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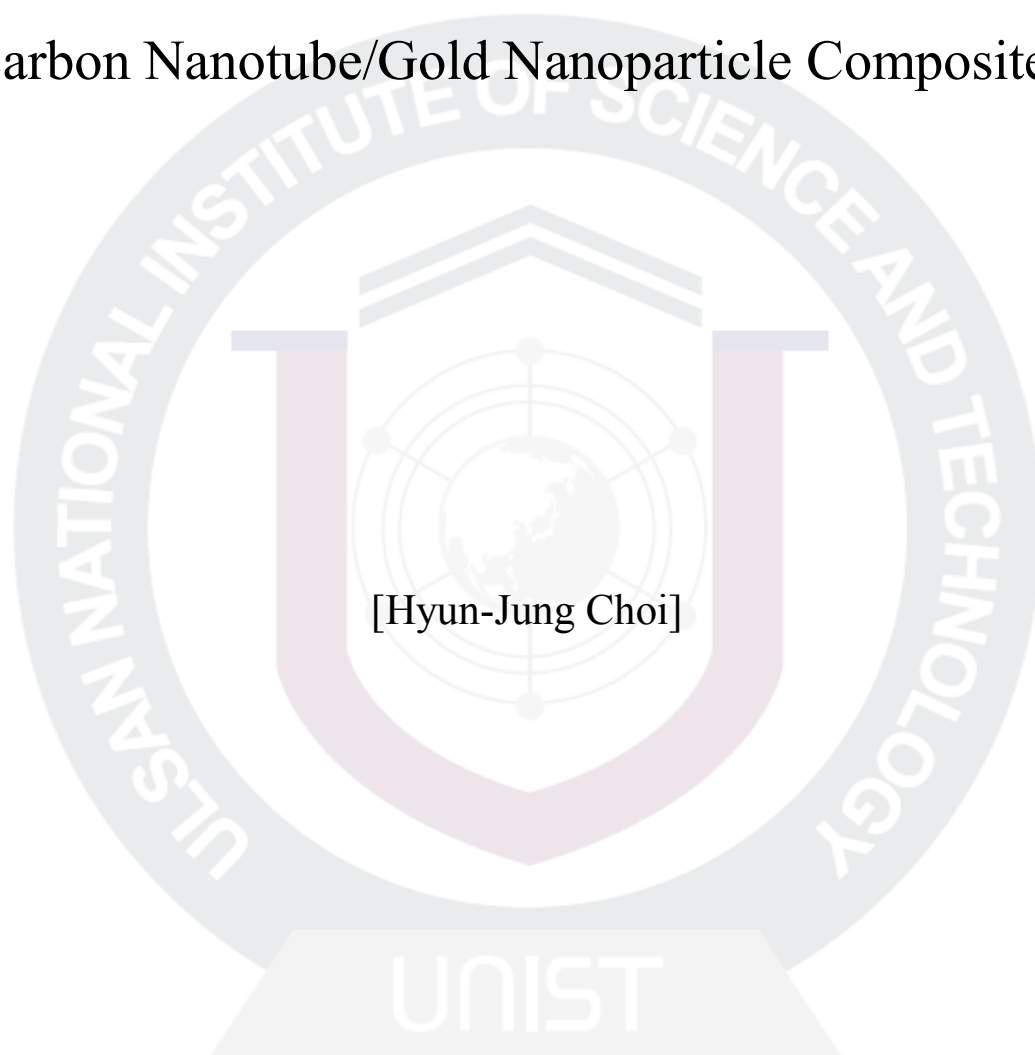
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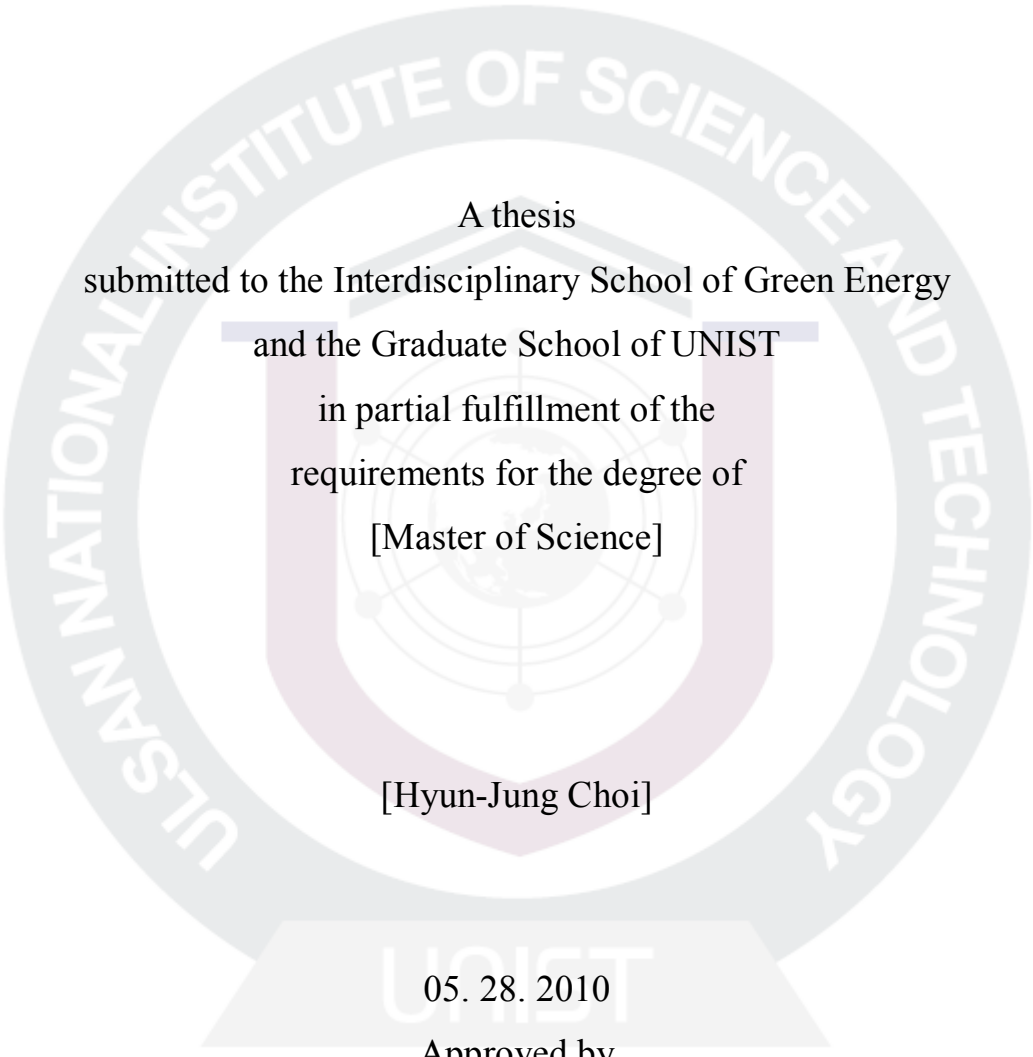
[Synthesis of Thiol Functionalized Multi-walled
Carbon Nanotube/Gold Nanoparticle Composites]



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[Synthesis of Thiol Functionalized Multi-walled Carbon Nanotube/Gold Nanoparticle Composites]

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A thesis
submitted to the Interdisciplinary School of Green Energy
and the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
[Master of Science]

[Hyun-Jung Choi]

