



SIMPLE WET CHEMICAL ROUTE FOR DECORATION OF MULTI-WALLED CARBON NANOTUBES WITH NICKEL NANOPARTICLES

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ABSTRACT

Due to high specific area and chemical stability, carbon nanotubes (CNTs) are considered to be an excellent support for metal nanoparticles. Carbon nanotube supported metal nanoparticles have applications in different fields. There are different techniques to attached metal nanoparticles on the surface of CNTs. This paper reports a simple wet chemical route to decorate the surface of oxidized multi-walled carbon nanotube (MWCNT) with nickel nanoparticles (NiNPs). The NiNPs decorated MWCNTs have different applications in different fields such as sensors, photocatalytic activity, hydrogen gas production, catalyst, to produce metallic nanowire etc. MWCNT was treated with nitric acid for purification and oxidation. Purification removes the impurities found in MWCNT and oxidation adds different oxygen functional groups. Raman spectroscopy shows the oxidation and attachment of nickel nanoparticles with the help of intensity, position and area ratio of D and G band. The introduction of an oxygen functional group on the surface of MWCNT after oxidation was studied by Infrared spectroscopy. Thermal analysis (thermogravimetric analysis; TGA and differential thermal analysis; DTA) revealed different thermal behavior of pristine, oxidized, and Ni decorated MWCNTs. TGA showed that the decomposition temperature decreased after oxidation and decoration with NiNPs. TGA also confirmed the purification of MWCNTs as well as the presence of nickel with the MWCNTs. Energy dispersive spectroscopy (EDS) also confirmed the presence of nickel in the sample.

Keywords: Decoration, Multi-walled carbon nanotubes, Nickel nanoparticles, Raman Spectroscopy, Thermal analysis

INTRODUCTION

Carbon nanotubes (CNTs) are one-dimensional nanostructures with extra-ordinary electronic, mechanical, and chemical properties which is also known as cylindrical fullerenes. They are a few nanometers wide, but range from micrometers to several millimeters in length (Wang *et al.*, 2009). They are composed of quasi-circular tubes with unique polygonal carbon ring microstructure units (Zheng *et al.*, 2015). CNTs are considered to be excellent support for different kinds of nanomaterials (Auer *et al.*, 1998). The CNT-based composites include metal, inorganic or organic components for specific application (Satishkumar *et al.*, 1996; Hernadi *et al.*, 2003; Cao *et al.*, 2002).

Decorating the external surface of CNTs with metal nanoparticles has attracted considerable attention due to its fundamental and technological interest. Combining the unique properties of CNTs (Dresselhaus & Avouris, 2001) and nanoparticles, (Alivisatos, 1996) a nanoparticle-nanotube composite structures is produced with different applications, such as nanoelectronics (Hu *et al.*, 1999), catalysis (Luo *et al.*, 2002), chemical sensors (Kong *et al.*, 2001), fuel cells (Che *et al.*, 1998), hydrogen storage (Yildirim & Ciraci, 2005).

Before decoration, the MWCNTs must be purified and oxidized in order to obtain optimal performance of CNTs in various fields which require high-purity of CNTs. The

impurities typically found in as-prepared CNTs are carbon species such as amorphous carbon, carbon nanoparticles, graphite flakes and transition metals that are introduced as a catalyst during synthesis. These impurities must be removed before proceeding to the next step. Purification removes the impurities present in raw or pristine CNTs and oxidation adds different oxygen functional groups on the surface of CNTs. Since the pristine CNTs are inert and poorly dispersible in common solvents, efforts have been made on the surface modification of CNTs mainly to enhance their solubility and process ability.

