FUNCTIONALIZATION OF CARBON NANOTUBES
BY DIRECT REDOX DEPOSITION OF MANGANESE OXIDE

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Abstract

Manganese dioxide (MnO_2) was coated on carbon nanotubes (CNTs) by simple immersion of the CNTs into a $KMnO_4$ aqueous solution. The synthesis mechanism was investigated by in situ monitoring of the reduction potential and pH of the solution. CNTs were found to act as a reducing agent and substrate for the heterogeneous nucleation of MnO_2 in an aqueous $KMnO_4$ solution. The morphology of the CNTs before and after MnO_2 deposition was examined using scanning electron microscopy, which showed MnO_2 deposited as a thin and uniform layer on the bare CNTs but as nano-flake of MnO_2 on the acid-treated CNTs. The MnO_2 was shown to be a Birnessite-type MnO_2 by Raman spectroscopy.

Introduction

There has been much interest lately in the sidewall chemistry of carbon nanotubes (CNTs). The research activities are motivated by modifying the inert nanotube sidewalls to deposit a metal or metal oxide. Covalent modification of nanotube sidewalls includes oxidation, fluorination, and formation of amide bonds. Noncovalent approaches utilize π-stacking or van der Waals interactions between aromatic molecules or polymers and nanotubes. Previous approaches to metal or metal oxide nanoparticle functionalization of nanotubes include physical evaporation, solid-state reaction, electroless deposition with the aid of reducing agents or catalyst. In this study, CNTs are functionalized by the acid-treatment using nitric acid to deposit manganese oxide on the sidewall of CNTs for electrochemical capacitor applications. Deposition mechanism is investigated by in-situ monitoring of solution chemistry during the synthesis of manganese oxide/CNTs nanocomposite.

Experimental

MnO_2 was spontaneously deposited onto the CNTs (multi-walled CNTs, ILJIN Nanotech, S = 200 m^2/g) by a direct redox reaction between the CNTs and MnO_4^-. CNTs were pretreated in a boiled nitric acid for 4hs. First, 200 ml of 0.1 M $KMnO_4$ (99+%, Aldrich) solutions were heated to 70^oC using a circulator (FP 40, Julabo) and then 1.0 g of bare and acid-treated CNTs was added to the solution. During the synthesis, temperature of the solution was maintained at 70^oC by the circulator. The reduction potential of the solution was monitored in situ by measuring the electrode potential (E) with a platinum electrode and a saturated calomel electrode using a potentiostat/galvanostat (VMP2, PRINSTON APPLIED RESEARCH). The pH variation of the solution was also in situ measured with a pH meter (720A, Thermo Electron Corporation) and a pH electrode (9107BN, Thermo Electron Corporation). The suspension was filtered and washed several times using distilled water, and then dried at 100^oC for 12 h in preparation for further analysis. In order to determine the structure of the MnO_2 on the CNTs, the Raman spectra were measured with a Jobin-Yvon LabRam HR with LN2 cooled CCD multichannel detector at room temperature using conventional backscattering geometry. The laser light source was the emission of the argon-ion laser at wavelength 514.5 nm. Scanning electron microscopy (SEM) (Sirion, FEI) was used to observe the morphology of the composite powder.

Results and discussion

In situ monitoring of E and pH

Fig. 1 shows the change in the E and pH of the solution with time during the deposition of MnO_2 on CNT in the 200 ml aqueous solution of 0.1 M $KMnO_4$ containing 1.0 g CNT at 70^oC. When the bare CNTs were added to the solution (around 2000 sec. in Fig.1), a rapid drop in the electrode potential and an increase in pH were observed while the acid-treated CNTs induced a rapid pH drop and an increase in the electrode potential.

Bare CNTs can be envisaged as roll-up graphene layer sheet, regarding their molecular structure. The basic sites, which consist of delocalized π – electrons, on the surface of the bare CNTs are responsible for the rise in pH right after the addition of bare CNT since they can act as Lewis bases capable of complexing protons to its π structure. After CNTs were treated in a boiled nitric acid, the acidic sites such as carboxyl groups on the acid-treated CNT are generated on the CNT surface and they can decrease pH in the solution. The E of the solution for the reduction of MnO_4^- ions to MnO_2 on CNT is a function of pH. The sharp change in E can be attributed to the sharp change in pH of the $KMnO_4$ solution caused by the CNT addition.