05. 28. 2010

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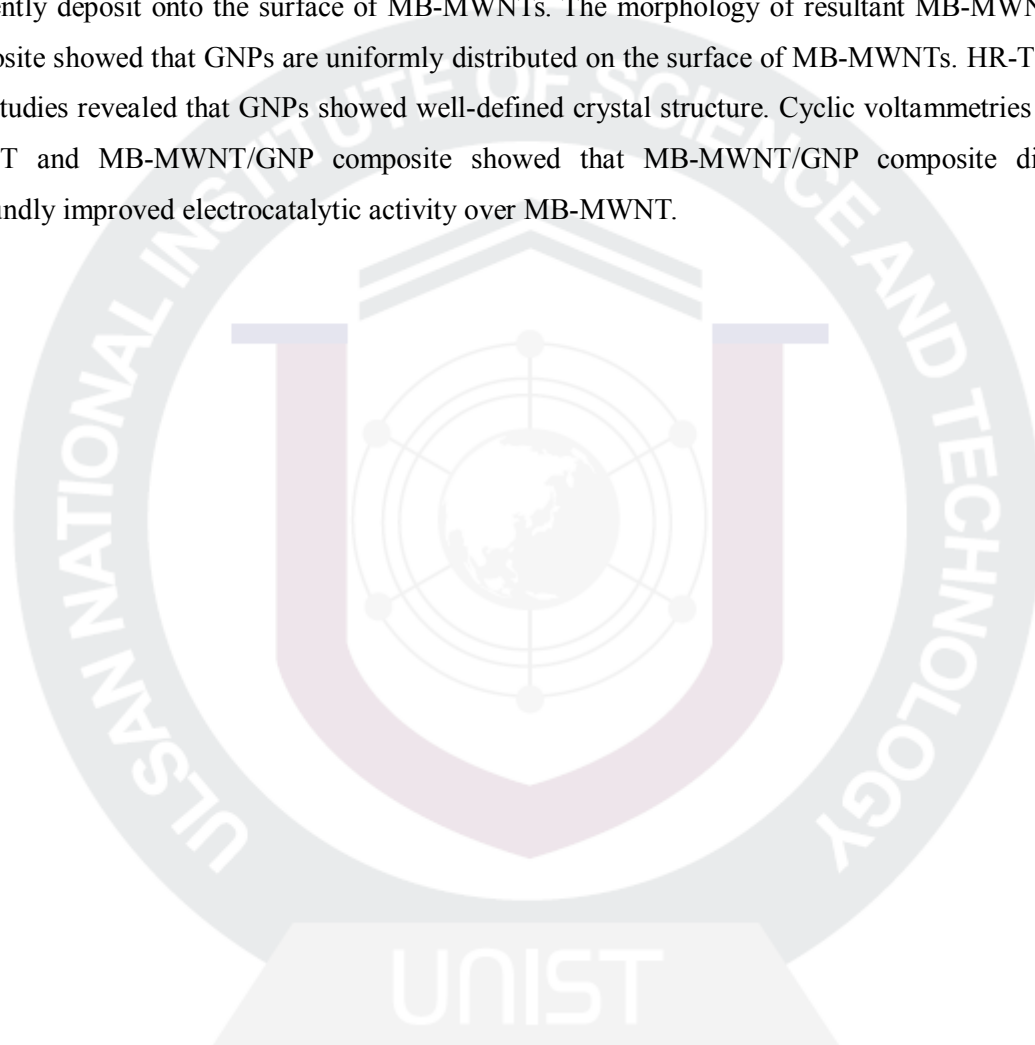
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ABSTRACT

Multi-wall carbon nanotubes (MWNTs) were functionalized with 4-mercaptopbenzoic acid (4-MBAc) in a polyphosphoric acid (PPA)/phosphorous pentoxide (P_2O_5). The resultant 4-mercaptopbenzoyl-functionalized MWNT (MB-MWNT) was used to immobilize gold nanoparticles (GNPs) via the covalent Au-S bonds. The process involved that GNPs were *in-situ* synthesized in the presence of MB-MWNT and stabilized by trisodium citrate and sodium borohydride ($NaBH_4$) to covalently deposit onto the surface of MB-MWNTs. The morphology of resultant MB-MWNT/GNP composite showed that GNPs are uniformly distributed on the surface of MB-MWNTs. HR-TEM and XPS studies revealed that GNPs showed well-defined crystal structure. Cyclic voltammeteries of MB-MWNT and MB-MWNT/GNP composite showed that MB-MWNT/GNP composite displayed profoundly improved electrocatalytic activity over MB-MWNT.





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Scheme 1. Synthesis of MB-MWNT and MB-MWNT/GNP composite.



Nomenclature

1. **CNTs**; Carbon nanotubes
2. **MWNTs**; Multi-walled carbon nanotubes
3. **4-MBAc**; 4-mercaptobenzoic acid
4. **MB-MWNT**; 4-Mercaptobenzoyl-functionalized MWNT
5. **GNPs**; Gold nanoparticles
6. **PPA**; polyphosphoric acid
7. **P₂O₅**; phosphorous pentoxide
8. **NaBH₄**; sodium borohydride
9. **FT-IR**; Fourier-transform Infrared
10. **EA**; Elemental analysis
11. **TGA**; Thermogravimetric analysis
12. **XPS**; X-ray photoelectron spectroscopy
13. **FE-SEM**; field emission scanning electron microscopy
14. **HR-TEM**; High resolution transmission electron microscope
15. **CV**; Cyclic voltammetry

I. Introduction

Carbon nanotubes (CNTs) are known to have excellent mechanical,¹ thermal,² electrical,³ efficient hydrogen storage properties.⁴ Owing to such unique properties, CNTs have been continuously attracting much interest from many areas of science and technology.⁵ Amongst them, CNTs-based metal nanoparticle composites have been tremendously studied due to their potential applications in catalysis,⁶ sensors,⁷ hydrogen storage, energy storage, optical and electronic devices.⁸ Various approaches for CNT/nanoparticle composites were suggested, such as, physical evaporation,⁹ chemical reaction with functionalized CNTs,¹⁰ and electrolysis deposition methods.¹¹ However, there are difficulties in dispersing metal nanoparticles with uniform dispersion and regular sizes in the CNT surfaces.¹²

To utilize CNTs as base materials for various applications, it is necessary to attach functional groups or to deposit other nanostructured materials onto their surfaces. Functionalized CNTs have been tremendously studied for dispersion enhancement in processing¹³ and/or for further chemical modifications.¹⁴ Unfortunately, however, although CNTs are generally considered as inert materials, significant damages to CNT frameworks are inevitable via reported common approaches to functionalize and/or disperse CNTs.^{15,16} To functionalize inert CNTs, it requires harsh treatment conditions in strong acids such as sulfuric acid, nitric acid,¹⁷ and/or their mixtures^{오류! 책갈피가 정의되어 있지 않습니다.} at elevated temperatures.

