Oxidation Mechanism of Nickel Oxide/Carbon Nanotube Composite

Tae-Hoon Kim,1 Min-Ho Park,1 Jiho Ryu,2 and Cheol-Woong Yang1,*

1School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, South Korea
2Department of Automobile Development, Ajou Motor College, Boryeong 355-769, Korea

Abstract: The oxidation mechanism and thermal stability of nickel oxide (NiO)/carbon nanotube (CNT) composites were investigated by examining composites with different NiO contents by thermogravimetric analysis and transmission electron microscopy (TEM). NiO acts as a catalyst in the oxidation of CNT in the composite. CNTs can be oxidized, even in a vacuum, by reducing NiO to nickel at temperatures lower than the normal oxidation temperature of CNTs. This phase transition was confirmed directly by in situ heating TEM observations. In air, reduction by CNT occurs simultaneously with reoxidation by gaseous O2 molecules, and NiO maintains its phase. The thermal stability decreased with increasing NiO content because of defects in the CNT generated by the NiO loading.

Key words: oxidation mechanism, NiO, CNT, composite, in situ heating, TEM, TGA, Raman spectroscopy

INTRODUCTION

Carbon nanotubes (CNTs), which were first discovered in 1991 by Iijima (1991), have been examined for many applications owing to their excellent properties. CNTs have great potential for a wide range of applications owing to their electrical, thermal, and mechanical properties (Avouris et al., 2007). In addition, the large specific area and small size of the CNTs make them suitable catalyst supports for catalytically active metal and/or metal oxide particles. Therefore, various metal/CNT and metal oxide/CNT composites have been investigated to take full advantage of the multifunctionality of the metal, metal oxide, and CNTs. In the case of metal oxide/CNT composites, CNT can provide a great reaction site because of the large specific area and high electronic conduction path to the metal oxide, which itself has relatively low conductivity (Avouris et al., 2007). Therefore, CNTs are expected to increase the electrochemical utilization of metal oxide. Among the various metal oxides, nickel oxide (NiO) is attractive in view of its low cost, low toxicity, well-defined electrochemical redox activity, and the possibility of enhanced performance through different preparative methods (He et al., 2006). For these reasons, NiO/CNT composites have been studied widely for many possible applications, such as catalysts, electrochromic films, gas sensors, and electrode materials (Xia et al., 2008; Wang et al., 2008; Lota et al., 2011).

For many applications, it is important to understand the oxidation resistance and thermal stability of CNTs in a NiO/CNT composite because they can limit the operation temperature and applicability of the composites. In general, CNTs are oxidized at 600–700°C (Ajayan et al., 1995). On the other hand, catalyst residues, amorphous carbon, and defects can reduce considerably their oxidative stability toward air. In contrast, the oxidative stability can be enhanced by high-temperature vacuum annealing, which produces more graphitic CNTs with a low defect concentration (Oswald et al., 2005; Behler et al., 2006). In addition, in NiO/CNT composites, the oxidation resistance and temperature of CNT can be affected by NiO around the CNT, and the oxidation state of the NiO/CNT composite can affect its characteristics and performance (Li et al., 2004; Aksel & Eder, 2010). Therefore, the oxidation mechanism and thermal stability of NiO/CNT composite should be examined in detail.

In this study, NiO/CNT composites with different NiO contents were prepared using a solution-based method. Thermogravimetric analysis (TGA) in air and N2 confirmed the NiO loading on CNT and the decrease in oxidation temperature with increasing NiO content. The oxidation mechanism was predicted from these data. Transmission electron microscopy (TEM), with ex situ and in situ heat treatment, was used to observe the microstructure.

MATERIALS AND METHODS

NiO/CNT composites were prepared by the thermal decomposition of nickel nitrate on CNTs. Multi-walled carbon nanotubes (MWCNT, M95, Carbon Nano-Material Technology Co. Ltd.) and Ni(NO3)2·6H2O with various contents (10, 30, 50 and 80 wt% NiO) were dissolved in ethanol. The samples were heat-treated in vacuum for 1 h at 300°C for the thermal decomposition of Ni(NO3)2·6H2O to NiO (Brockner et al., 2007). Subsequently, TGA (TA Instruments Q500) was conducted to determine the NiO loading on the CNT and examine the variations of the oxidation temperature as a function of the NiO content and atmosphere (air and N2). The samples were analyzed in a platinum pan from room
temperature to 900°C at a heating rate of 5°C/min. Raman spectroscopy (Renishaw RM 1000-In Via) was used to examine the quantity of defects in the CNTs. The *ex situ* heat treatment was conducted at 600°C for 30 min in vacuum or in air. TEM (JEM-2100F, JEOL Co. Ltd.) was employed to observe microstructure of the NiO (50 wt%)/CNT composite. In addition, selected area diffraction (SAD) was used to confirm the phase transition. The *in situ* heating experiments were performed in the TEM (JEM-3011 with a LaB₆ filament operating at 300 keV, JEOL Co. Ltd.). A model EM-21130 JEOL heating holder was used to resistively heat the samples.