In the case of bare CNT, right after the rapid drop in the E and the increase in pH, protons, adsorbed at basic sites on the bare CNT surface, are expected to be desorbed as MnO_4^- ions were absorbed, thereby producing a heterogeneous MnO_2 film

on the CNTs. Protons desorbed from the surface of the CNTs contributed to the slight decrease in pH and the slight increase in E. It should be noted that the pH stayed relatively constant after the initial change. This is possibly related to the reduction reaction of MnO_4^- ions, since this reaction consumes protons from the CNT surface. In the case of acid-treated CNT, right after the sharp increase in E and decrease in pH, the protons, generated from the acidic sites on the surface of acid-treated CNT, are consumed rapidly for the reduction reaction of MnO_4. It is expected that this helps keep the solution pH increase.

After rapid change in E and pH, a potential plateau with respect to time, which represents the reduction of MnO_4^- ions to MnO_2 by the CNTs, was observed. The potential plateau corresponds to the reduction potential of MnO_4^- ions in the aqueous solution containing the CNTs. At the end of the plateau, i.e., when all the MnO_4^- ions are reduced, E shifts downward significantly and is indicative of the complete reduction of MnO_4^- ions. There is no difference in overall change in the solution E and pH with time between bare and acid-treated CNTs during the reduction of MnO_4^- ions to MnO_2 by CNT. However, it should be pointed out that the reduction reaction time between the moment of CNT addition and the time for the negative shift of E, i.e., the time required for the complete removal of MnO_4^- ions from the solutions, are shortened by using acid-treated CNT. This indicates that the reduction reaction rate of MnO_4^- ions by acid-treated CNT is much faster than that by bare CNT. Since more protons in the solution become available for the given concentration of MnO_4^- ions, an increase in the reaction rate for the reduction of MnO_4^- ions MnO_2 on CNT is expected when using acid-treated CNT.

A slight decrease in E and small increase in pH is observed after the complete reduction of MnO_4^- ions. The measured E corresponds to the equilibrium in an aqueous solution after the reaction for given electrochemical cells. No further reaction followed.
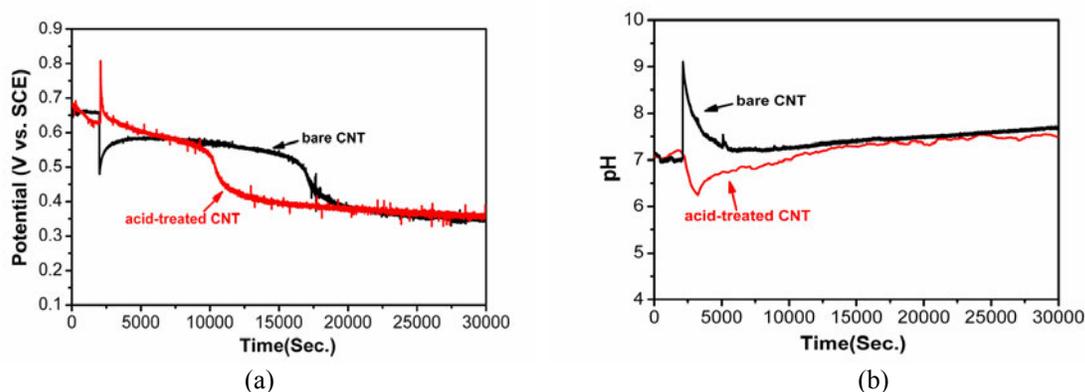

(a)   (b)

Figure 1. (a) E vs. time curves and (b) pH vs. time curves measured during the reduction of MnO_4^- ions by 1.0 g CNT in the 200 ml aqueous solution of 0.1 M $KMnO_4$ at 70^oC

Morphology of MnO_2 on CNT

Fig. 2 shows SEM images of the CNTs before and after MnO_2 deposition in the 200 ml aqueous solution of 0.1 M $KMnO_4$ containing 1.0 g CNT at 70^oC. Each CNT particle is around 20~30 nm in size, as shown in Fig. 2(a). After MnO_2 deposition, the CNT particles became a little thicker with size increased to approximately 30~50 nm. This indicates that the CNTs acted as a substrate for the heterogeneous precipitation of a very thin layer of MnO_2, as shown in Fig. 2(b) and (c).

