

Polymer–Copper-Modified MWNTs by Radiation-Induced Graft Polymerization and Their Efficient Adsorption of Odorous Gases

Kyo-Il Kim,¹ Sang-Hyeb Oh,² Hai-Doo Kwen,¹ Seong-Ho Choi¹

¹Department of Chemistry, Hannam University, Daejeon 305-811, Republic of Korea

²Korea Research Institute of Standards and Science, Daejeon 305-600, Republic of Korea

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ABSTRACT: Polymer–copper-modified multi-walled carbon nanotubes (MWNTs) were prepared by radiation-induced graft polymerization of epoxy-containing glycidyl methacrylate and subsequent amination and Cu complexing. Two amines, triethyldiamine and imidazol, were used as polymeric ligand compounds. The Cu-modified MWNTs were confirmed by high-resolution transmittance electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy,

and thermal gravimetric analysis. The dynamic adsorption of odor gases, such as CH₃SH and H₂S, on the Cu-modified MWNTs and amine-modified MWNTs was also evaluated. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: radiation-induced graft polymerization; polymer–copper-modified MWNTs; amine-modified MWNTs; odor gas

INTRODUCTION

Radiation-induced graft polymerization (RIGP) is a unique technique for direct grafting of new functional polymers (grafts) into polymer substrates in which the functional polymers retain characteristics such as thermal stability, mechanical strength, electronic properties, and crystallinity.^{1–3} Research has probed graft polymerization's mechanisms and also news methods for grafting including chemical transformation of grafts in battery separators, absorber resins, and polymer electrolyte membranes.^{4–6}

Carbon nanotubes (CNTs) possess superlative mechanical, thermal, and electrical properties⁷ making them potentially suitable for a wide range of applications, such as conductive and high-strength polymer composites, energy storage and conversion devices, and field emission displays.^{8–11} However, their insolubility in most solvents and matrices has limited their application. To overcome solubility problems, noncovalent and covalent modifications have been attempted.^{12,13} Among them, a covalent reaction of CNTs with polymers is widely used, as long polymer chains aid the nanotubes' dispersion in a wide range of solvents. Recently, polymer-grafted CNTs have been prepared by methods such as anionic polymer-

ization,¹⁴ ring-opening polymerization,¹⁵ atom transfer radical polymerization,¹⁶ reversible addition-fragmentation chain transfer polymerization,¹⁷ and radiation-induced polymerization.^{19,20} RIGP of various vinyl monomers onto aqueous multi-walled carbon nanotubes (MWNTs) at room temperature has been performed to introduce functional groups onto the nanotubes' surfaces for electrochemical biosensing.^{21–23} However, a search of the literature found nothing regarding the modification of MWNTs' surfaces with polymer–metal complexes by aqueous RIGP at room temperature.

Polymer–metal complexes are typified by remarkably specific structures in which a central metal ion is surrounded by a bulky polymer chain. The polymeric ligands' complicated conformations lead to complexes showing interesting and important characteristics. For example, different catalytic activities arise from polymeric complexes compared with ordinary, lower molecular weight, metal complexes. This work's aim was to prepare graft polymer–metal complexes for possible use as gas adsorbents to remove odorous gases.

RIGP of glycidyl methacrylate (GMA) was performed on the surfaces of aqueous MWNTs at room temperature. GMA vinyl monomer was chosen for its epoxy group, something easily converted to alcohols, amines, phosphonic acid, sulfonic acid, etc. Triethylene diamine (TEDA) and imidazol were subsequently introduced onto these grafted epoxy groups to introduce amine groups into the ligands. Finally, polymer–Cu-modified MWNTs were produced by complexing the aminated-poly(GMA) and copper

Correspondence to: S.-H. Choi (shchoi@hnu.kr).

