). Electrical conductivity of the Ag-MWNTs/PANI was measured at room temperature using a four probe digital multi meter Ag Hydrazine Ag Aniline APS AgNO₃ <MWNTs> <A-MWNTs> <Ag-MWNTs> <Ag-MWNTs/PANI> PANI H₂SO₄/HNO₃ HOC O COH O COH O COH O HOC O HOC O

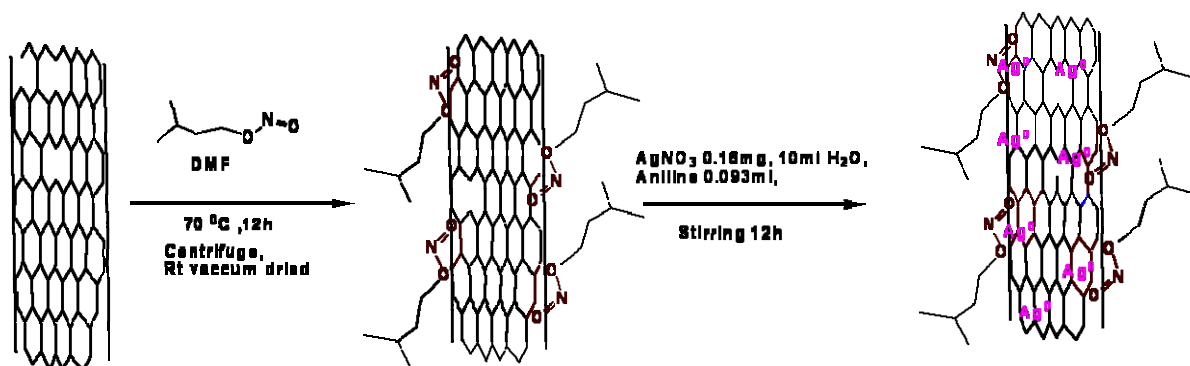


Figure 1: Schematic diagram showing the preparation of Ag-MWNTs and Ag-MWNTs/PANI

RESULTS AND DISCUSSION

Characterization of Ag-MWNTs

Figure 2 shows the XRD patterns for the pristine MWNTs and Ag-MWNTs. The pristine MWNTs revealed reflections corresponding to the C(002) and C(100) planes of crystalline graphite-like materials at 2θ 26.1 and 43.1, respectively, whereas the Ag-MWNTs show those corresponding to three main crystallographic planes of Ag, namely, Ag (111), Ag (200), and Ag (220). These results indicate that Ag nano particles are successfully decorated on to the MWNTs by the chemical reduction method.

Figure 2: XRD patterns for the pristine MWNTs (a) and Ag-MWNTs (b)