In general, CNTs are chemically treated with acids, which introduce various functional groups, such as carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$), and carbonyl ($>\text{C}=\text{O}$), onto the carbon surface (Ebbesen *et al.*, 1996). After the acid treatments, the nanotubes formed a well-dispersed colloid in water and ethanol (Schaffer *et al.*, 1998). Different methods have been reported to decorate metal and metal oxide nanoparticles onto the surface of CNTs. These include liquid phase (Sun *et al.*, 2005), vapor-liquid deposition (Sadeghi *et al.*, 2011), electrode deposition (Tsai *et al.*, 2006), microwave irradiation (Nadagouda & Varma, 2008), thermal decomposition (Xue *et al.*, 2001), hydrothermal (Jayalakshmi *et al.*, 2007), and gamma irradiation (Oh *et al.*, 2005).

This paper reports a simple wet chemical route for decoration of nickel nanoparticles on the surface of oxidized MWCNTs. This method has several advantages

of decorating CNTs such as; simple chemicals can be used, the amount and size of metal nanoparticles can be controlled, don't need any sophisticated instruments, and consume less energy compared to other methods.

MATERIALS AND METHODS

Starting materials

MWCNTs, synthesized by a catalytic chemical vapor deposition (CVD) process (Iljin Nanotech, Korea), were used in this research work. Ethylene glycol, nickel chloride from Qualigens (SQ), and nitric acid, sodium hydroxide from Fisher Scientific were used without further purification.

Deposition of Ni nanoparticles

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

Oxidation and purification

There are several methods for the purification/oxidation of carbon nanotubes. An acid oxidation method was used in this process. Many oxidants have been used to oxidize CNT surfaces (Lyth *et al.*, 2007; Datsyuk *et al.*, 2008). In this work, nitric acid was used for purification/oxidation of MWCNTs. During this process, MWCNTs (0.1 g) was first sonicated (~15 mins) in HNO₃ and then refluxed for about 4 hours. This was filtered using membrane filter paper of pore size: 0.2 μm with the help of suction filter equipment. It was then washed with distilled water until pH 7 and dried in an oven at 100 °C for one hour, as described elsewhere (Shrestha *et al.*, 2010).

Deposition of Ni-nanoparticles on oxidized MWCNTs

The deposition of metal nanoparticle on the surface of CNTs can be achieved by two main pathways. One of the methods is to grow and/or deposit naked nanoparticle directly onto the CNT surface. In an alternative approach, the nanoparticle is pre-formed and connected to CNTs using covalent linking. In the present work, the NiNPs were decorated on the surface of oxidized MWCNTs by wet chemical route using ethylene glycol as a reducing agent. In this decoration procedure, nitric acid-treated MWCNTs (0.05 g) were dispersed in ethylene glycol. To this well-dispersed suspension, NiCl₂.H₂O (0.1 g) in ethylene glycol (2 mL) was added. The pH of the mixture was adjusted to 9 by adding 2 M NaOH and stirred while heating with the help of a magnetic stirrer. The mixture was then filtered through membrane filter paper of pore size 0.2 μm, washed several times with distilled water and dried in an oven at 100 °C for one hour.

Characterization

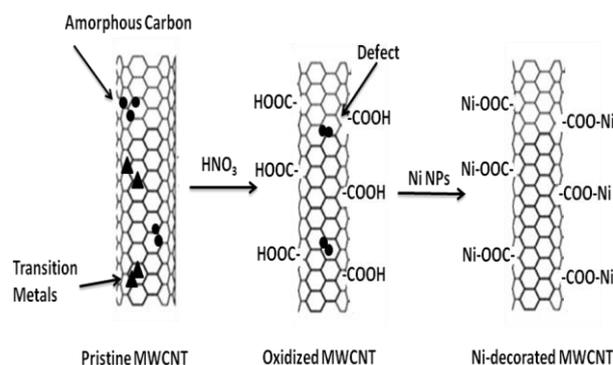
Solid-state Raman spectra of pristine purified Ni/MWCNTs composite were obtained on a renishaw RM-1000. The combined thermogravimetric and

differential thermal analysis (TG-DTA) was carried out on a TG/DTA 6200 (Seiko) instrument. The analysis was performed at a heating rate of 10 °C/min over the temperature range, 50-1000 °C, in open air. Infrared spectroscopy was recorded on IR Prestige- 21 (Shimadzu) by powdered method.

