Self-Assembly of Colloidal γ-Fe$_2$O$_3$ and FePt Nanoparticles on Carbon Nanotubes by Dip-Coating Process

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The chemically synthesized colloidal γ-Fe$_2$O$_3$ and FePt nanoparticles (NPs), with the diameter of $\sim$10 nm and $\sim$4 nm, respectively, adsorbed and assembled on the surface of carbon nanotubes (CNTs) by dip-coating process, through van der Waals interaction between NP and CNT. Repeating the steps of dip-coating and removing the surfactants from NPs significantly increased the amount of NPs as forming multilayers on the CNT. In addition, the electrochemical activities of FePt/CNTs for methanol oxidation were investigated for the potential application as catalysts of direct methanol fuel cells.

Keywords: Iron Oxide, Iron Platinum, Nanoparticle, Carbon Nanotubes, Adsorption, Dip-Coating.

1. INTRODUCTION

The nanocomposites of carbon nanotubes (CNTs) containing nanoparticles (NPs) have been investigated as promising units for various applications including nanoelectronics,[1] nanomagnetics,[2] catalysts for fuel cells,[3] photocatalysts for environmental treatment,[4] chemical and biological sensor,[5] and so on. These applications are pursued through combining the characteristics of a high strength, good electrical and thermal conductivity, and large specific surface area of CNT, and specific functionality of NPs.

The direct synthesis of NPs on CNT surface has been employed in order to form NPs/CNT nanocomposites.[6–8] In particular, an electrochemical deposition is used to deposit NPs on the CNT surface through the nucleation and growth of NPs in the solution.[6] Though the density and size of NPs can be controlled by applied potential and deposition time, the statistical nature of the nucleation and growth of NPs causes a wide distribution of size and density of NPs.[6] Another approach is to attach the preformed colloidal NPs on CNT through the intermolecular

force between surface-modified NPs and CNT.[9, 10] Compared to direct synthesis, the attachment of preformed NPs achieves the high density and uniform assembly of NPs on CNT. However, the chemical treatment on CNT and NPs with functional groups such as carboxyl, carbonyl, hydroxyl groups as glue molecules has to be preceded to attach the NPs to CNT.[9, 10] The attachment of NPs through intermolecular force by using glue molecules or surface treatment has also been employed to attach NPs on planar substrates[11] and on nanospheres.[12]

On the contrary, we have previously demonstrated the adsorption of colloidal maghemite (γ-Fe$_2$O$_3$) NPs, stabilized by oleic acid surfactants, on Si, Si$_3$N$_4$, and SiO$_2$ substrates, without using any glue molecules or surface treatment. During dip-coating of substrates into NPs solution, the NPs adsorbed on the surface of substrate and assembled upon evaporation of solvent after taking out the substrate from the solution. The amount of adsorbed NPs was found to increase as increasing van der Waals interaction.[13]

In this study, we investigated the NPs adsorption on CNTs by dip-coating process. The distinctive aspect is that the NPs adsorb and assemble on CNT surface by van der Waals interaction, without any surface treatment,

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during dip-coating of CNT layers grown on substrates into colloidal solution. As model systems, we studied the adsorption of γ-Fe$_2$O$_3$ NPs in ~10 nm diameter and iron platinum (FePt) NPs in ~4 nm diameter on CNTs. The adsorption of NPs on CNTs by van der Waals interaction is thought to provide viable scheme for producing NPs/CNT composites, in particular for the system where the proper chemical modification of NPs and CNTs is not available for the adsorption of NPs on CNTs. Also, we investigated the electrochemical activities of FePt NPs on CNTs as catalyst for direct methanol fuel cell (DMFC).

2. EXPERIMENTAL DETAILS

The γ-Fe$_2$O$_3$ NPs were chemically synthesized by following the method developed by Hyeon et al.,[14] through decomposition of iron pentacarbonyl (Fe(CO)$_5$) and stabilization of NPs with oleic acid (C$_{18}$H$_{34}$O$_2$) surfactants. The diameter of NP is about 10 nm and its phase is maghemite.[14, 15] The oleic acids encapsulating NP surface prevent the aggregation of NPs in the solution. The γ-Fe$_2$O$_3$ NPs were dissolved in hexane with a concentration of ~2.7×10^{13}/ml. Iron platinum (FePt) NPs were synthesized through reduction of platinum acetylacetonate (Pt(acac)$_2$) and decomposition of iron pentacarbonyl (Fe(CO)$_5$), as reported by Sun.[16] The FePt NPs with a diameter of ~4 nm were stabilized by oleic acid and oleylamine (C$_{18}$H$_{34}$N). They have a face-centered cubic (fcc) structure,[16] which was confirmed by diffraction pattern analysis. Their composition was Fe:Pt = 0.47:0.53, as measured using inductive coupled plasma atomic emission spectroscopy (ICP-AES). The FePt NPs were dispersed in hexane with a concentration of ~1.6×10^{15}/ml.