We have developed an efficient method to introduce desired organic functional groups onto the surface of CNTs in a polyphosphoric acid (PPA, 83 % assay)/phosphorous pentoxide (P₂O₅) medium via “direct” Friedel-Crafts acylation reaction.¹⁸ We expect that PPA is a mild and less destructive reaction medium and plays two important roles for the effective and thus uniform covalent attachment on the surface of carbon nanomaterials. The one is its moderate acidic nature promotes deaggregation to help homogeneous dispersion without damaging CNT. The other is viscous character helps to impede reaggregation after dispersion, which is achieved by shear force during high torque stirring. In the present study, we would like to functionalize MWNT with 4-mercaptobenzoic acid via Friedel-Crafts acylation reaction to afford 4-mercaptobenzoyl functionalized MWNT (MB-MWNT). The resultant MB-MWNT contains many thiol groups on its surface, which are well known to interact with gold nanoparticles (GNPs).¹⁹ Hence, GNPs could be conveniently immobilized onto the surface of MB-MWNT without agglomeration.²⁰ The MB-MWNT/GNP composite is expected to exhibit excellent electrocatalytic activity.

II. Experimental

2.1 Materials

All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received, unless otherwise mentioned. Multi-walled carbon nanotubes (MWNTs, CVD MWNT 95 with diameter of ~20 nm and length of 10-50 nm) was obtained from Hanwha Nanotech Co., LTD, Seoul, Korea.²¹

2.2 Instrumentations

To study the functionalization of MWNTs, Fourier-transform Infrared (FT-IR) spectra were recorded on a Jasco Fourier transform spectrophotometer model 480 Plus. All of the samples were mixed with dried KBr and pressed to form the semi-transparent pellets. The FT-IR spectra were collected in the wavelength range from 650 to 4000 cm^{-1} . Elemental analysis (EA) was performed with a CE Instruments EA1110. Thermogravimetric analysis (TGA) was conducted in air atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ with a TA Q200. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Fisher K-alpha employing a monochromatic Al $\text{K}\alpha$ radiation as the X-ray source. The field emission scanning electron microscopy (FE-SEM) used in this work was FEI NanoSem 230. High resolution transmission electron microscope (HR-TEM) employed in this work was a JEOL JEM-2100F (Cs) operating at 200 kV. The TEM samples were prepared by dipping holey carbon micro-grids into dispersed samples in ethanol. The CV experiment was conducted with Solartron SI1287.

2.3 Synthesis of 4-mercaptobenzoyl-functionalized MWNT (MB-MWNT)

4-Mercaptobenzoyl-functionalized MWNT were prepared according to the literature procedure.²² In brief, a mixture of 4-mercaptobenzoic acid (4-MBAc, 5.0 g), and MWNT (5.0 g), PPA (83 % assay, 200.0 g) and P_2O_5 (50.0 g) was placed in a 500 mL resin flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet. The mixture was stirred under dry nitrogen purge. The reaction mixture was heated to 130 $^{\circ}\text{C}$ for 72 h. Due to dispersion of MWNT, the initially dark mixture (MWNT) with a little white powder (4-MBAc) became black as the reaction progressed. At the end of the reaction, the color of the mixture was dark shiny black-brown. The mixture was poured into distilled water. The resulting powdery precipitates were collected by suction filtration, washed with distilled water, Soxhlet-extracted with water for three days to completely remove

residual reaction medium and with methanol for three more days to remove unreacted 4-MBAC, respectively. Finally, the sample was freeze-dried under reduced pressure (0.05 mmHg) to give 8.67 g (91.76 % yield) of dark black powder. Anal. Calcd. for $C_{19.84}H_5OS$ (calculation based on % yield): C, 81.77; H, 1.73; S, 11.01. Found: C, 80.63; H, 1.37; S, 11.09.

2.4 Synthesis of MB-MWNT/GNP composite

Gold nanoparticles (GNPs) were prepared according to a literature method.²³ Briefly, a 20 mL aqueous solution containing 18.4 mL of deionized water, 0.5 mL of an aqueous 0.05 M $HAuCl_4 \cdot 3H_2O$ solution, and 0.5 mL of an aqueous 0.05 M trisodium citrate solution was prepared in a conical flask. Next, 0.6 mL of an ice cold aqueous 0.1 M $NaBH_4$ solution was added in one portion with vigorous stirring. The solution turned red immediately after the addition of the $NaBH_4$ solution, indicating GNP formation. MB-MWNTs (50 mg) were dispersed in 30 mL ethanol by ultrasonic agitation for 3 min. Then black suspension was added into the solution containing gold colloids (20 mg) at room temperature. The mixture was stirred for 1 day. A homogeneous, well distributed solution of MB-MWNT/GNP composite was collected by filtration, washed with water several times and freeze-dried under reduced pressure (0.05 mmHg) to give 48mg of dark black powder.

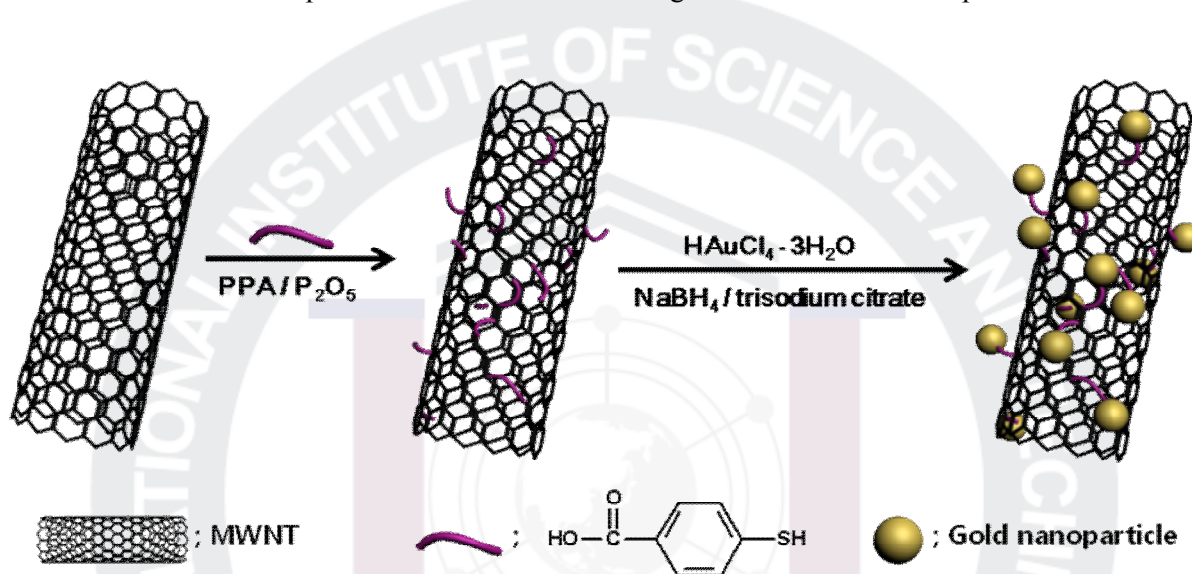
2.5 Electrocatalytic activity

To study the electrocatalytic activities, a conventional three-electrode system, which is consisted of a carbon cloth electrode as working electrode, an Ag/AgCl (sat. KCl) as reference electrode and platinum mesh as counter electrode, was used at room temperature. . All potential values are reported as a function of Ag/AgCl. The CV was measured in 0.1 M aqueous sulfuric acid solution with a scan rate of 10 mV/s and in the potential range of 0 and 1.4 V. To prepare MB-MWNT, MB-MWNT/GNP modified carbon cloth electrode, MB-MWNT, MB-MWNT/GNP in aqueous solution were coated on the carbon cloth electrodes, respectively, and then vacuum dried for 24 h at 50 °C prior to test.