RESULTS AND DISCUSSION

Formation of Ni-nanoparticles on oxidized MWCNTs

The NiNPs were decorated on the surface of the MWCNTs in the following steps. The first step is the purification/ oxidation process, during the purification process, impurities were removed from the pristine CNTs, but on the other hand, several defect sites were generated on the surface of the CNTs. The second step involved the addition of oxygen functional groups into the defect sites. The final step involves decorating the surface of the CNTs with NiNPs. These are shown in schematic diagram 1.



Schematic diagram 1. Decoration of MWCNT with Ni-nanoparticles

The reaction of Ni-atoms on the defect site of MWCNTs is given (eqn.1) by a simple general ion exchange reaction, replacing the proton of the carboxylic group of the nanotubes with metal ions M⁺.



Raman spectroscopy

Raman spectroscopy is a very valuable tool for the characterization of carbon-based nanostructures. Graphitization of pristine, functionalized, and metal attached MWCNTs was comparatively analyzed based on the destruction level due to acid treatment. Figure 1(a) shows the Raman Spectra of pristine, oxidized, and Ni-deposited MWCNTs respectively. Each of them consists of the characteristic bands at 1351 cm⁻¹ (Pristine), 1353 cm⁻¹ (oxidized), and 1356 cm⁻¹ (Ni-MWCNTs) is due to the D band (Shrestha *et al.*, 2010). The D-band was attributed to the presence of defect or disordered in the graphitic structure in the CNT samples (Eklund *et al.*, 1995). Similarly, the band at 1585 cm⁻¹ (pristine), 1586 cm⁻¹ (oxidized), and 1589 cm⁻¹ (Ni-MWCNTs) was due to

the G band, arise from in-plane tangential stretching of the carbon-carbon bonds in graphite sheets (Zdrojek *et al.*, 2004).

In the study of the Raman response of the acid-treated MWCNTs in respect of the pristine sample, Costa and Borowiak (2009) showed that the vibronic and electronic properties of the nanotubes were strongly affected by the acid treatment. When we compared the Raman spectrum of oxidized MWCNT to that of pristine MWCNT, the intensity of D- band increased after treatment with HNO₃ (Table 1). HNO₃ contains oxygen atoms and this oxygen can be easily attached to the sides of the defect in the CNT bond network which leads to changes in the defect band. The guest molecule can either intercalate the walls (Fisher, 2002) or react with the defects in the surface creating attached functional groups (Kim *et al.*, 2007). It is known that both cases lead to an increase in the number of defects in the CNT (Costa *et al.*, 2008).

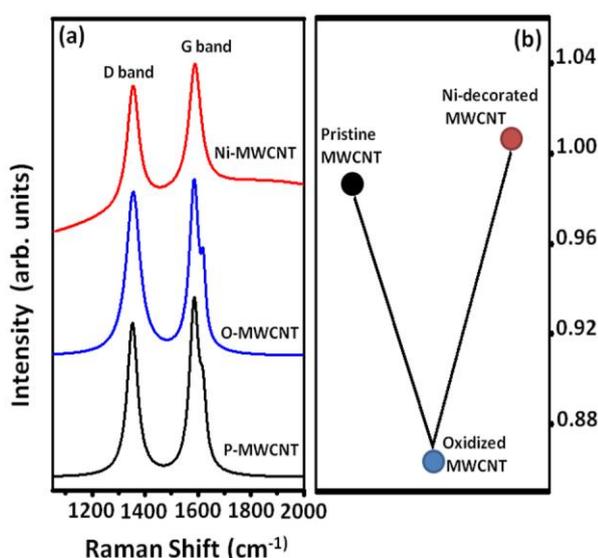


Fig.1. Raman spectra of (a) pristine, oxidized and Ni-decorated MWCNT (b) area ratio of G and D band with oxidation and decoration with nickel nanoparticles