The multiwall CNTs were grown on Si substrates. For the growth of CNTs, iron nitrate (Fe(NO$_3$)$_3$) solution was dropped on Si substrate as catalyst and introduced into the growth chamber. Xylene (C$_6$H$_4$(CH$_3$)$_2$) was carried by argon gas as a carbon source and the ammonia was used as reduction gas. The reaction was performed at 800 °C and the nominal thickness of grown CNT layer was about 10 μm.

For the adsorption of NPs on CNTs, the substrates were vertically dipped in colloidal NPs solution and pulled out at a speed of 0.01 mm/sec. In order to form the multilayers of NPs on CNTs, the annealing was subsequently carried out at 200 °C for 30 minutes in air environment to desorb the surfactants from the NPs layer after dip-coating step.[15] Then, the dip-coating and annealing steps were repeated five times for additional adsorption of NPs on top of the NPs layer on CNTs. The adsorption of NPs on CNTs was characterized by scanning electron microscopy (SEM).

The electrochemical activities of FePt NPs on CNTs were investigated by cyclic voltammetry (CV). For CV analysis, the CNTs were coated on the gas diffusion layer (GDL10BB, SGL Technologies GmbH), which is carbon

fiber-based nonwovens and typically used for fuel cell. The CNTs were first pretreated in an acidic solution (aqua regia) for 72 hours and washed with distilled water several times. A proper amount of pretreated CNT was dispersed in a mixture of 5% Nafion solution and 2-propanol. The resultant solution was then sprayed onto the gas diffusion layer. Then, the FePt NPs were adsorbed on CNTs by repeating dip-coating and annealing steps five times. The current–voltage measurement was conducted in a conventional three-electrode electrochemical cell using Pt and Ag/AgCl as a counter electrode and a reference electrode, respectively, at room temperature. The catalytic activity for methanol oxidation was evaluated in a solution of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ with a voltage range from −0.2 to 1.0 V versus Ag/AgCl.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of γ-Fe$_2$O$_3$ NPs on CNTs after dip-coating once. The γ-Fe$_2$O$_3$NPs assembled and formed monolayer on the surface of CNTs. Since the surface of CNT was not chemically modified for binding γ-Fe$_2$O$_3$ NPs, the adsorption of γ-Fe$_2$O$_3$ NPs is thought to be driven by van der Waals interaction between NP and CNT. Because the γ-Fe$_2$O$_3$ NP is much smaller than CNT, it could be assumed that the γ-Fe$_2$O$_3$ NPs adsorbed on planar surface of CNT. The van der Waals interaction energy of NPs on planar CNT surface is expressed as,[17]

$$E_{vdW} = -\frac{A}{6}\left[\frac{R}{C-R} + \frac{R}{C+R} + \ln\left(\frac{C-R}{C+R}\right)\right]$$

where R is the radius of NP (~5 nm), C is the distance from NP center to CNT surface (~7 nm by assuming the length of surfactant of ~2 nm), and A is the Hamaker constant between γ-Fe$_2$O$_3$ and CNT mediated by hexane. From the data of Hamaker constant of 4.28×10^{-20} J of hexane,[14] 3.19×10^{-19} J of CNT,[18] and 4.14×10^{-19} J of
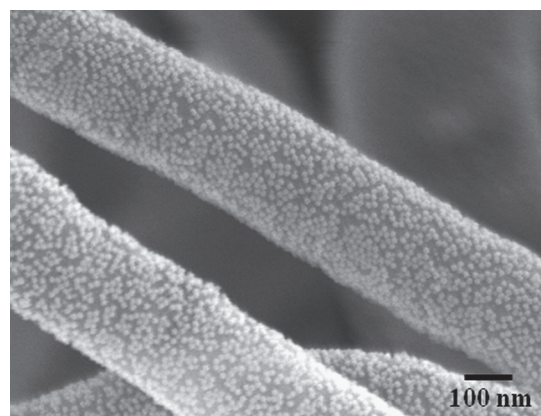
Fig. 1. SEM micrograph of γ-Fe$_2$O$_3$ NPs adsorbed on CNTs surface after dip-coating once.

