Facile production of very small nickel metal nanoparticle on the surface of oxidized multiwalled carbon nanotubes

Suman Thapa[*], **Lok Kumar Shrestha**[**]**and Sabita Shrestha**[***]

[*] Department of Chemistry, Trichandra Multiple College, Ghantaghar, Kathmandu, Nepal.

[**] National Institute for Materials Science (NIMS), MANA, Japan.

[***] Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal.

Abstract: Carbon nanotubes have been considered as excellent support materials for metal catalysts due to their high specific surface area, thermal and chemical stability. Metallic nanoparticles decorated with carbon nanotubes are gaining extensive attention due to their fundamental and technological importance. In this contribution, we report facile production of nickel nanoparticles (2 – 3 nm) decorated on aqua regia treated multi-walled carbon nanotubes (MWCNTs) *via* wet-chemical method using ethylene glycol as reducing agent for nickel salt and stabilizing agent for nanotubes. High-resolution transmission electron microscopy (HR-TEM), energy-dispersive x-ray spectroscopy (EDS) and elemental mapping confirmed the formation of nickel nanoparticles with average diameter in the range of 2 – 3 nm which are uniformly distributed on the external surface of multiwalled carbon nanotubes. The results of Raman Spectroscopy, Infrared Spectroscopy and Thermal analysis (TG, DTA) are also reported.

Keywords: Multiwalled carbon nanotubes; nickel nanoparticles; Raman spectroscopy; Thermal analysis.

Introduction

Nanomaterials have emerged as an amazing class of materials that consists of a broad spectrum of examples with at least one dimension in the range of 1 to 100 nm. The term nanometer was first used in 1914 by Richard Adolf Zsigmondy. The American physicist and Nobel Prize laureate Richard Feynman introduced the specific concept of nano technology in 1959 in his speech during the American Physical Society's annual meeting. This is considered as the first academic talk about nanotechnology[1].

The unique properties of materials are explored when size becomes nanoscale in dimension. Nanomaterials have emerged as an exciting class of materials that are in high demand for a range of practical applications. However, the history of nano material utilization is ancient, and human beings used these materials a long time ago for diverse applications, unintentionally. About 4500 years ago, humans utilized asbestos nanofibers to reinforce ceramic mixtures[2]. The ancient Egyptians were familiar with PbS nanoparticles about 4000 years ago and used them in an ancient hair-dyeing formula[3, 4]. The Lycurgus Cup is another fascinating example from the past. It is a dichroic cup produced by the Romans in the 4th century A.D. It resembles jade in direct light, whereas it shows a translucent ruby color in the case of transmitted light. It shows color variations depending on the incident light. These color variations appear due to the presence of nanoparticles of Ag and Au[5].

Carbon nanotubes are an essential member of the carbon nanomaterial family, and they entered the carbon family in

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Author for correspondence: Sabita Shrestha, Central Department of Chemistry, Tribhuvan University, Kathmandu, Nepal.
Email: sabita.shrestha@cdc.tu.edu.np; https://orcid.org/0009-0005-3025-3783

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1991 after being discovered by S. Iijima[6]. Multi-walled carbon nanotubes (MWCNTs) offer superior properties, critical mechanical quality, including a high specific surface area, excellent chemical stability, increased tensile strength and toughness, and exceptional thermal and electrical conductivity Moreover, CNTs can be used as support material and as a catalyst[7, 8].

Metal nanoparticles (NPs) on Multi-Walled Carbon Nanotubes (MWCNTs) create advanced nanocomposites. Combining the unique properties of CNTs and nanoparticles produces a nanoparticle–nano tube composite structure that is attractive to a broad range of advanced applications, such as nanoelectronics, catalysis, chemical sensors, fuel cells, bifacial counter electrodes for dye-sensitized solar cells hydrogen storage etc [9, 10, 11,]. The nanocomposite was formed by decorating the MWCNTs surface (often after oxidation for functional groups) using methods like wet chemical reduction (e.g., ethylene glycol), high-temperature chemical evaporation, electron beam irradiation etc[11].