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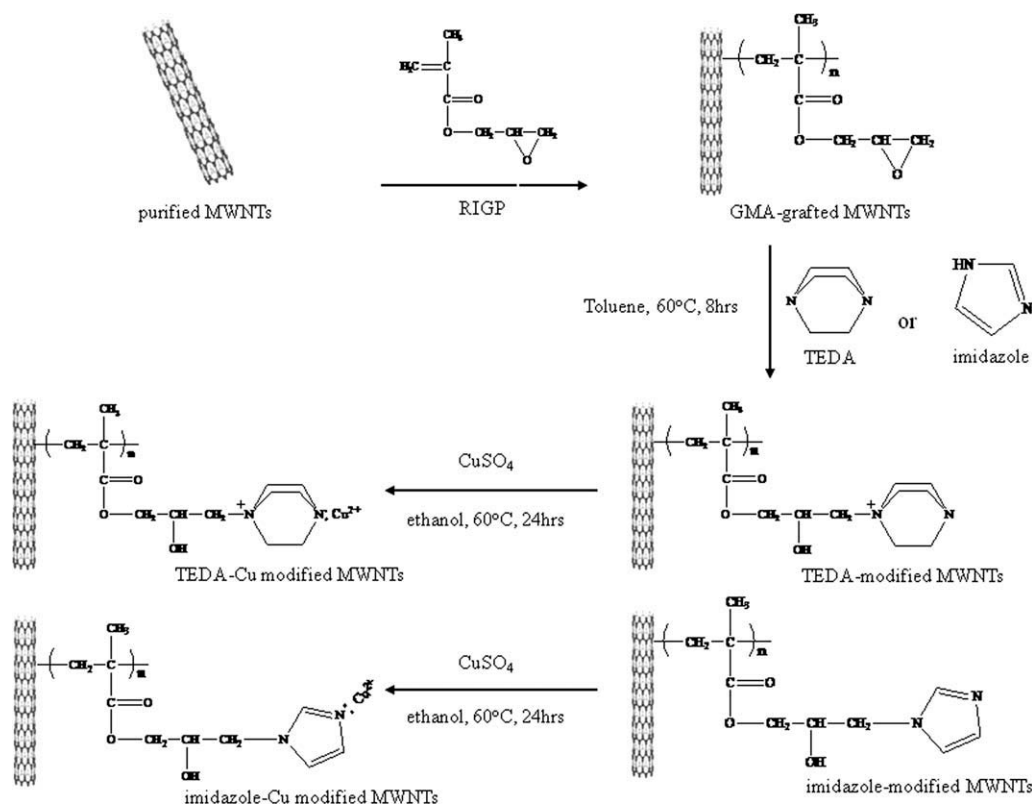


Figure 1 Schematic preparation procedure of polymer-Cu complex-modified MWNTs by RIGP.

ions in ethanol. The polymer-copper-modified MWNTs and amine-modified MWNTs were evaluated by high-resolution transmittance electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA) to assess their dynamic adsorption of odorous gases, such as CH_3SH and H_2S , at room temperature.

EXPERIMENTAL

Chemicals

GMA, TEDA, imidazole, and copper sulfate ($CuSO_4$, 99%) were of analytical reagent grade (ζ -Aldrich) and used without further purification. MWNTs (CM-95) were supplied by Hanwha Nanotech Corp. (Korea). The standard odorous gases, CH_3SH , and H_2S (both of 1000 ppm) were obtained from the Korea Research Institute of Standards and Science. Water was purified in a Milli-Q plus water purification system (Millipore Co., final resistivity of $18.2M \Omega \text{ cm}^{-1}$) and degassed before each measurement. Other chemicals were of reagent grade.