III. Results and discussion

3.1 Synthesis of MB-MWNT/GNP composite

As shown in Scheme 1, 4-mercaptobenzoyl-functionalized MWNT (MB-MWNT) was prepared as followed by literature procedure via “direct” Friedel-Crafts acylation reaction in PPA/P₂O₅ medium.²² The formation of MB-MWNT was traced by elemental analysis and FT-IR. The synthesis of MB-MWNT/GNP composite was carried out following the modified literature procedure.²⁴



Scheme 1. Synthesis of MB-MWNT and MB-MWNT/GNP composite.

3.2 FT-IR study

The progress of the reaction was conveniently monitored with FT-IR. FT-IR spectroscopy was used to confirm the chemical modification of the MWNTs with 4-MBAC. The spectra of MWNTs, 4-MBAC and MB-MWNTs are shown in Figure. 1. The spectrum of pristine MWNTs exhibits absorption peaks at 2921 and 2850 cm⁻¹ corresponding to sp² C-H and sp³ C-H stretching bands, respectively. 4-MBAC shows thiol group at 2564 cm⁻¹, aromatic carbonyl peak at 1680 cm⁻¹, and C=C bond at 1594 cm⁻¹. To our surprise, The MB-MWNT does not to show thiol peak around 2564 cm⁻¹, due to a tight π - π interaction between grafted 4-MBAC and MWNT. However, it is apparent that there is a strong aromatic carbonyl band at 1675 cm⁻¹ and C=C bond at 1587 cm⁻¹. The result is clear evidence for the covalent attachment of 4-MBAC moieties on the surface of MWNT. In addition, MB-MWNTs display C-H vibration bands around 2922 and 2852 cm⁻¹. The data could be used to further support that Friedel-Crafts acylation reaction between 4-MBAC and MWNT at the reaction condition

had indeed taken place. Furthermore, EA result further support that the CHOS contents are agreed well between theoretical and experimental values (see Experimental section).

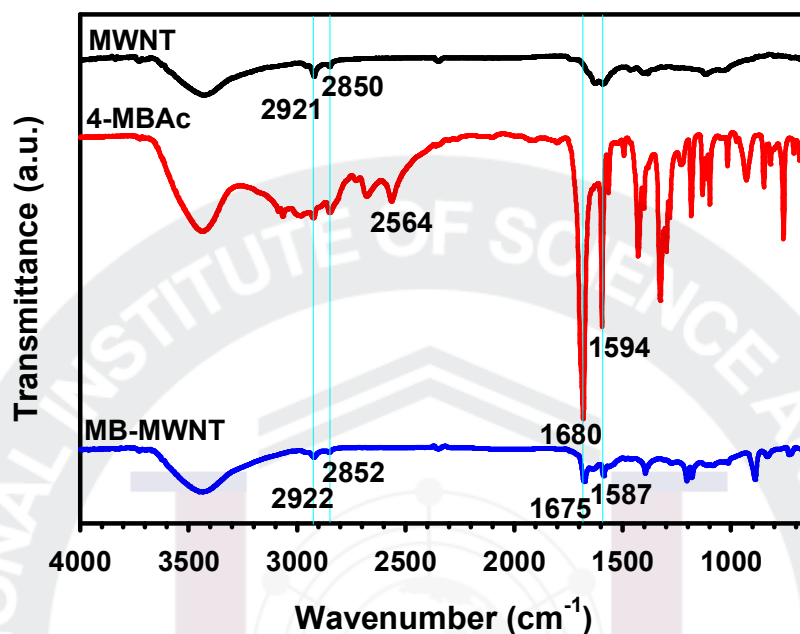


Figure 1. FT-IR (KBr pellet) spectra of pristine MWNT, 4-MBAc and MB-MWNT.

3.3 Thermal Properties

The samples were subject to thermogravimetric analysis (TGA) with heating rate of 10 °C/min in air. The TGA thermograms obtained from the powder sample of pristine MWNT, MB-MNWT and MB-MWNT/GNP composite showed that the temperatures at which 5 % weight loss ($T_{d5\%}$) in air was occurred at 584, 365 and 374 °C, respectively (Figure 2). It could be confirmed that organic pendants were covalently attached to the surface of MWNT from the change of inclination at around 380 °C in air. The char yields of MWNT and MB-MWNT/GNP composite were 1.5 and 21 %, respectively, while the MB-MWNT had the values approached to 0 %. The result indicated that the residual amount of MWNT due to catalytic residues and stable carbonaceous fragments. After functionalization to the MB-MWNT, those impurities were almost completely eliminated in mild acid treatment.²⁵ Hence, the residual amount of MB-MWNT/GNP composite at 800 °C should be due to GNPs. It was a strong indication that GNP was successfully attached to the surface of MB-MWNT and the residual value at 800 °C was the amount of GNP load.

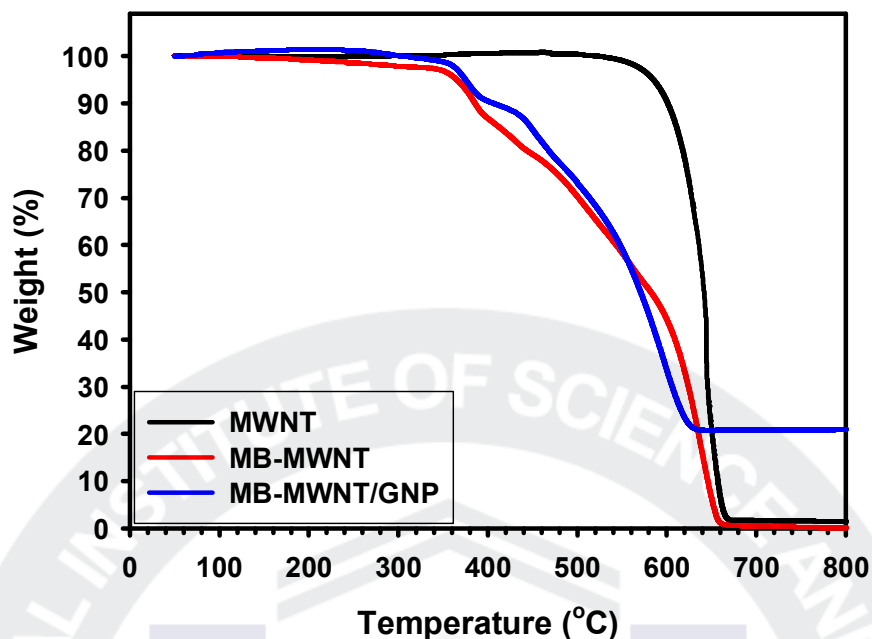


Figure 2. TGA thermograms obtained with heating rate of 10 °C/min in air

3.4 X-ray photoelectron spectroscopy (XPS) spectra

To confirm the existence of Au, S, O and C in the MB-MWNT/GNP composite, XPS experiment was employed for the surface chemical composition of the samples. XPS survey of the MB-MWNT shows a significant S2p, S2s and O1s signals from 4-MBAC moiety, and a C1s signal mainly contributed to MWNTs (Figure 3a). The deconvoluted C1s peak shows a major C1s peak at 284.4 eV and a minor peak at 285.4 eV. The former could be assignable to the carbon in the graphitic C and the latter to that in the C=O group. In the C1s in the high energy region, the peak was broad due to the mixture of sp² carbon and carbon atom bound to sulfur atom. A peak at 532.2 eV is corresponded to O1s. There are S2p with shoulder and S2s peaks at 163.8 and 228.0 eV, respectively.²⁶ The deconvolution of S2p separates two peaks 163.8 and 165.1 eV, which are closely related to the states of -SH, confirming the 4-MBAC grafted onto the surface of MWNT. The peaks are assignable to S2p_{1/2} and S2p_{3/2} electrons, respectively.²⁷

In the case of MB-MWNT/GNP as shown in Figure 3b, XPS spectrum shows that a strong C1s peak at 285 eV, S2p peak at 164.1 eV and S2s peak at 227.9 eV are appeared. New peaks at 84.2 and 87.8 eV are appeared from Au4f, which are corresponded to Au 4f_{7/2} and Au 4f_{5/2}, respectively. The emission of 4f photoelectrons from Au is identified in two peaks of the XPS spectra. They are assignable to Au⁰ (84.2 and 87.8 eV).²⁸ These are typical values of Au⁰, strongly indicating that the formation of GNPs on the sidewalls of the MB-MWNT.