All the D band and G bands were fitted according to Lorentz fitting to calculate the area ratio. The area ratio decreased from pristine to oxidized MWCNTs after acid treatment as shown in Fig. 1(b). That is due to the increase in defect sites on the surface of MWCNTs. These defect sites may be amorphous carbon generated during oxidation, conversion of sp² carbon to sp³ carbon etc. And again this ratio increased after nickel deposition. This suggests that the defect sites generated by the shortening and thinning of the MWCNTs during oxidation can be passivated by decoration with the metal nanoparticles (Shrestha *et al.*, 2010). Characterization of the nanotube surface area helps to elucidate these interactions and the material activity. The shifting of D band and G band

together with the first decrease of area ratio and the increase after nickel deposition strongly supported the attachment of nickel with MWCNTs (Kim *et al.*, 2007).

Table 1. Band positions of pristine, oxidized and Ni-MWCNTs

Sample	D-band (cm ⁻¹)	G-band (cm ⁻¹)	A _(G/D)
Pristine MWCNTs	1351	1585	0.98
Oxidized MWCNTs	1353	1586	0.87
Ni-MWCNTs	1356	1589	1.0

Infrared spectroscopy

Infrared Spectroscopy is used to gain information about the sample composition in terms of chemical groups present and also used to check the purity of the sample. Here, this technique was used to detect the oxygen functional on the surface of oxidized MWCNTs after treatment with acid. Acidic oxidative treatment of the MWCNTs may cause major changes in the structural properties. Figure 2 shows the infrared spectrum of pristine-MWCNTs. The spectra do not show any sharp infrared peak.

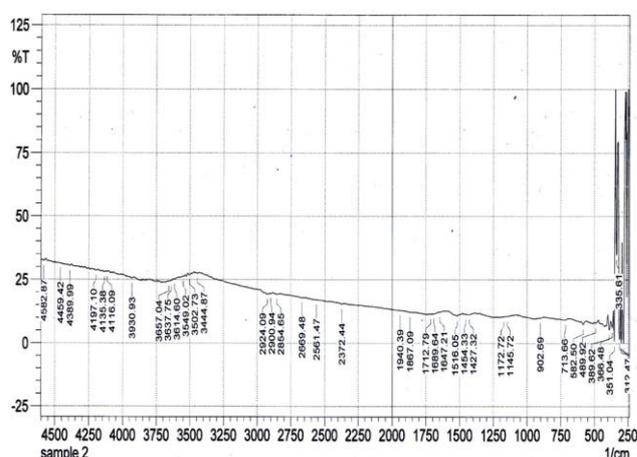


Fig. 2. IR spectrum of the pristine MWCNTs

Figure 3 shows the infrared spectrum of oxidized MWCNTs. If we compare the infrared spectrum of pristine MWCNTs to that of oxidized MWCNTs, we can see many changes. The spectrum shows the number of peaks at different wavelengths. The integrity of the hexagonal structure on the pristine MWCNTs was confirmed by the appearance of a peak at 1527 cm⁻¹ elucidating the existence of carbon double bonding (C=C). Appearance of peak at 1689 cm⁻¹ assigns carbonyl (C=O) stretching vibration of carboxyl groups indicating the expansion of carboxylation on the surfaces of purified and functionalized MWCNTs. Peak at 2800-2900 cm⁻¹ appeared after purification and functionalization corresponding to the C-H asymmetric and symmetric

stretching vibration, derived from the long alkyl chain. Appearance of peak at 3032 cm^{-1} assigns aromatic rings (Yudianti *et al.*, 2011; Silverstein *et al.*, 1981).