**Results and Discussion**

Figure 1 shows TGA results of the NiO/CNT composite with various NiO contents in air and N₂. Weight losses were observed in each sample and derivative plots were obtained in both atmospheres. The NiO loading after CNT oxidation was confirmed by the weight loss curves in air. The amount of residue remaining increased with increasing NiO loading (see Fig. 1a). On the other hand, in N₂ atmosphere, there was less residue remaining (see Fig. 1b). Derivative plots (DTG) in N₂ revealed peaks at ~540°C (Fig. 1b). In contrast, in air, the peaks were observed at ~400°C with increasing NiO content from 10 to 80 wt% (Fig. 1a). As a reference, the MWCNTs, which were used for this study, were oxidized at ~600°C (data not shown). In other words, NiO affects the oxidation stability and decreases the oxidation temperature of CNT. The main peaks at ~540°C in both atmospheres are believed to have occurred via the same mechanism. Unlike an air atmosphere, which supplies oxygen continuously, in a N₂ atmosphere, there is no oxygen source to oxidize the CNTs except for the oxygen in NiO itself. Therefore, the CNTs were oxidized at the interface between NiO and CNT by consuming oxygen from the NiO and reducing NiO to nickel. This was confirmed by TGA in a N₂ atmosphere, which showed less residue with increasing NiO loading (see Fig. 1b). The number of reaction sites that cause CNT oxidation increased with increasing NiO content, and more oxygen could be consumed through CNT oxidation. Consequently, less residue remained in the N₂ atmosphere. In the air atmosphere, however, oxygen vacancies generated by the oxidation of CNT diffuse from the interface between NiO and CNT to the surface of NiO and are regenerated by gas-phase oxygen (Mars & Krevelen, 1954; Aksel & Eder, 2010). Therefore, in air atmosphere, NiO can keep its phase without a transition to nickel, and the amount of residue shown in the TGA results (Fig. 1a) can be understood in the same context.

To confirm and observe the microstructure and phase transition directly through the oxidation of CNT by reducing NiO to nickel, comparative TEM analysis was conducted selectively for the NiO (50 wt%)/CNT composite samples before and after the *ex situ* heat treatment at 600°C for 30 min in vacuum and air atmosphere. Figure 2 shows the TEM results before and after heat treatment. After heating in a vacuum, the phase transition of NiO to nickel was confirmed by the SAD pattern and fast Fourier transform (FFT) image (Figs. 2b, 2d). During the oxidation of CNT by reducing NiO to nickel in a vacuum, the oxygen in NiO diffuses to the CNT surface and carbon diffuses into nickel because carbon has some solid solubility in nickel (Singleton & Nash, 1989). This was confirmed by the formation of graphitic shell covering the nickel particles, which was formed by the precipitation of supersaturated carbon from nickel with cooling down (Fig. 2b). In contrast, NiO in the sample after heating in air maintains its phase without a transition because reduction by CNT and reoxidation by gaseous O₂ molecules in NiO occur simultaneously (Fig. 2c).

The oxidation mechanism of CNT with reducing NiO can be explained using the Ellingham Diagram. To oxidize CNT, O₂ molecules were adsorbed on the CNT surface first, a C–O bond was formed, and the C–O pair was desorbed.
with breaking C–C bonds (Zhu et al., 2000; Park et al., 2001). In the Ellingham Diagram, the position of the line for a given reaction shows the stability of the oxide as a function of temperature and can determine the relative ease of reducing a given metallic oxide to metal. Reactions closer to the top of the diagram are the most noble metals, and their oxides are unstable and reduced easily. Toward the bottom of the diagram, the metals become progressively more reactive and their oxides become more difficult to reduce (Ellingham, 1944). To examine the reduction of NiO by CNT, the $2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$ line and $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ line can be used because a CO molecule was desorbed from the adsorbed phases by breaking the C–C bonds after O$_2$ adsorption. Both lines are crossed at $\sim 500^\circ\text{C}$. At temperatures $<500^\circ\text{C}$, the $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$ line takes place at the bottom of the $2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$ line and CNT cannot be oxidized by reducing NiO. On the other hand, at temperatures $>500^\circ\text{C}$, the positions of both lines are reversed and the heat of formation of carbon monoxide is smaller than NiO at $\sim 500^\circ\text{C}$. Therefore, the main DTG peak at $\sim 540^\circ\text{C}$ in the TGA results in air and N$_2$ atmospheres with the same mechanism, i.e., because of the oxidation of CNT by consuming oxygen from NiO and generating oxygen vacancies.