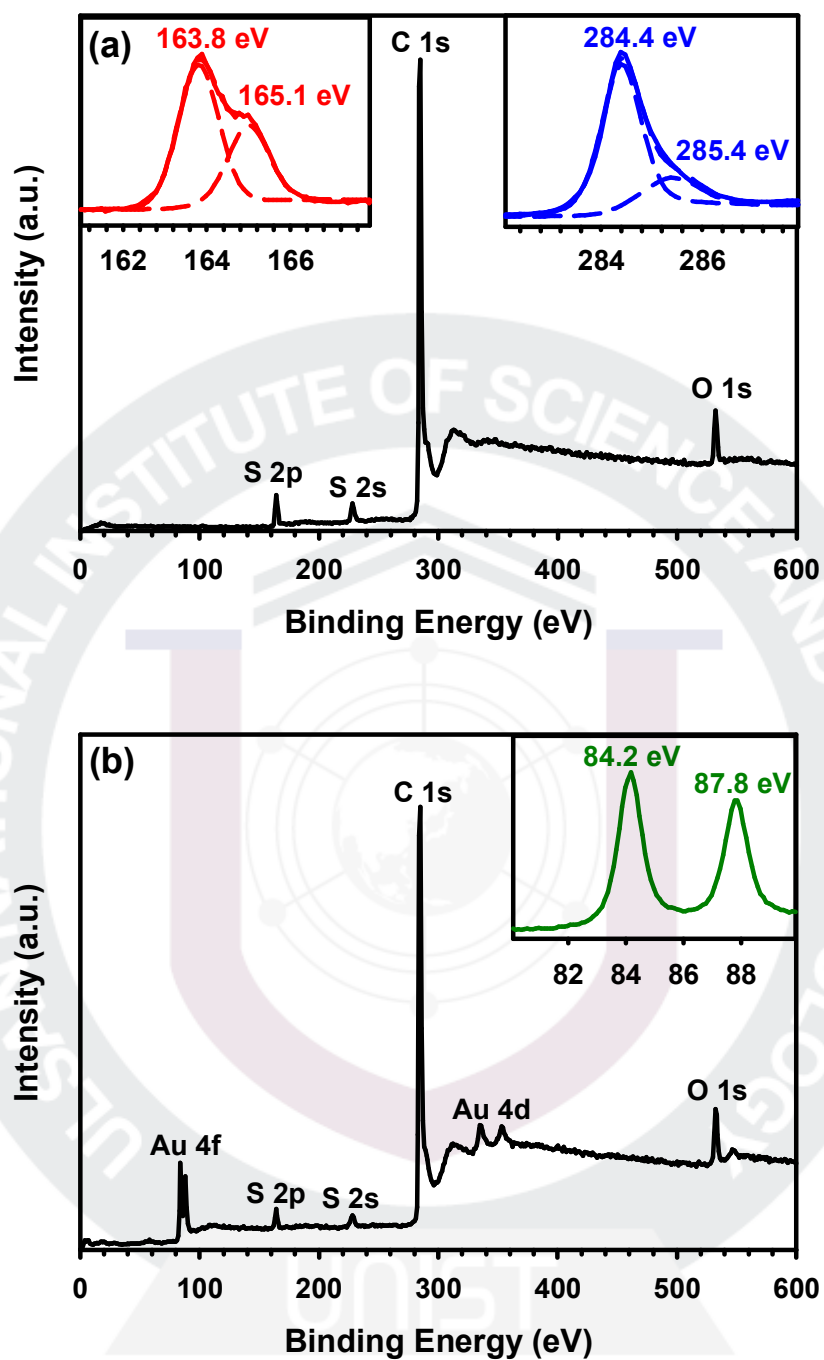


Figure 3. XPS spectra of (a) MB-MWNT [Inset: the S 2p doublet (top-left) and C 1s (top-right)]; (b) MB-MWNT/GNP composite (Inset: the Au 4f doublet).

3.5 Scanning electron microscopy (SEM) study

The SEM images presented in Figure 4 are obtained from the MB-MWNT and MB-MWNT/GNP composite. The MB-MWNT shows that the surface of tubes are decorated MBAC. The thickness was in the range of 30-60 nm (Figure 4a), whose value is approximately 2-3 times larger than that of pristine MWNT (~20 nm). The result strongly support that the functionalization is successful. The SEM image obtained from MB-MWNT/GNP composite is shown in Figure 4b. A numerous white dots are uniformly deposited on the surface of MB-MWNT. The result visually assure that the GNPs are successfully loaded.

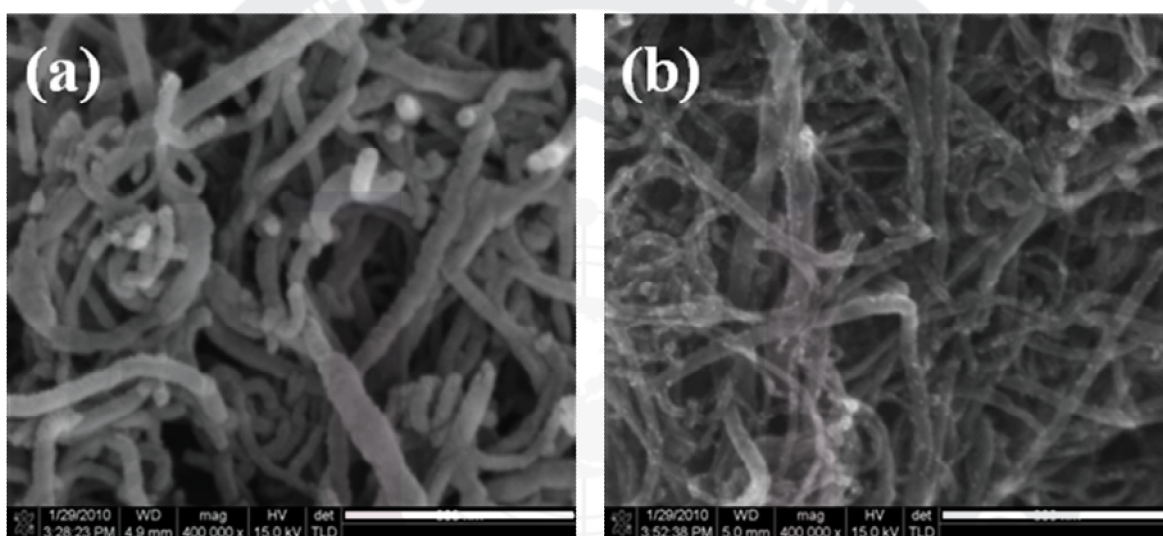


Figure 4. SEM images obtained from (a) MB-MWNT; (b) MB-MWNT/GNP composite. Scale bars are 300 nm.