Characterization of Ag-MWNTs /PANI

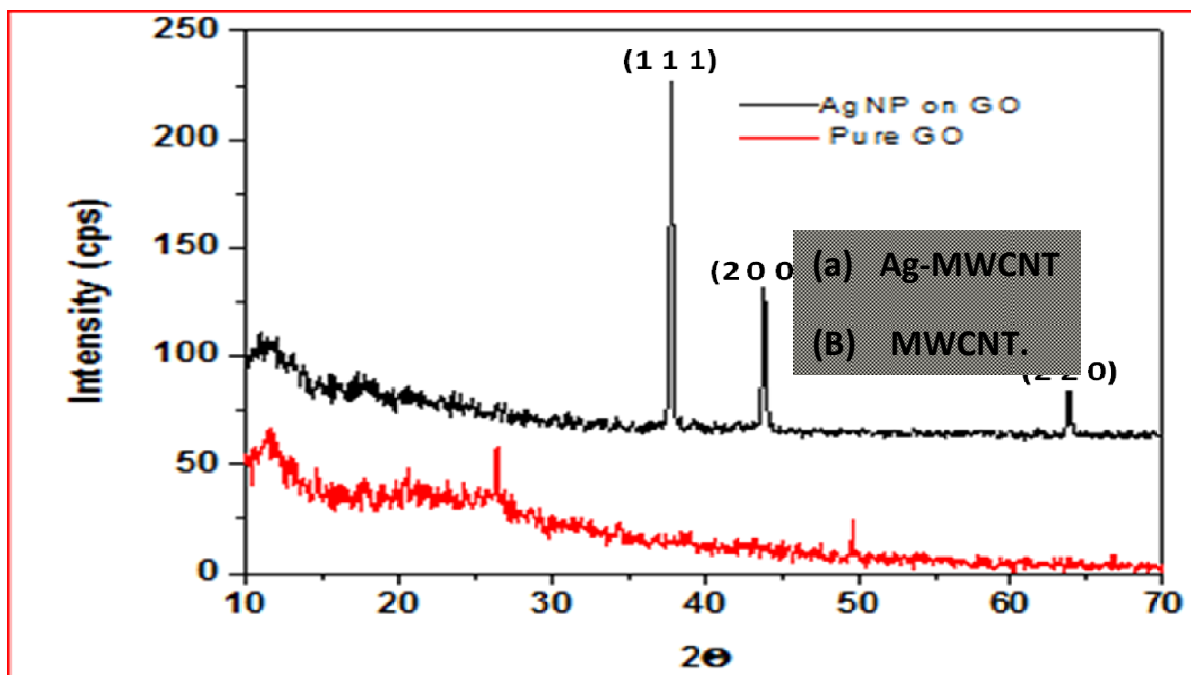


Figure 3 shows the FT-IR spectra of MWNTs, A-MWNTs, Ag-MWNTs, and Ag-MWNTs/PANI. There are no characteristic peaks for pristine MWNTs. In oxidized MWNTs, the appearance of a broad band at 4000 cm^{-1} and absorbance at 1385 cm^{-1} is, respectively, attributed to hydroxyl groups and carbonyl groups on the surface of the oxidized MWNTs, resulting from the fictionalization of the MWNTs. However, the relative intensity of the peak at 1385 cm^{-1} in the Ag-MWNTs is lower than in A-MWNTs, indicating the decrease of electron density of the carboxyl ($\text{C}=\text{O}$) oxygen atom, probably due to the interaction between silver nitrate and the $\text{C}=\text{O}$ group of the A-MWNTs¹⁰. In Ag-MWNTs/PANI, the bands around 579 and 498 cm^{-1} are characteristic stretching bands of nitrogen quinoid ($\text{N}=\text{Q}=\text{N}$) and benzenoid ($\text{N}-\text{B}-\text{N}$), resulting from the conducting state of the polymer. The 452 cm^{-1} band are assigned to the bending vibrations of $\text{N}-\text{H}$ and asymmetric $\text{C}-\text{N}$ stretching modes of polar on structure of PANI, respectively. The prominent absorption band around 1120 cm^{-1} ($\text{C}-\text{N}$ stretching) is due to the charge delocalization over the polymeric backbone.

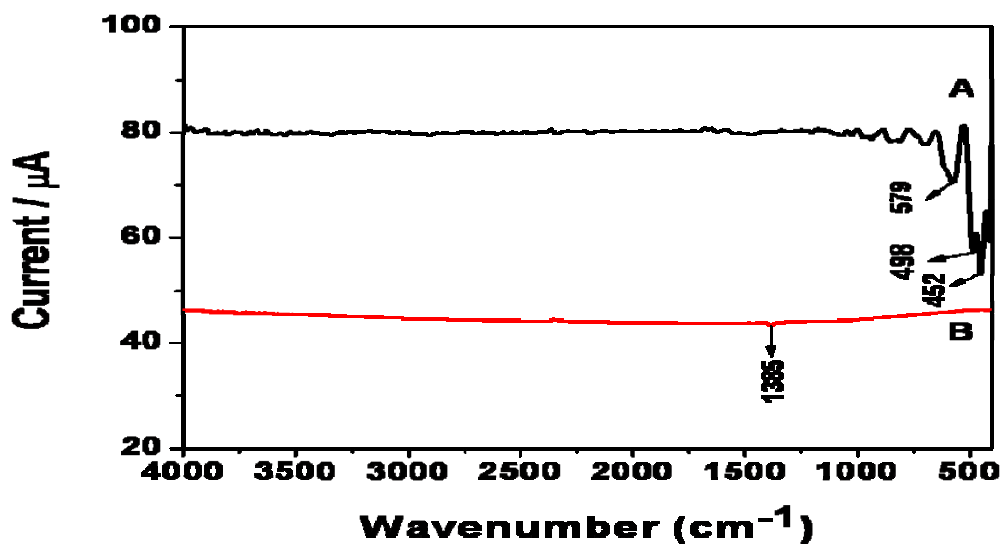


Figure 3: FT-IR spectra of MWNTs, A-MWNTs, Ag-MWNTs, (a) and Ag-MWNTs/PANI, (b)