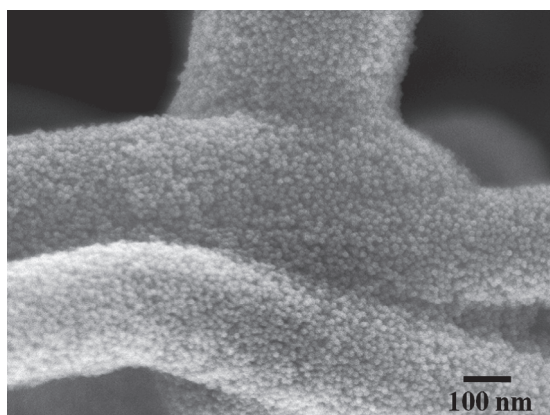**Fig. 2.** SEM micrograph of γ-Fe$_2$O$_3$ NPs on CNTs after repeating the steps of dip-coating and annealing at 200 °C for 30 min for five times.
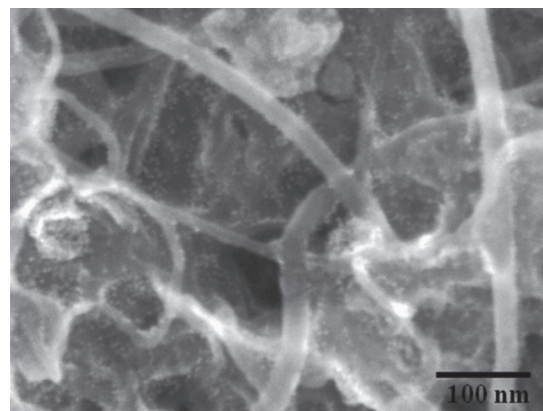

Fig. 3. SEM micrograph of FePt NPs on CNTs after repeating the steps of dip-coating and annealing at 200 °C for 30 min for 5 times.

γ-Fe$_2$O$_3$,[13] the van der Waals interaction energy is calculated to be ∼7.1 kT, that is sufficiently higher than thermal fluctuation at room temperature. As a result, the γ-Fe$_2$O$_3$ NPs could adsorb on the surface of CNTs by van der Waals interaction. Though it is not shown here, the γ-Fe$_2$O$_3$ NPs on CNT remains almost the same after repeating only the dip-coating for five times. The reason for this is that the NPs do not adsorb on the surface of NPs layer because the oleic acids covering NPs prevent the additional adsorption of NPs on the surface of NPs layer.

However, repeating the steps of dip-coating and subsequent annealing for five times formed the multilayers of γ-Fe$_2$O$_3$ NPs on CNTs as shown in Figure 2. As previously confirmed by Fourier transform infrared spectroscopy, the oleic acids (surfactants) desorbed from γ-Fe$_2$O$_3$ NPs surface after annealing at 200 °C.[15] Therefore, repeating the steps of dip-coating and subsequent annealing to desorb the surfactants led to the repeated adsorption of γ-Fe$_2$O$_3$ NPs on γ-Fe$_2$O$_3$ NPs layer and formed multilayers. It verifies that large amount of NPs can be attached on CNTs without employing any glue molecules or chemical treatment.

Figure 3 shows the SEM micrograph of FePt on CNTs after repeating the steps of dip-coating and subsequent annealing at 200 °C for 30 min for five times. Compared to the adsorption of γ-Fe$_2$O$_3$ NPs in Figure 2, the amount of FePt NPs is much smaller. Since the Hamaker constant of FePt (∼4 × 10⁻¹⁹J)[19] is similar to that of γ-Fe$_2$O$_3$, a smaller size of FePt results in a weaker van der Waals interaction energy of ∼1.4 kT than ∼7.1 kT for γ-Fe$_2$O$_3$ NPs. As a result, the weaker interaction causes the smaller amount of FePt NPs on CNTs than γ-Fe$_2$O$_3$. Nevertheless, increasing the number of dip-coating and annealing steps is thought to further increase the coverage to multilayer. Regarding the adsorption of NPs without chemical linkers, the hydrophobic force between the surfactants and CNT surface can be also considered as a driving force for the adsorption. However, the amount of adsorbed γ-Fe$_2$O$_3$

NPs is larger than that of FePt though both NPs are covered with oleic acid and oleylamine surfactants with the same alkyl chains of hydrophobic end. Hence, though further study is needed, the adsorption of NP is thought to be mainly driven by the van der Waals interaction between NP and CNT.