3.6 Transmission electron microscopy (TEM) study

Because MB-MWNT/GNP composite was either powder or friable lump, it was dispersed in ethanol. The carbon coated holey carbon grid was dipped into the mixture and taken out to dry in a vacuum oven. The TEM images of MB-MWNT/GNP composite (Figure. 5a) show that GNPs are uniformly distributed on the surface of MB-MWNT. Free GNPs are not observed in the background of TEM images, indicating that strong interactions between MB-MWNT and GNPs. This indicated that there were active sites on the MB-MWNT, which provided the nucleation sites for GNP growth on its surface. Figure 5b shows magnified image from the interface between the GNPs and MB-MWNT. The lattice fringes associated to the GNPs have an interplanar spacing of 0.24 nm, consistent with the (111) planes of fcc Au.²⁹ The lattice of CNT has an interplanar spacing of 0.34 nm, which

are related to (002) plane of CNT or graphite.³⁰ Figure 5c is a statistical result counted from 300 GNPs showing the distribution of the particle size. The diameters are in the range of 2~8.86 nm and the average diameter is approximately 4.3 nm. Surely, introduction of mercapto groups on the surface of MWNT suggests the uniform dispersion and stabilization of GNPs.

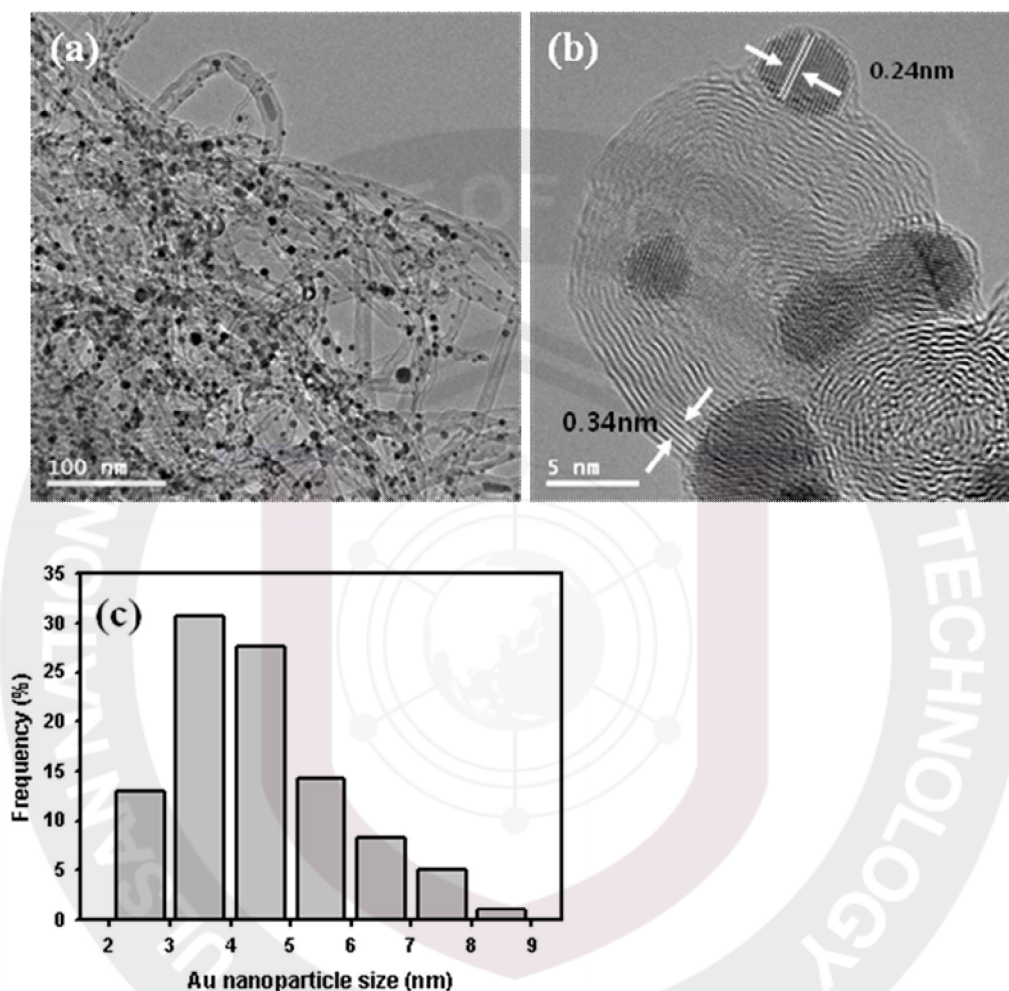
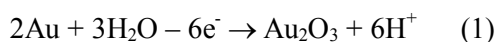


Figure 5. TEM images: (a) MB-MWNT/GNP composite; (b) magnified image; (c) size distribution of GNP on MB-MWNTs.

3.7 Electrochemical property

The deposition of GNPs on the surface of MB-MWNT greatly affects their electrochemical properties. According to literature,³¹ higher electroactive surface area of the carbon nanotubes-based nanomaterials always shows higher electrocatalytic activity resulting higher sensitivity. Cyclic voltammetry (CV) studies were performed in aqueous solution of 0.1M H₂SO₄, in the potential range from 0 V to 1.4 V versus Ag/AgCl at sweep rate of 10 mV/s. Hence, CV was used to estimate the

electroactive surface of the modified electrodes. The 10th CV curve recorded on carbon cloth coated with a MB-MWNT and MB-MWNT/GNP composite (Figure 6). While MB-MWNT shows a small oxidation peak at 0.34 V and a small reduction peak at 0.25 V, MB-MWNT/GNP composite shows two oxidation peaks at 0.32 and 1.17 V, and three reduction peaks at 0.30, 0.70 and 0.92 V. According to equation (1)³² the oxidation peaks indicate the formation of an oxide monolayer on the GNP.



The MB-MWNT/GNP composite coated electrode shows typical features of gold surface. The oxidation on the forward scan (at 1.17 V) and the reduction on the reverse scan (at 0.70 and 0.92 V) were observed. A clear pair of peaks appears at 0.32 and 0.30 V for the MB-MWNT/GNP catalyst, which are assignable to carbon-oxygen functionalities on the surface of pretreated MWNT.³³ The difference between the two peaks of oxidation and three peaks of reduction potentials indicates that the redox reaction is irreversible, which means the gold oxide is not entirely reduced at the returning sweep, i.e. from 1.4 to 0 V versus Ag/AgCl.

Compared to MB-MWNT electrode, the peak currents at MB-MWNT/GNP composite electrode were significantly increased, illustrating that the MB-MWNT/GNP electrode possesses much higher electrocatalytic activity.