Preparation of the polymer-Cu-modified MWNTs by RIGP

Figure 1 outlines the preparation of the polymer-Cu-modified MWNTs adsorbents. To remove odorous gas, MWNTs were first purified to remove the

catalyst and noncrystallized carbon impurities by treatment with phosphoric acid at 50°C for 12 h. The purified MWNTs were used as substrates for grafting with the epoxy groups of GMA. The MWNTs (2.0 g) and GMA (2.0 g) were then mixed in aqueous solution (400 mL). Nitrogen gas was bubbled through the solution for 30 min to remove oxygen gas, and the solution was irradiated by a Co-60 source under atmospheric pressure and ambient temperature. A total dose of 30 kGy was administered at $1.0 \times 10^4 \text{ Gy/h}$. The obtained samples were separated by centrifuge at 3000 rpm, and then dried in a vacuum oven at 50°C for 18 h.

The GMA-grafted MWNTs were immersed in 0.5M TEDA or 0.5M imidazole in toluene at 60°C for 8 h, sufficient to reach final conversion. The modified MWNTs were sequentially washed with toluene, acetone, methanol, and hot de-ionized water, and then dried under reduced pressure. The polymer-Cu-modified MWNTs were prepared by complexing the amine-modified MWNTs (0.1 g) with 0.1 g $CuSO_4$ in 50 mL ethanol at 60°C for 24 h. They were then washed thrice with ethanol.

Adsorption of odorous gases

An adsorption chamber was made as shown in Figure 2. 0.1 g samples were placed in a Petri dish covered with a shield in the adsorption chamber with

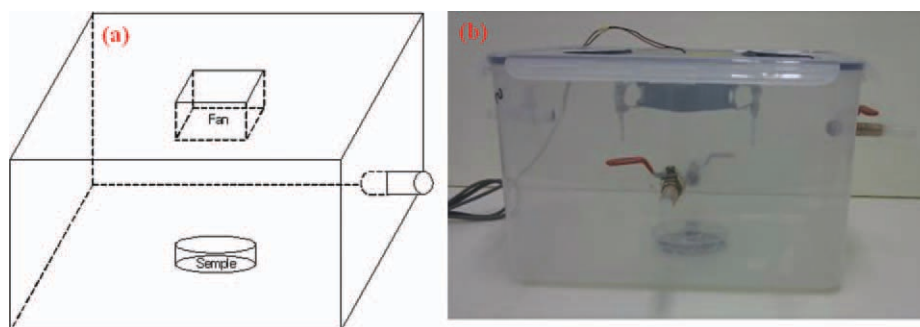


Figure 2 A diagram chamber (a) and photograph (b) for adsorption of odor gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

odorous gas of 15 ppm at room temperature under atmospheric pressure. The shield was then removed to allow gas adsorption. Initial and final gas concentrations were determined using a GASTEC detector tube sensor (Safety Equipment Institute, SEI).

Instrumentation

X-ray photoelectron spectra were obtained using a MultiLab ESCA2000 (Thermo Fisher Scientific, Barrington, IL, USA). Surface morphologies were determined by HR-TEM (JEOL, JEM-2010, Peabody, MA, USA) and scanning electron microscopy (SEM; Hitachi, S-4700, Tokyo, Japan). Fourier transform infrared spectra were recorded between 400 and 4000 cm^{-1} (with 4 cm^{-1} resolution) from KBr pellets using a Perkin-Elmer Spectrum 1000 system (Perkin-Elmer Life and Analytical Sciences, Waltham,

MA, USA). TGA was conducted on a Scinco TGA S-1000 (Seoul, Korea) under N_2 flow from 25 to 700°C at 20°C/min.