Characterization of Ag-MWNTs /PANI

Figure 4 Showing the UV= Spectra of Ag-MWCNTs, Ag-MWCNTs/PANI. UV-visible spectrum of MWCNT and Ag nanoparticles decorated, Ag-MWCNTs/PANI. The UV-visible spectrum of silver nanoparticles modified, Ag-MWCNTs / PANI give two characteristic peaks. A peak at 230 nm indicates the formation of silver nanoparticles whereas the peak at 402 nm arises due to emeraldine form of polyaniline. From this study it is concluded that the silver nanoparticles

decorated, Ag-MWCNTs/PANI can be synthesized by a single step reduction of silver nitrate followed by incorporation on to, Ag-MWCNTs/PANI surface using aniline as reducing and stabilizing agent.

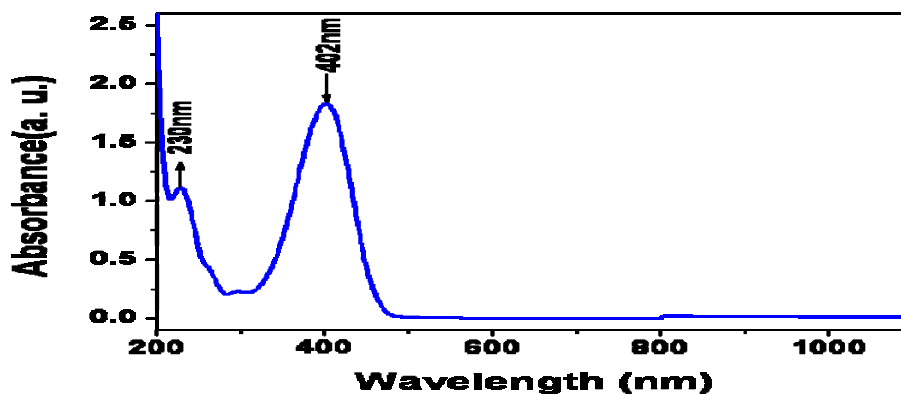


Figure 4: UV= Spectra of Ag-MWCNTs, (a) and Ag-MWCNTs/PANI (b)

CONCLUSIONS

The Silver nano particle modified, Ag-MWCNTs/PANI was synthesized through in situ chemical reduction of AgNO_3 by aniline in presence of DMF. It was synthesized successfully in good percentage of yield. These structures were confirmed and characterized by different physical, analytical, spectral data from XRD, FT-IR, and UV-Visible spectroscopy. All the data showed the expected results. This effective approach can be extended for the assembly of other important inorganic materials and it has opened new possibilities for the fabrication of optical and electronic nano devices.

REFERENCES

1. Ureta-Zanartu M.S, Electrooxidation, *Electrochimica Acta* ,2002;47:2399-2406.
2. Kim K-S , Park S J ,Silver-Decorated MWCNT,*Journal of Solid state Chemistry* 2011;184:2714-2730.
3. Salvatierra Rodrigo V, Carbon Nanotubes /polyaniline, *Chem .Mater.*, 2010;22:5222-5234.
4. Dyke Christopher A ,Tour James M , Solvent –Free Functionalization of carbon Nanotubes ,*J.AM.CHEM.SOC* 2003;5:1156-1157
5. Van Hoa Nguyen, Jae-jin Shim, Characterization of carbon nanotubes ,*Synthetic Metals* 2011;161:2078-2802.

6. Paulraj P, Polyaniline Protected Silvernanoparticles, Colloids and surface A: physicochem. Eng, Aspects , 2011;377:28-34.
7. Daping He, Chao Zeng, Cheng Xu, Niancai Cheng , Huaiguang Li, Shichun Mu, Mu pan , polyaniline-Functionalized carbon Nanotube , 2011;27:5582-5588.
8. Yong Taik Lim, O Ok park ,Hee-Tae Jung, Gold nanolayer-encapsulated silica particles, journal of colloid and interface Science,2003;263:449-453
9. Wolfgang Maser, Teresa Martinez M, Benito M, electro active Polymers and Carbon Nanotubes, 2007;0930;1-3.
10. Bohua Wu, Yinjie kung, Xiaohua Zhang,Jinhua chen, noble metal nanoparticles/ carbon nanotubes nanohybrids , 2011;6;75-90.
11. Xiaojun zhang, Guangfeng wang, xiaowang Liu, Jing jing Wu, Ming Li Jing gu , Huan Liu Bin Fang, Different CuO Nanostructures: Synthesis, characterization, J.Phys.Chem.C, 2008; 112; 16845-16849.