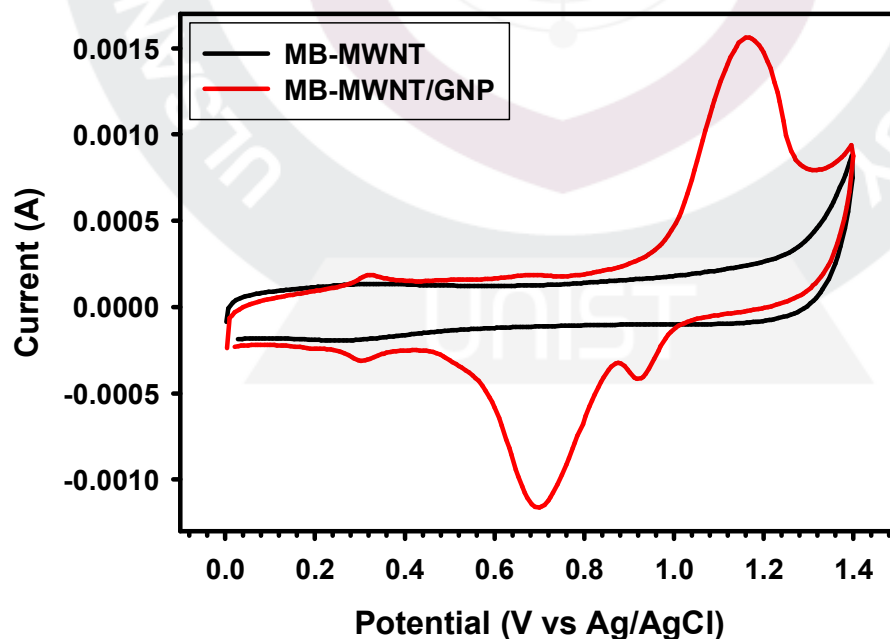


Figure 6. CV curves at the carbon cloth electrode coated with the MB-MWNT and MB-MWNT/GNP composite, respectively, in 0.1 M H₂SO₄. Scan rate is 10 mV/s.

IV. Conclusion

The functionalization of MWNT with 4-mercaptopbenzoic acid was indeed viable to introduce thiol functionality, which provided anchoring sites for gold nanoparticles (GNPs). The resultant MB-MWNT was used as substrate for GNP deposit to afford MB-MWNT/GNP composite. MB-MWNT/GNP composite was characterized with a various analytical techniques such as EA, FT-IR, TGA and XPS. The morphology of the composite was studied with SEM and TEM, showing that GNPs were uniformly distributed onto the surface of MB-MWNT. MB-MWNT/GNP composite clearly showed redox peaks. Compared to MB-MWNT electrode, the MB-MWNT/GNP composite electrode displayed much higher electrocatalytic activity.



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Appendix

TEM mapping

TEM mapping was used as an additional means to characterize the assembly of the gold nanoparticles at the surface of the MB-MWNTs, as shown in Figure 1. It can be seen from the Scanning TEM image. Figure 1 indicates the presence of O and S from the 4-MBAC molecules, C from MWNTs and 4-MBAC and Au from GNPs. The presence of O and S in the elemental mapping images confirms that a significant amount of the 4-MBAC molecule is present at the surface of the MWNTs. And the elemental mapping of Au was well matched with S. It indicated that GNPs were successfully grafted onto the surface of MB-MWNTs.

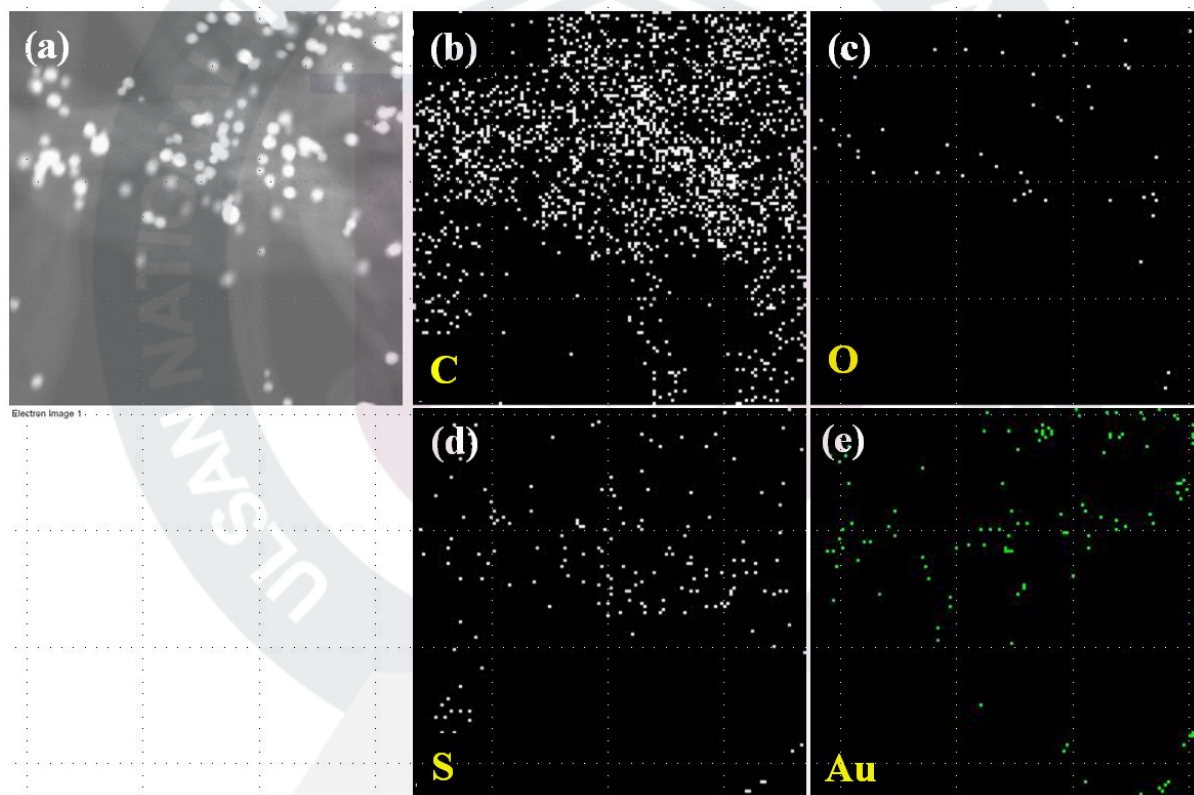


Figure S1. (a) Scanning TEM image of MB-MWNT/GNP composite; (b) elemental mapping of C present in part a; (c) elemental mapping of O present in part a; (d) elemental mapping of S present in part a; and (e) elemental mapping of Au present in part a.

Electrochemical properties.

Figure 2 presents CV curves of MB-MWNT and MB-MWNT/GNP composites on a glassy carbon electrode in 0.1M aqueous solution of KOH saturated with N_2 or O_2 with a scan rate of 0.1 V/s. Featureless voltammetric currents within the potential range of -0.3~-0.6 V were observed for MB-MWNT and MB-MWNT/GNP composites in N_2 saturated KOH solution. In contrast, the remarkable catalytic reduction of oxygen of MB-MWNT and MB-MWNT.GNP composites occurred at the potential of -0.48 V and -0.43 V, respectively, when the electrolyte solution is saturated with O_2 . The results indicate that the MB-MWNT/GNP composites have an excellent electrocatalytic activity for oxygen reduction.