RESULTS AND DISCUSSION

Figure 3 shows TEM images of the polymer-Cu-modified MWNTs. Purified MWNTs average diameter was 40 nm [Fig. 3(a)]. After RIGP, this increased to 60 nm for poly(GMA)-g-MWNTs [Fig. 3(b)]. TEDA introduction to the epoxy groups of the poly(GMA)-g-MWNTs further increased diameters to 80 nm due to the swelling effects of the reaction solvents. Irradiation initiated radical polymerization of the GMA on the surfaces of MWNTs. Hence, tubular MWNTs were produced in a one-step reaction. After grafting, amination was conducted with TEDA and

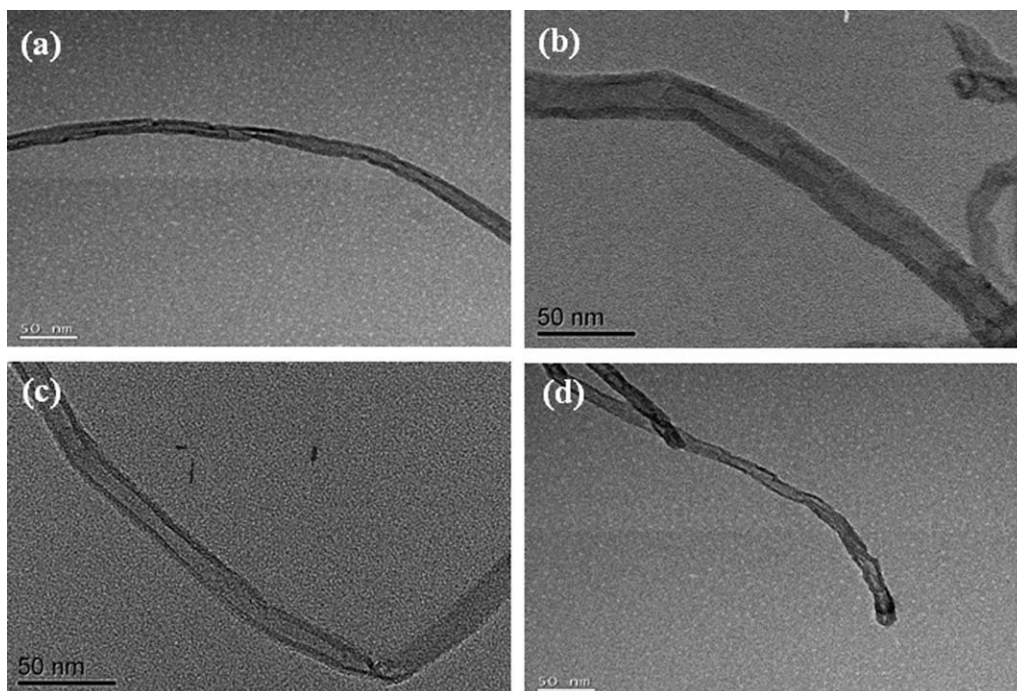


Figure 3 TEM images of the purified MWNTs (a), poly(GMA)-g-MWNTs (b), TEDA-modified MWNTs (c), and polymer-Cu complex-modified MWNTs (d) prepared by RIGP.

TABLE I
Adsorption Efficiency of the TEDA-, TEDA-Cu, Imidazole- and Imidazole-Cu-modified MWNTs Adsorbents for CH₃SH and H₂S in 25 cm × 25 cm Chamber

| | | TEDA (%) | TEDA-Cu (%) | Imidazole (%) | Imidazole-Cu (%) |
|--------------------|---------|----------|-------------|---------------|------------------|
| CH ₃ SH | 60 min | N/A | 40 | N/A | 17 |
| | 180 min | N/A | 100 | N/A | 100 |
| H ₂ S | 60 min | 46 | 80 | 50 | 42 |
| | 180 min | 87 | 100 | 100 | 100 |

imidazol, as TEDA can induce ionic properties via tetra-amine and unpaired electrons via triamine (see structure in Fig. 1). Amine groups with ionic charges and unpaired electrons are expected to facilitate efficient adsorption of odorous gas. However, only some adsorption of odorous gas was observed by amine-modified MWNT adsorbents in practical experiments (Table I). Efficiency was increased by the introduction, through complexing, of copper ions to the amine-modified MWNT adsorbents.