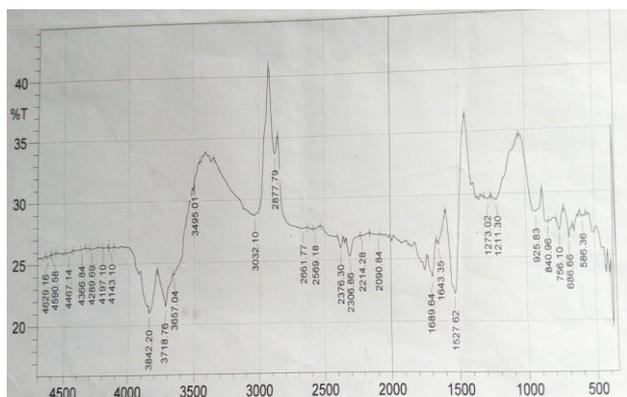


Fig. 3. IR Spectrum of oxidized MWCNTs

Thermal analysis

Figures 4(a), (b), and (c) show the TGA/DTA thermograms for pristine, oxidized, and Ni-MWCNTs respectively. In pristine MWCNTs, the constant weight was maintained up to $550\text{ }^{\circ}\text{C}$. as shown in Fig. 4(a). That means the pristine MWCNTs was hydrophobic in nature and did not contain any water molecule as well as other functional groups. It was thermally stable up to $550\text{ }^{\circ}\text{C}$. Then drastic weight loss occurred from 550 to $650\text{ }^{\circ}\text{C}$ with a single exothermic peak around $625\text{ }^{\circ}\text{C}$. Almost all MWCNTs were burned out at this temperature. After $650\text{ }^{\circ}\text{C}$, continuous heating up to temperature $1000\text{ }^{\circ}\text{C}$ did not show any change in weight loss. The weight remaining was about 8% , which may be due to the oxides of transition metal, used as a catalyst during the synthesis of CNTs (Dillon *et al.*, 1999).

Figure 4 (b) shows the TGA/DTA curve of HNO_3 treated MWCNTs. If compare this thermogram to that of pristine, changes can be seen. The weight loss from 90 - $180\text{ }^{\circ}\text{C}$ was due to the loss of water molecules because oxidized MWCNTs are hydrophilic in nature. At around $250\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$, some weight loss was seen in the TGA curve with a small exothermic peak around $300\text{ }^{\circ}\text{C}$. Here, this weight loss may be due to the loss of some amorphous carbon, which was generated during oxidation and different oxygen functional groups formed after acid treatment (Dillon *et al.*, 1999). This confirmed the introduction of oxygen functional groups after acid treatment. The drastic weight loss ($\sim 70\%$) occurred from 500 to $600\text{ }^{\circ}\text{C}$, which was due to the combustion of MWCNTs. If we compare the burning temperature of pristine and oxidized MWCNTs, the burning of oxidized MWCNTs occurred at a lower temperature than pristine MWCNTs. That may be due to the rupture of the wall of MWCNTs by acid treatment. After heating to $1000\text{ }^{\circ}\text{C}$ less than 1% of weight remained. This confirmed that most of the impurities were removed after treatment with acid.

Figure 4(c) shows the TGA/DTA curve for nickel decorated MWCNTs. Weight loss at $100\text{ }^{\circ}\text{C}$ was due to the moisture contained in it during the experiment. At around 250 - $300\text{ }^{\circ}\text{C}$ a small loss (with exothermic peak at $300\text{ }^{\circ}\text{C}$) is due to amorphous carbon and oxygen functional group. Between $450\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, a large weight loss was seen having a large exothermic peak at $575\text{ }^{\circ}\text{C}$, in which almost all the MWCNTs were burned. After $600\text{ }^{\circ}\text{C}$ no weight loss was observed up to $1000\text{ }^{\circ}\text{C}$. The total residual weight left in the decorated sample was approximately 30% , which was due to the formation of stable Ni-oxide. This also confirmed the presence of Nickel nanoparticles on the surface of oxidized MWCNTs.