This paper reports a simple method for production of very small size nanoparticles on the surface of oxidized MWCNTs. In general, pristine MWCNTs are chemically inert and it was treated with acids, to create active sites for attachments of metal nanoparticles, by introducing various functional groups, such as carboxyl (–COOH), hydroxyl (–OH), carbonyl (>C=O) etc. on the carbon surface[12]. Here aqua regia was used for purification and oxidation of MWCNTs. After the acid treatments, the nanotubes formed a well-dispersed colloid. The production of Ni nanoparticles were performed by liquid-phase reduction using ethylene glycol as the reducing agent.

The attachment of Ni-nanoparticles on the surface of MWCNTs were confirmed by transmission electron microscope, energy-dispersive X-ray spectroscopy and elemental mapping. Raman spectroscopy also revealed the oxidation and functionalization of the nanotubes. Infrared spectroscopy again confirmed the attachment of oxygen functional group on MWCNTs. Thermogravimetric analysis showed the thermal behavior of pristine, oxidized and Ni nanoparticles deposited MWCNTs.

Experimental Methods

Starting Materials

MWCNTs, which were synthesized by a catalytic chemical vapor deposition (CVD) process, were used in this research work. Ethylene glycol, $NiCl_2.6H_2O$ was purchased from Qualigens.

Deposition of Ni Nanoparticles

The deposition of Ni-nanoparticles on the surface of MWCNTs was done in following two steps.

Oxidation and purification of MWCNTs

There exist several different methods for the purification/oxidation of carbon nanotubes such as oxidation, acid oxidation, filtration, ultrasonication, etc. Here, acid reflux process was carried out for the purification and oxidation process. This was first described by Rinzer et al[13]. in which raw nanotube materials was refluxed in acid to remove the metals and impurity carbons. Acid-treated nanotubes are thought to have carboxylic acid groups at the tube ends and, possibly, at defects on the sidewalls. In this acid reflux process, aqua regia was used for oxidation and purification. The MWCNTs was first sonicated for about 10 mins and refluxed in aqua regia for about 30 mins. This was filtered by using membrane filter paper of pore size: 0.2 μm. Then it was washed with distilled water until pH 7 and dried in oven at 100 °C for one hour.

Deposition of Nickel Nanoparticles on the Surface of Oxidized Multiwalled Carbon Nanotube

The deposition of metal nanoparticles on the surface of CNTs can be achieved through two main pathways. One method involves the direct growth and/or deposition of naked nanoparticles onto the CNT surface. In an alternative approach, nanoparticles are pre-formed and connected to CNTs via covalent linking through organic fragments. In this work, the deposition of Nickel nanoparticles on the surface of aqua regia treated MWCNTs was done by liquid-phase reduction using Ethylene Glycol. In the deposition procedure, aqua regia treated MWCNTs (0.05 g) was dispersed in Ethylene Glycol (40 mL) by ultrasonication and $NiCl_2.6H_2O$ (0.05

g) was added in Ethylene Glycol (5 mL) and ultrasonicated for an hour which finally mixed with well dispersed suspension. The pH of the mixture was adjusted to 9 by adding 2M NaOH and the mixture was heated with constant stirring for four hours. Then the product was filtered by using membrane filter paper (pore size: 0.2 μm), washed with distilled water and dried in an oven at 100 ^{o}C for one hour.

Physico-Chemical Measurements

The purified/oxidized and nickel deposited samples were studied using different instrumental techniques, such as Thermal analysis (TG/DTA 6200 Seiko instrument), Raman Spectroscopy (Renishaw RM-1000), Energy dispersive spectroscopy and Transmission electron microscopy (JEOL Model JEM-2100F operating at 200 kV). Infrared spectroscopy (IR Prestige 21, Shimadzu) was done by powdered method.