The TEM images of the polymer-Cu-complex-modified MWNTs did not distinguish Cu, as the TEM analysis was performed on copper grids. Cop-

per's presence was established through SEM. Figure 4 shows SEM images of (a) purified MWNTs; (b) poly(GMA)-g-MWNTs; (c) TEDA-modified MWNTs; and (d) TEDA-Cu-modified MWNTs prepared by RIGP. When amine groups from TEDA were introduced to the epoxy group of the grafted poly(GMA), the MWNTs aggregated due to hydrogen bonding [Fig. 4(c)]. Subsequent complexing with Cu ions was confirmed by SEM and copper appears as blue dots in Figure 4(d). Therefore, the successful preparation of polymer-Cu-modified MWNTs was demonstrated.

Figure 5 shows XPS spectra of (a) poly(GMA)-g-MWNTs; (b) TEDA-modified MWNTs; (c) imidazole-modified MWNTs; (d) TEDA-Cu-modified MWNTs; and (e) imidazole-Cu-modified MWNTs. The XPS data show significant changes upon introduction of TEDA and imidazole to the poly(GMA)-g-MWNTs; for example, the appearance of the characteristic N 1s peak at 399 eV. This implies the successful preparation by RIGP of MWNTs supporting TEDA with positive charge via tetra-amine and unpaired electrons via triamine. These amine groups are expected to lead to strong gas adsorption. However, as mentioned above, there was only low gas