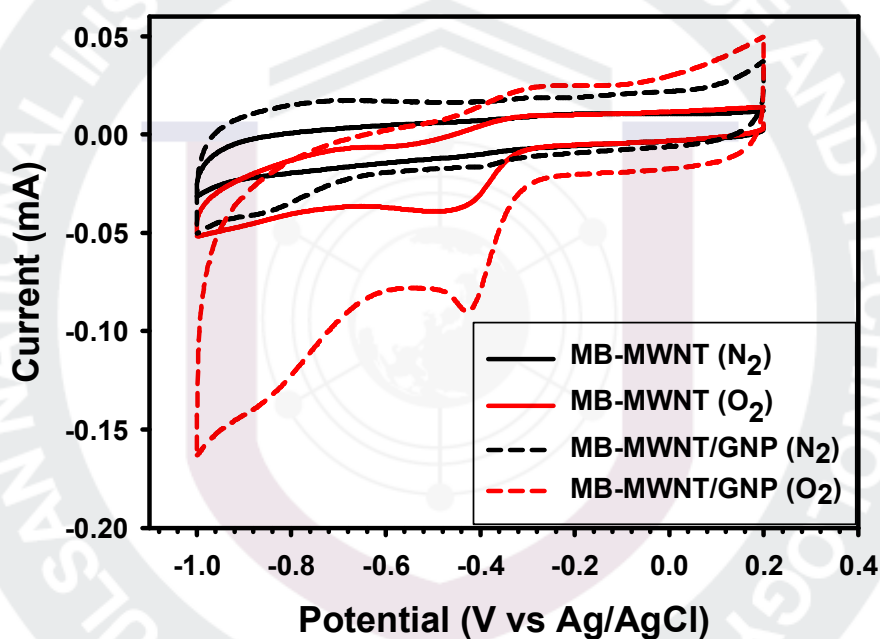


Figure S2. CV curves of the MB-MWNT and MB-MWNT/GNP on a glassy carbon electrode in an N_2 saturated and an O_2 saturated 0.1 M aqueous solution of KOH with a scan rate of 0.1 V/s.

The electrocatalytic properties of MB-MWNT and MB-MWNT/GNP composites for oxygen reduction reaction have been investigated by linear sweep voltammetry in O₂ saturated 0.1 M aqueous solution of KOH with a scan rate of 0.01 V/s. The corresponding results are presented in Figure 3. The peak current densities of MB-MWNT and MB-MWNT/GNP composite are -0.02 and -0.048 mA/cm², respectively. The peak current densities of MB-MWNT/GNP composites are almost 1.5 times as much as that of MB-MWNT.

The above results imply that sample MB-MWNT/GNP composites possesses higher electrocatalytic activities for the oxygen reduction reactions. The increase in the electrocatalytic activities may mainly be attributed to the higher active surface area of MB-MWNT/GNP composites.

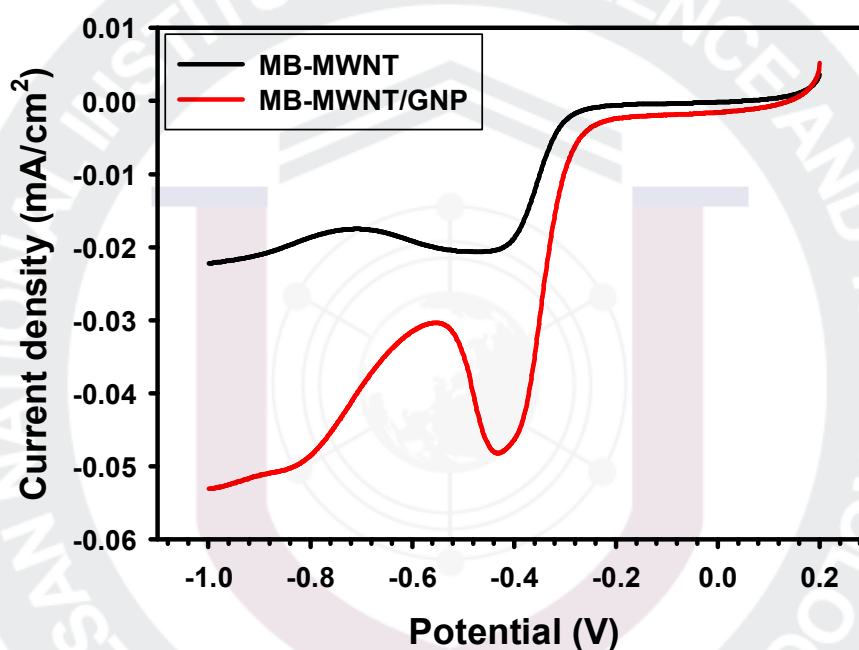


Figure S3. LSV of the MB-MWNT and MB-MWNT/GNP composites on a glassy carbon electrode in an O₂ saturated 0.1 M aqueous solution of KOH with a scan rate of 0.01 V/s.

Manuscript

International

1. Hyun-Jung Choi, In-Yup Jeon, Jong-Beom Baek "**Stable anchoring of gold nanoparticle onto thiol-functionalized multi-walled carbon nanotube and its electrochemical properties** " MRS. 2009 fall meeting, Prepr. Boston, MA, November 30-December 4.
 2. Hyun-Jung Choi, In-Yup Jeon, Loon-Seng Tan, Jong-Beom Baek "**Synthesis and properties of gold nanoparticle/thiol-functionalized multi-walled carbon nanotube composites**" Polym. Prepr. 2009, 49(2), Salt Lake, UT, March 22-26.
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Domestic

1. Hyun-Jung Choi, Jong-Beom Baek "**GNP/mercaptobenzoyl-functionalized multi-walled carbon nanotube composites.**" The polymer Society of Korea 2010, 35(1), (Daejeon, April 8-9).
 2. Hyun-Jung Choi, Jong-Beom Baek "**Synthesis of thiol-functionalized multi-walled carbon nanotube/gold nano-particle composites and its electrochemical properties**" The polymer Society of Korea 2009, 34(2), (Gwangju, October 8-9).
 3. Hyun-Jung Choi, Jong-Beom Baek "**Synthesis and properties of gold nanoparticle/thiol-functionalized multi-walled carbon nanotube composites**" The Polymer Society of Korea 2009, 34(1) (Daejeon, April 9-10).
 4. Hyun-Jung Choi, Loon-Seng Tan, Jong-Beom Baek "**Thiol-functionalized multi-walled carbon nanotube/gold nanoparticle composite**" The Polymer Society of Korea 2008, 33(2). (KINTEX, ILSAN, October 9-10, 2008).
 5. Hyun-Jung Choi, Sang-Wook Han, Loon-Seng Tan, Jong-Beom Baek "**Synthesis and properties of thiol-functionalized multi-walled carbon nanotube/gold nanoparticle composites**" The Polymer Society of Korea 2008, 33(1) (Daejeon, April 11-12).
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Acknowledgement

Foremost, I would like to express my sincere gratitude to my advisor Prof. Jong-Beom Baek for the continuous support of my master course study and research, for his kindness, patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my master course study.

Besides my advisor, I would like to thank the rest of my thesis committee: Prof. Yongseok Jeon and Prof. Hyeonsuk Shin for their encouragement and insightful comments.

And I want to express my gratitude to my colleagues: Jong-Kwan Lim, Sang-Wook Kang and Ji-Ye Kang for the stimulating discussions, for the sleepless nights we were working together before deadlines. I was really happy about the times we shared together. And I wish you good luck.

I thank my fellow labmates in High Performance Polymer Synthesis lab: In-Yup Jeon, Kyung-Su Kim, Seo-Yoon Bae, Yeon-Ran Shin and Gyoung-Ju Shon for all the fun we have had in the last two years. Also I thank my friends in UNIST.

Last but not the least, I would like to thank my family: my parents Young-Tai Choi and Sak-soon So, for their support and who raised me with their loving and gentle care. And I also thank my younger brother Byung-Jin Choi.