Results and Discussion

Raman Spectroscopy

Raman spectroscopy is a highly powerful technique for the characterization of carbon-based materials. It enables the identification of the disorder-induced D band and the G band corresponding to the crystalline graphitic structures. The intensity ratio of these D and G band is used to quantify the oxidation process. The graphitization of pristine, functionalized and metal decorated MWCNTs was comparatively analyzed based on structural disorder induced by acid treatment. Figure 1 (a), (b) and (c) showed the Raman Spectra of Pristine, oxidized and Ni-deposited MWCNTs respectively. Each of them consists of three characteristic bands (Table 1) of MWCNTs. The bands at 1325 cm^{-1} (Pristine), 1331 cm$^{\mathbf{-1}}$ (oxidized) and 1335 cm$^{\mathbf{-1}}$ correspond to D band. The D-band is generally attributed to the presence of amorphous or disordered carbon in the CNT samples. The carbon structural disorder is due to the finite or nanosized graphitic planes and other forms of carbon, such as rings along with defects on the nanotube walls, vacancies, heptagon-pentagon pairs and hetero atoms. The band at 1580 cm$^{\mathbf{-1}}$ (pristine), 1583 cm$^{\mathbf{-1}}$ (oxidized) and 1587 cm$^{\mathbf{-1}}$ (Ni-MWCNTs) is due to G band, which arises from in –plane tangential stretching of the carbon-carbon bonds in graphite sheets. The shoulder band near G band around 1620 cm^{-1} is due to D' band, which is also a double resonance feature induced due to defect and disorder[14].

In the study of the Raman response of the acid treated (H_2SO_4, HNO_3, HCl) MWCNTs in comparison with the pristine sample, it was found that the vibronic and electronic properties of the nanotubes are strongly affected by the acid treatment. The most pronounced modifications of the Raman modes of MWCNTs were observed for the samples treated with H_2SO_4 and HNO_3. This is attributed to the presence of oxygen in their molecular structures and their stronger interaction with the MWCNTs structure [15].

All the D band and G bands were fitted according to Lorentz fitting to calculate the area ratio. The area ratio was decreased (figure 2) from pristine to oxidized MWCNTs after acid treatment. That is due to increase of defect sites. These defect sites may be amorphous carbon generated during oxidation, conversion of sp^2 carbon to sp^3 carbon etc. And this ratio was slightly increased after nickel deposition. The shifting of D and G band together with first decrease of area ratio and the increase after Nickel deposition strongly support the attachment of Nickel with MWCNTs[11].

Thermal Analysis (TGA and DTA):

Thermo gravimetric analysis is a valuable tool for determining the overall quality of the material, as it provides information on the various carbon structures in the sample based on differences in their decomposition temperatures. Figure 3 (a), (b), and (c) show the TG-DTA thermograms of pristine, oxidized and Ni nanoparticle decorated MWCNTs. In case of pristine MWCNTs the constant weight maintained up to 550 ^{o}C. That means the pristine MWCNTs was hydrophobic in nature and also it did not contain any other funtional groups. Then drastic weight loss occurs from 550 ^{o}C to 650 ^{o}C with single exothermic peak around 625 ^{o}C. This means that almost all the MWCNTs were burned out at this temperature range. After continuous heating up to temperture 1000 ^{o}C there was no change in weight loss and no any combustion was seen. The weight remaining is about 8 %,

Table 1: Different band positions of pristine, oxidized and Ni-MWCNT.

Sample	D- band	G-band	D′-band
Pristine MWCNTs	1325 cm^{-1}	1580 cm^{-1}	1620 cm^{-1}
Oxidized MWCNTs	1331 cm^{-1}	1583 cm^{-1}	1620 cm^{-1}
Ni-MWCNTs	1335 cm^{-1}	1587 cm^{-1}	1620 cm^{-1}