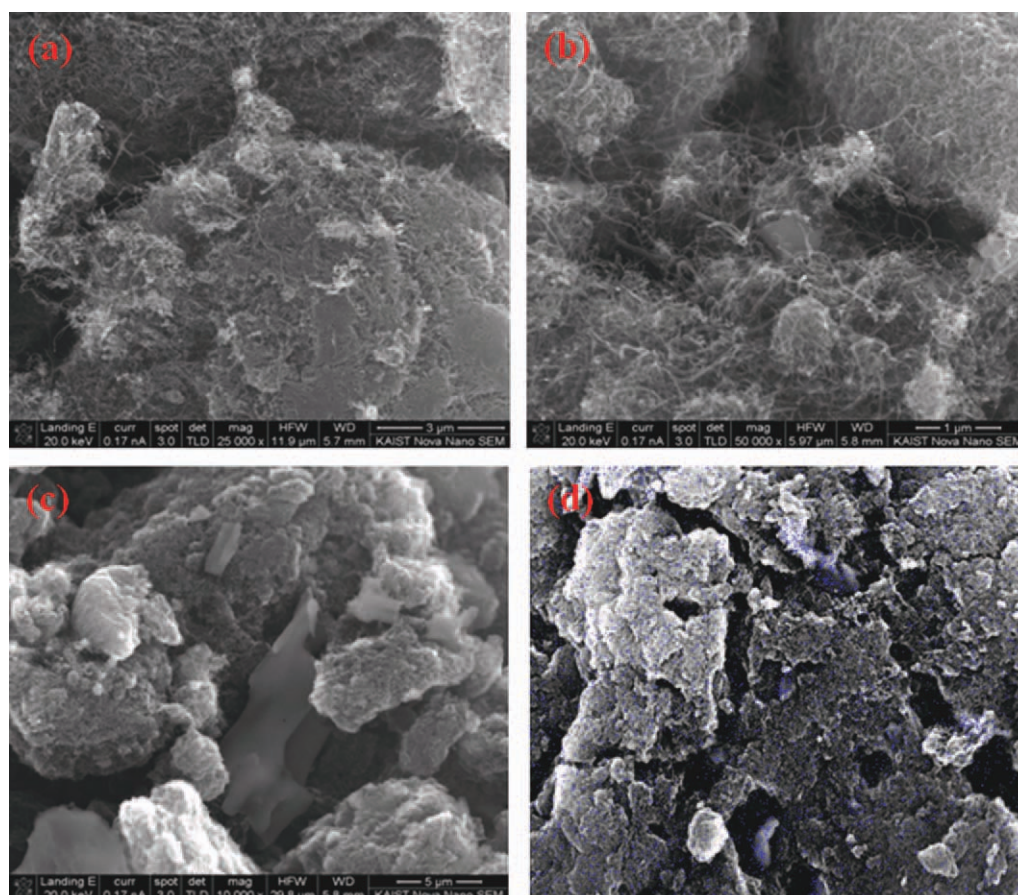


Figure 4 SEM images of the purified MWNTs (a), poly(GMA)-g-MWNTs (b), TEDA-modified MWNTs (c), and polymer-Cu complex-modified MWNTs (d) prepared by RIGP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

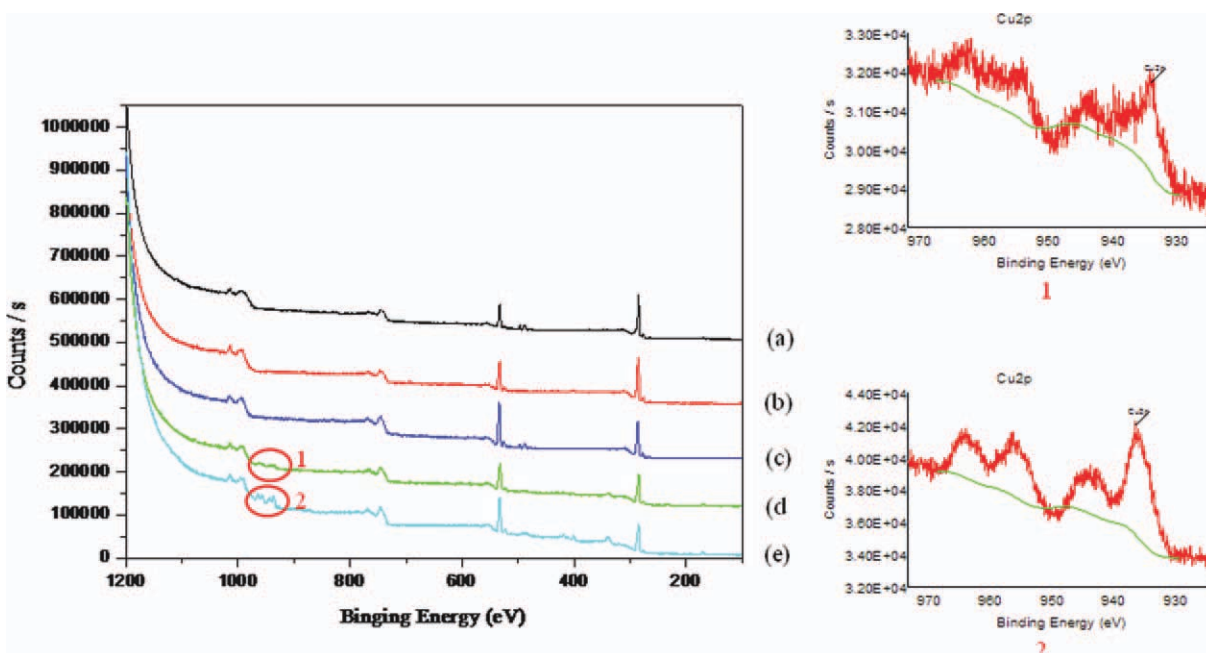


Figure 5 XPS survey scan spectra of the base carbon (a), TEDA-modified carbon (b), imidazole-modified carbon (c), TEDA-Cu complex-modified carbon (d), and imidazole-Cu complex-modified carbon (e) prepared by RIGP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adsorption in the practical adsorption tests. Its efficiency was increased by the introduction through complexing of copper ions onto amine-modified MWNTs, which led to the characteristic Cu 2p peak at 935 eV. These polymer-copper-modified MWNTs adsorbents then showed efficient gas adsorption.