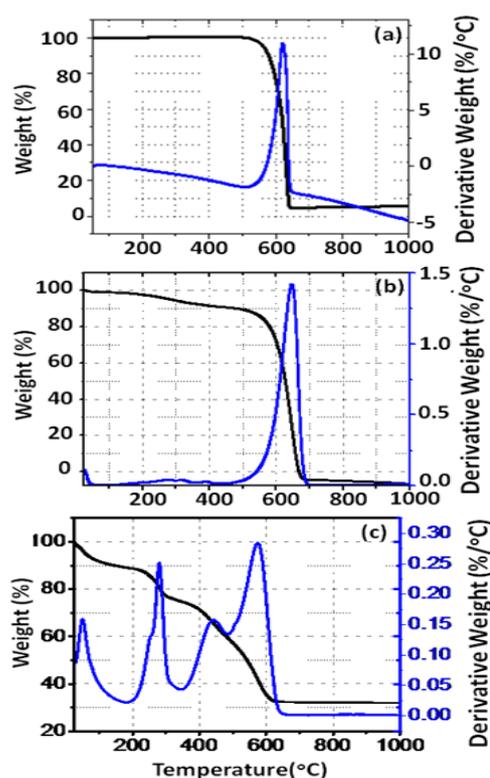


Fig. 4. TG-DTA thermograms of (a) pristine (b) oxidized and (c) Ni-decorated MWCNTs

Energy dispersive spectroscopy

EDS was used for the elemental analysis or chemical characterization of a sample. Its characterization capability is due to its fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its X-ray emission spectrum. Figure 5 shows the EDS spectrum of Nickel decorated MWCNTs. The presence of the expected nickel in the sample was confirmed by their EDS spectra.

CONCLUSION

By using a simple chemical reduction method, the NiNPs can be decorated on the surface of oxidized MWCNT.

The oxidized and Ni decorated MWCNTs were characterized by various techniques such as Raman spectroscopy, IR spectroscopy, Thermal analysis, and EDS. Raman spectroscopy showed the characterization of MWCNTs at various stages. The G and D bands were seen in pristine, oxidized and Ni deposited MWCNTs. The position of these bands and area ratio of G and D bands clarified the purification and deposition of Ni on the surface of MWCNTs.

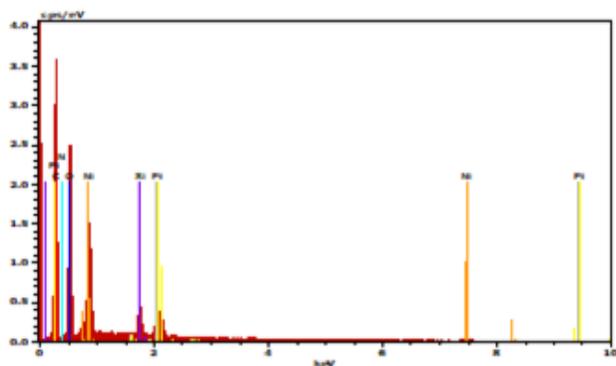


Fig. 5. Energy dispersive spectroscopy of nickel deposited MWCNTs

The increased area ratio of G and D bands in oxidized MWCNTs and shifting of G and D band showed the attachment of nickel. The infrared spectrum of oxidized MWCNTs indicated the addition of oxygen functional groups. The presence of Nickel on the surface of MWCNTs was confirmed by energy dispersive spectroscopy. At the same time, TGA/DTA analysis showed different thermal behavior of pristine-MWCNTs, oxidized-MWCNTs, and Ni deposited MWCNTs. The combustion temperature in oxidized-MWCNTs was decreased, which is due to the rupture of walls and the introduction of defects in MWCNTs. Again, TGA/DTA of oxidized MWCNTs showed the presence of an oxygen functional group. The TGA thermogram of Ni-MWCNTs showed the total residual weight of the Ni-deposited sample was approximately 30 %, which is due mainly to Ni-oxide. This also confirmed the presence of Ni with MWCNTs. After decoration, its applications in various fields can be explored.

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