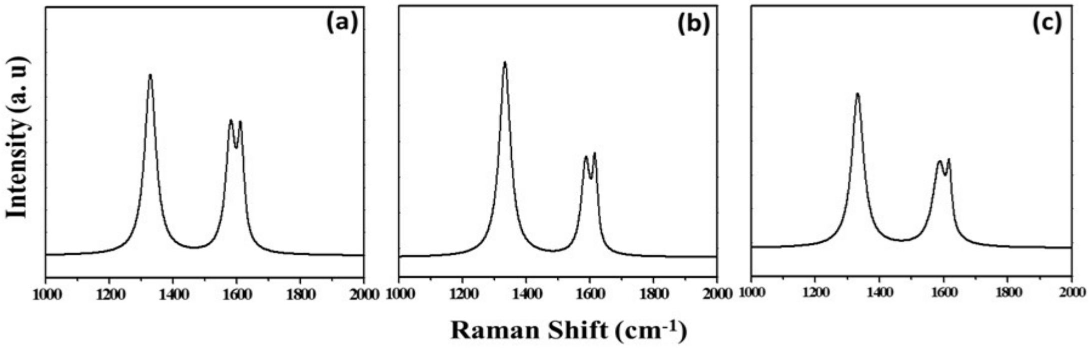

Figure 1: Raman Spectra of (a) pristine (b) oxidized and (c) Ni-MWCNT.

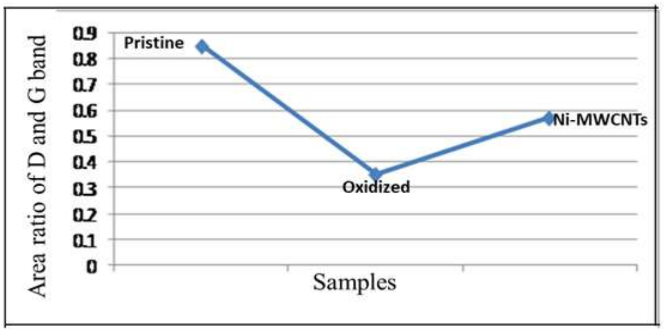

Figure 2: Area ratio of D and G bands of different samples.

which may be due to the oxides of transition metal, used as catalyst during synthesis of CNTs which is considered as impurities[16].

Figure 3 (b) shows the TG-DTA thermogram of oxidized MWCNTs. If we compare these two thermograms figure 3 (a) and (b) many changes can be observed. In the case of the oxidized MWCNTs, a gradual weight loss was observed at the initial stages of heating. The weight loss from 80-150 °C is due to loss of water molecules, because oxidized MWCNTs are slightly hydrophilic in nature. At around 300 °C some weight loss is seen in TGA curve with small exothermic peak. Here, this weight loss may be due to loss of some amorphous carbon, which was generated during oxidation and different oxygen functional group formed after acid treatment. The acid treatment not only removes most of the metal but also produces carboxyl, aldehyde and other oxygen-containing functional groups[13]. The drastic weight loss (~70 %) occur from 450 °C to 550 °C, which is due to combution of MWCNTs. After heating up to 1000 °C less than 1 % weight is remained. The remaining lower weight is definite evidence of the removal of the metal impurities by the acid treatment[11].

If we compare the burning temperature of pristine and oxidized MWCNTs, the burning of oxidized MWCNTs occurs at lower temperature than pristine MWCNTs. That may be due to possible destruction of MWCNTs structure during chemical oxidation[17].