Figure 6 shows TGA curves of the TEDA-Cu complex-modified MWNTs (left side) and imidazole-Cu complex-modified MWNTs adsorbents (right side). (a) The purified MWNTs; (b) poly(GMA)-g-MWNTs; (c,c') amine-modified MWNTs; and (d,d') amine-Cu-modified MWNTs adsorbents. As shown in Figure 6, the first weight loss from 50 to 200°C for the poly

(GMA)-g-MWNTs, amine-modified MWNTs, and polymer-Cu-modified MWNTs is due to moisture loss as the grafted poly(GMA), amine groups, and polymer-Cu complexes are all hydrophilic. This weight loss increased after the introduction of amine and copper ion because of their strong hydrophilic properties. The second weight loss from 250 to 600°C occurred due to the grafted poly(GMA), as shown in Figure 6(b) (left and right sides). The results show graft yield of *ca.* 45% by RIGP of GMA monomer, confirming the successful preparation of poly(GMA)-g-MWNTs. However, there were no remaining MWNTs after the introduction of TEDA

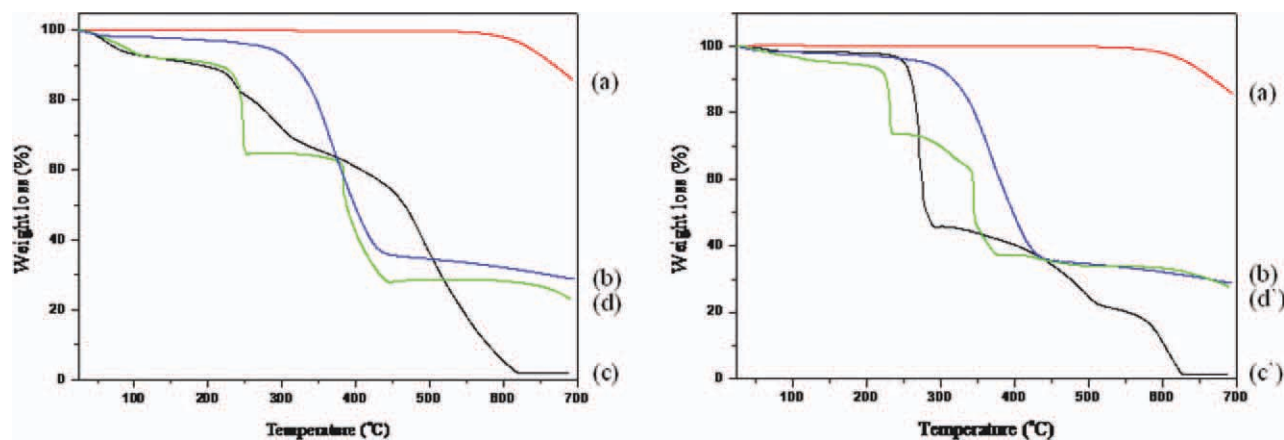


Figure 6 TGA curves of the TEDA-Cu complex-modified MWNTs (left side) and imidazole-Cu complex-modified MWNTs adsorbents (right side). (a) the purified MWNTs; (b) poly(GMA)-g-MWNTs; (c and c') amine-modified MWNTs; and (d and d') amine-Cu-modified MWNTs adsorbents prepared by RIGP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(left side) and imidazole (right side), as shown in Figures 5(c,c'). This may be through the weakening of the MWNTs physical and chemical properties during amination in toluene at high temperature. Copper yields of *ca.* 30% after complexing demonstrated the successful preparation of polymer–Cu-complex MWNTs adsorbents.