The electrochemical activities of FePt/CNTs were analyzed by using cyclic voltammetry for methanol oxidation, as shown in Figure 4. From the FePt/CNTs sample after dip-coating once, no oxidation peak was observed probably due to the small amount of FePt NPs on CNTs. However, the oxidation peaks during forward and backward scans were obtained from the sample after repeating dip-coating and annealing for five times. A prominent anodic peak (I_f) around 0.66 V in the forward scan comes from the methanol oxidation.[20] In the reverse scan, the oxidation peak (I_b) around 0.52 V is attributed to the removal of the incompletely oxidized carbonaceous species, carbon monoxide, CO, which is formed in the forward scan and adsorbed on Pt surface. It is well known that the second metal in the Pt-based bimetallic alloy catalysts, Fe in this case, can enhance the oxidative removal of poisonous intermediates, such as CO, with the adsorbed hydroxyl species.[21] The CO molecules can be further oxidized to CO_2 by reacting with hydroxyl species, Fe-(OH)$_{ad}$, on the catalyst surface. The ratio of the forward oxidation peak current density (I_f) to the reverse peak current density (I_b), I_f/I_b which is measured to be ∼0.57, represents the catalyst tolerance to the CO poisoning.[22] The higher value of I_f/I_b implies the higher tolerance of catalyst to the CO poisoning, so the larger fraction of catalyst surface is free of adsorbed CO molecules. The long-term oxidation of methanol at a constant voltage of 0.5 V versus Ag/AgCl revealed that the current density remained to be ∼70% of its initial value after 20 minutes. It should be further studied on the effect of composition and amount of NPs on CNT surface on the electrochemical activities. Nevertheless, these results demonstrated that the colloidal NPs could be attached on the surface of CNTs and applied
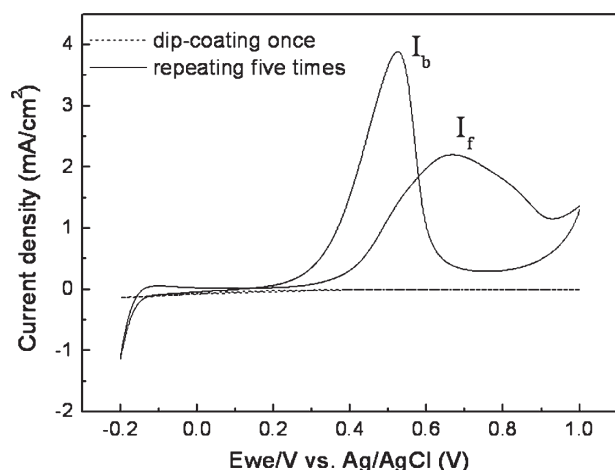
<div style="text-align: right">**RESEARCH ARTICLE**</div>

Fig. 4. Cyclic voltammogram of FePt/CNT electrode on carbon tape in 0.5 M CH_3OH and 0.5 M H_2SO_4 solution.

to various applications depending on the functionality of NPs, such as electrocatalyst for fuel cell.

4. CONCLUSION

The colloidal γ-Fe₂O₃ and FePt NPs adsorbed and assembled on the surface of CNTs by van der Waals interaction between NP and CNT by dip-coating process. The larger amount of γ-Fe₂O₃ NPs than that of FePt on CNTs is caused by the stronger van der Waals interaction due to the larger size of γ-Fe₂O₃ NPs than FePt. Repeating dip-coating and subsequent annealing to desorb the surfactants from NPs formed multilayers on CNT. The catalytic effects on methanol oxidation were obtained with FePt/CNT. The approach of NPs adsorption on CNTs by van der Waals interaction without employing chemical modification of CNT and NP surface is expected to provide the viable solution for producing various NPs/CNTs nanocomposites.

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