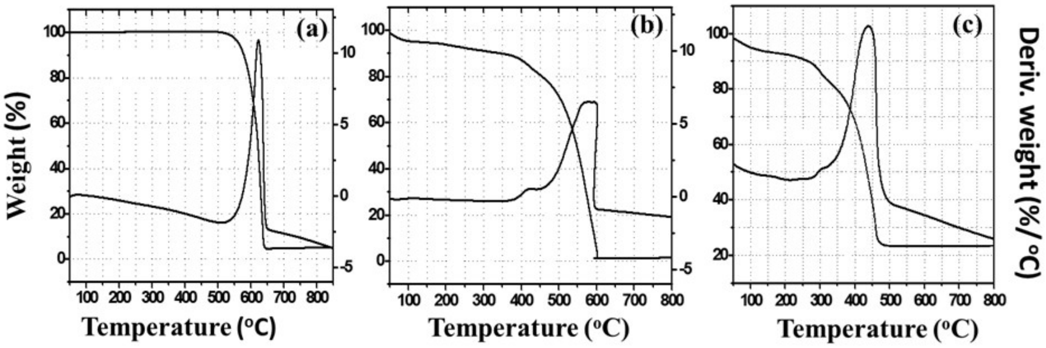

Figure 3: TGA-DTA thermograms of (a) pristine, (b) oxidized and (c) Ni-MWCNTs

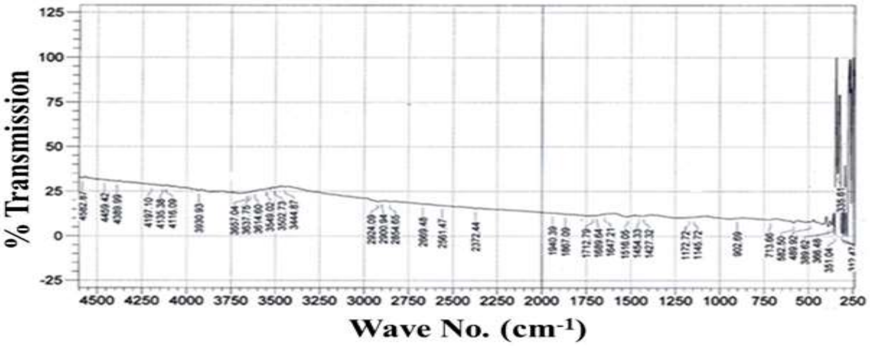

Figure 4: (a) Infrared spectrum of pristine MWCNTs.

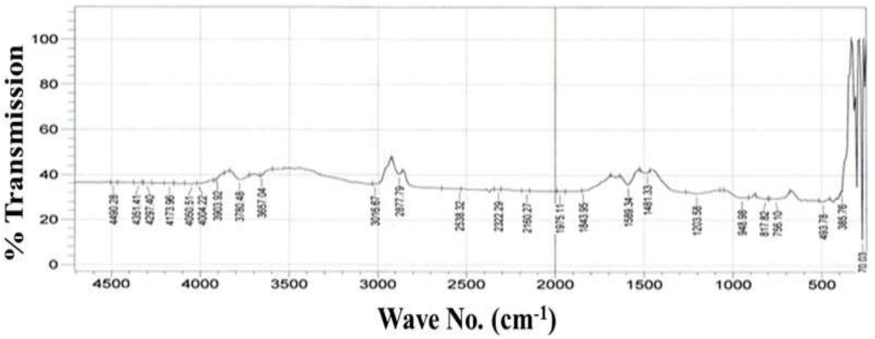

Figure 4: (b) Infrared spectrum of oxidized MWCNTs.

Figure 3 (c) shows the TGA/DTA thermogram of Nickel deposited MWCNTs. The trend of weight loss below 300 °C was similar to that of the oxidized sample The weight loss up to 200 °C may be due to the moisture content in it during the experiment.

The weight loss around 275 °C to 350 °C with a slight exothermic peak at 300 °C may due to the combustion of oxygen functional group in it and also the amorphous carbon present during the process [13]. At around 350 °C to 460 °C a large weight loss was seen with a large exothermic peak at 440 °C, which was the burning of all the MWCNTs. Beyond 460 °C no weight loss was observed up to 1000 °C, which is due to the formation of stable Ni-oxide. The total residual weight of the Ni-deposited sample was approximately 23 %, which is due to mainly oxide of Nickel (~22 %).

Infrared Spectroscopy

Acidic oxidative treatment of the MWCNTs may cause major change in the structural properties. Fig. 4 (a) and (b) show the infrared spectra of pristine and oxidized MWCNTs. If we compare these two spectra many changes can be observed. The spectrum of pristine MWCNTs does not show any sharp infrared peak i. e it does not contain any functional groups.