Table I shows dynamic adsorption efficiencies of the TEDA-, TEDA–Cu, imidazole-, and imidazole–Cu-modified MWNTs adsorbents for CH₃SH and H₂S in a 25 cm × 25 cm chamber. Unmodified MWNTs showed no adsorption. Also, the solely amine-modified MWNT adsorbents failed to adsorb CH₃SH. 150 ppm H₂S was adsorbed at 87% efficiency by the TEDA-modified MWNTs adsorbents after 180 min, compared with the imidazole-modified MWNTs 100%. TEDA–Cu and imidazole–Cu-modified MWNTs showed *ca.* 100% adsorption efficiency of both 150 ppm CH₃SH and H₂S after 180 min. Therefore, polymer–Cu-modified MWNTs adsorbents are potentially beneficial materials for removing odorous gas from the environment. Further adsorption efficiency studies are in progress.

CONCLUSIONS

Novel polymer–Cu-modified MWNTs adsorbents were synthesized by RIGP. They were confirmed by HR-TEM, XPS, and thermal gravimetric analysis. Their adsorption efficiency of odorous gases, CH₃SH and H₂S, was *ca.* 100% after 180 min with an initial gas concentration of 150 ppm at room temperature and atmospheric pressure. RIGP therefore demonstrated its worth in the preparation of novel adsorbents.

References

1. Choi, S. H.; Nho, Y. C. *J Appl Polym Sci* 1999, 71, 2227.
2. Choi, S. H.; Nho, Y. C. *Radiat Phys Chem* 2000, 57, 187.
3. Sawada, S.; Yamaki, T.; Kawahito, S.; Asano, M.; Suzuki, A.; Terai, T.; Maekawa, Y. *Polym Degrad Stab* 2009, 94, 344.
4. Gwon, S. J.; Choi, J. H.; Sohn, J. Y.; Lim, Y. M.; Nho, Y. C.; Ihm, Y. E. *J Ind Eng Chem* 2009, 15, 748.
5. Klein, E. *J Membr Sci* 2000, 179, 1.
6. Peighambardoust, S. J.; Rowshanzamir, S.; Amjadi, M. *Int J Hydrogen Energy* 2010, 35, 9349.
7. Spitalsky, Z.; Tasis, D.; Papagelis, K.; Galiotis, C. *Prog Polym Sci* 2010, 35, 357.
8. Ma, P. C.; Siddiqui, N. A.; Marom, G.; Kim, J. K. *Composites A* 2010, 41, 1345.
9. Snook, G. A.; Kao, P.; Best, A. S. *J Power Sources* 2011, 196, 1.
10. Zhao, J.; Chen, X.; Xie, J. R. H. *Anal Chim Acta* 2006, 568, 161.
11. Kim, K. I.; Lee, J. C.; Robards, K.; Choi, S. H. *J Nanosci Nanotechnol* 2010, 10, 3070.
12. Yang, D. S.; Jung, D. J.; Choi, S. H. *Radiat Phys Chem* 2010, 79, 434.
13. Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* 2006, 44, 1624.
14. Yang, M.; Gao, Y.; Li, H.; Adronov, A. *Carbon* 2007, 45, 2327.
15. Yang, Y.; Qiu, S.; He, C.; He, W.; Yu, L.; Xie, X. *Appl Surf Sci* 2010, 257, 1010.
16. Jeon, J. H.; Lim, J. H.; Kim, K. M. *Polymer* 2009, 50, 4488.
17. Xu, G.; Wu, W. T.; Wang, Y.; Pang, W.; Zhu, Q.; Wang, P.; You, Y. *Polymer* 2006, 47, 5909.
18. Kim, K. I.; Kang, H. Y.; Lee, J. C.; Choi, S. H. *Sensors* 2009, 9, 6701.
19. Junga, C. H.; Kima, D. K.; Choi, J. H. *Curr Appl Phys* 2009, 9, S85.
20. Piao, M. H.; Son, P. S.; Chang, C. H.; Choi, S. H. *Anal Sci Tech* 2010, 23, 165.
21. Piao, M. H.; Yang, D. S.; Yoon, K. R.; Lee, S. H.; Choi, S. H. *Sensors* 2009, 9, 1662.
22. Ryu, H. N.; Choi, S. H. *Carbon Lett* 2010, 11, 216.