On the other hand, with increasing NiO loading (50 and 80 wt%) in air, the peak moved from $\sim 540$ to $400^\circ\text{C}$. This is caused by another mechanism, and is due to defects of CNT, which occur with increasing NiO content. To quantify the increase in defects due to the NiO loading, Raman spectroscopy was carried out with excitation at 633 nm. Figure 3 shows the Raman spectra of the CNTs with various NiO contents. The number of defects can be estimated from the D band in the Raman spectrum. Two characteristic peaks near 1,320 and 1,600 cm$^{-1}$ were observed in the NiO/CNT composites. The former, which is known as the D band, originates from the first-order scattering process of sp$^3$ carbon by the presence of in-plane substitutional hetero-atoms, vacancies, grain boundaries, or other defects, and by finite size effects; all of these reduce the crystalline symmetry of the quasi-infinite lattice (Brown et al., 2001). The latter, which is known as the G band,
represents the sp$^2$ carbon states related to the graphitic hexagon-pinched mode (Osswald et al., 2007). Owing to the origin of the respective bands, the $R$ value (i.e., the D band/G band ratio) indicates the quantity of defects (disordered carbon) in the tube walls (Lee et al., 2011). More defects are generated on CNTs with increasing NiO content, which was demonstrated by an increase in $R$ value from 1.008 for 10 wt% to 1.318 for 80 wt%. The adsorption energy of an O$_2$ molecule on defects is much larger than that on a nondefective tube wall. Furthermore, the desorption barriers of the C–O pair from the defects are much lower than those at nondefective wall (Zhu et al., 2000; Park et al., 2001). Therefore, the oxidation rate of disordered carbon and defective tubes by O$_2$ molecules is much faster than that of the nondefective wall and oxidation occurs at $\sim$400°C (Osswald et al., 2005; Behler et al., 2006). The temperature when a phase transition occurs was examined directly by observing the dynamic changes in the diffraction patterns of NiO as a function of temperature through an $\textit{in situ}$ heating experiment. Figure 4 shows the $\textit{in situ}$ results. In the SAD patterns, the (200) plane of nickel began to appear at $\sim$500°C, and the (111) and (220) plane of NiO decreased with continued heating. These $\textit{ex situ}$ and $\textit{in situ}$ TEM results are consistent with the TGA results.

**CONCLUSION**

This study examined the thermal stability and oxidation mechanism of the NiO/CNT composite. The NiO/CNT composites were prepared by a solution-based method with various NiO contents. The oxidation mechanism was suggested based on the comparative TGA and TEM results in air and N$_2$ atmosphere and Ellingham Diagram. In addition, phase transitions were observed directly by $\textit{in situ}$ heating TEM. NiO decreases the oxidation temperature of CNTs and acts as a catalyst. CNTs can be oxidized by reducing NiO to nickel by consuming the oxygen of NiO, even in a N$_2$ atmosphere. In air, NiO maintains its phase because reduction by CNT and reoxidation by O$_2$ molecules occur simultaneously. Moreover, with increasing NiO content, the oxidation temperature decreased to much lower temperature because of defects in CNT generated by the NiO loading. The thermal stability of the NiO/CNT composite was examined, and it was affected by NiO and the quantity of defects.

**ACKNOWLEDGMENTS**

This work was supported by the National Research Foundation of Korea (NRF) grants funded by the Korea government (MEST; No. 2011-0017257, No. 2011-0019984, and No. 2011-0030803). The authors gratefully appreciate technical support from the Cooperative Center for Research Facilities (CCRF) at Sungkyunkwan University.

**REFERENCES**


Brockner, W., Ehrhardt, C. & Gjikaj, M. (2007). Thermal decomposition of nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O, in comparison to Co(NO₃)₂·6H₂O and Ca(NO₃)₂·6H₂O. Thermochim Acta 456, 64–68.