The spectrum of acid treated MWCNTs shown in figure 4(b) shows number of peaks at different wavelengths such as 1203 cm^{-1}, 1589 cm^{-1}, 2322 cm^{-1} and 2879 cm^{-1}. Appearance of peak at 1589 cm^{-1} assigns carbonyl (C=O) stretching vibration of carboxyl groups indicating the expansion of carboxylation on the surfaces of purified and functionalized MWCNTs. The peak at 2800-2900 cm^{-1} appears after purification and functionalization corresponding to the C-H asymmetric and symmetric stretching vibration, derived from long alkyl chain and appearance of peak at 3016 cm^{-1} assigns aromatic rings[18]. So, the IR study proves the presence of carboxylic acid groups in oxidized MWCNTs which corroborate the Raman results about the cause of structural defects in oxidized MWCNTs.

TEM, EDS, Elemental Mapping

Figure 5. (a) shows the TEM image of Nickel deposited MWCNTs. The image showed the uniform deposition of Ni nanoparticle on the surface of MWCNTs. The presence of the expected metal nanoparticles was confirmed by their corresponding EDS spectra shown in Figure 1(b). The size of Ni nanoparticles [red circle in Figure 1 (a)] is about 2 nm. Figure 3 (c) and (d) show the elemental mapping of Carbon (numbers of small dots) on Ni deposited MWCNTs and distribution of Nickel nanoparticles (showing numbers of small dots) on surface of MWCNTs based on EDS respectively.

The Ni-nanoparticles were deposited on the defect sites of the MWCNTs in the following three simple steps:

Purification step: In this step many impurities such as amorphous carbon and metals are removed and defect sites are produced.

Oxidation step: Addition of different oxygen functional groups at defect sites.

Deposition of Nickel by simple exchange reaction

$$\text{CNT-COOH} + M^+X^- \longrightarrow \text{CNT-COOM} + H^+X^-$$

(M = Ni)

Conclusions

Very small size nickel metal nanoparticle (2-3 nm) was formed on the surface of aquaregia treated multiwalled carbon nanotubes by using a simple chemical reduction method. Such nanocomposite materials from metal nanoparticles and carbon nanotubes are promising materials with applications in different fields such as nanoscale devices, hydrogen production, sensors, catalysts, nanoelectronics etc. The Ni deposited MWCNTs was characterized by various techniques such as: Raman spectroscopy shows the characterization of MWCNTs at various stages. The G and D bands were seen in pristine, oxidized and Ni deposited MWCNTs. These bands and area ratio of D and G bands showed the purification and deposition of Ni on the surface of MWCNTs. The increase area ratio of D and G bands in oxidized MWCNTs and shifting of D and G band in Ni deposited MWCNTs shows the attachment of Ni. The infrared spectroscopy shows the addition of oxygen functional group on the surface of oxidized MWCNTs. The size and distribution of Ni nanoparticles on the surface of MWCNTs were studied by TEM image, Energy Dispersive Spectroscopy and elemental mapping. At the same time TGA/DTA analysis shows different

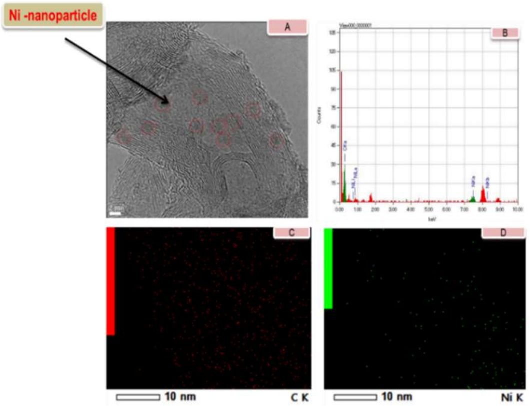

Figure 5: (a) TEM image of Nickel deposited MWCNTs. Nickel Nanoparticles are in red circles. (b) Energy Dispersive Spectroscopy of Nickel deposited MWCNTs (c) Elemental mapping of carbon (d) Elemental Mapping of Nickel nanoparticles.

thermal behavior of pristine-MWCNTs, oxidized-MWCNTs, and Ni deposited MWCNT

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