The roughness of the MnO_2 deposit on the acid-treated CNTs was much higher than that on the bare CNT. MnO_2 deposit on the acid-treated CNTs Fig. 2(c) consisted of nano-flake MnO_2 while that on the bare CNT in Fig. 2(b) was of a thin film form. This suggests that the reduction rate of MnO_4^- ions to MnO_2 by CNT might affect the morphology of the MnO_2 deposit on the CNTs. As shown in Fig. 1(a), the shorter time was required for the complete removal of MnO_4^- ions in the case of acid-treated CNT, i.e., reduction reaction rate of MnO_4^- ions by acid-treated CNT is much faster than that by bare CNT. Therefore, it was observed that the increased reduction rate by using acid-treated CNT roughened the morphology of MnO_2.
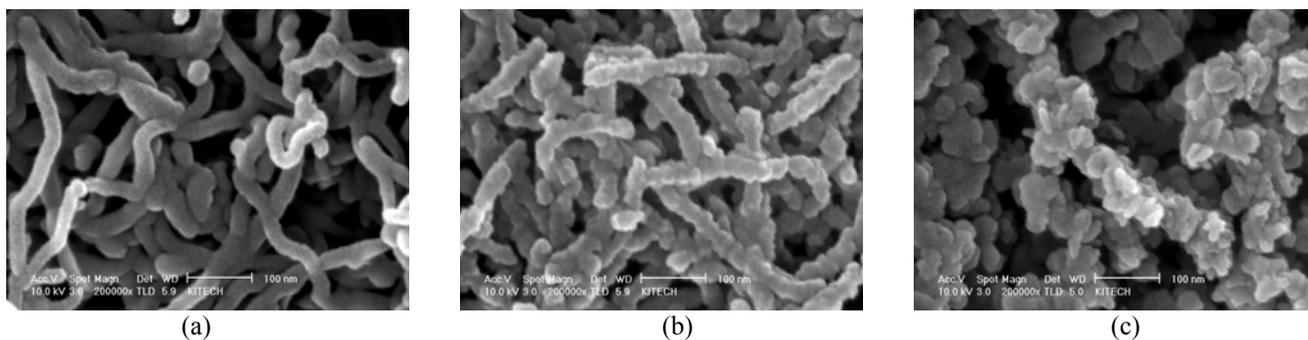
Figure 2. SEM images of (a) pristine CNT and MnO_2 coated CNT prepared in the 200 ml aqueous solution of 0.1 M $KMnO_4$ containing 1.0 g of (b) bare CNT and (c) acid-treated CNT

Structure of MnO_2 on CNT

Raman techniques are useful for analyzing the local structure of MnO_2. Many MnO_2 materials have similar gross structural features, namely the MnO_6 octahedral units building the MnO_2 frame work. MnO_2 compound classifications are based on the nature of the polymerization of the MnO_6 units, in which six oxygen atoms surround a central manganese cation in approximately octahedral coordination. Raman shifts are correlated with the M–O bond order and bond lengths.

Fig. 3 shows the Raman spectra of MnO_2/CNT nanocomposites synthesized by the reduction of MnO_4^- ions to MnO_2 in the 200 ml aqueous solution of 0.1 M $KMnO_4$ containing 1.0 g of bare CNT and acid-treated CNT at 70°C. Three major features for MnO_2 can be recognized at 500, 575 and 640 cm^{-1}. The two high wave number bands are dominant in all of the spectra, while the bands in the low-frequency region appear with a significantly weaker intensity. The Raman band at 640 cm^{-1} can be recognized as the symmetric stretching vibration (Mn–O) of the MnO_6 groups. The band located at 575 cm^{-1} is usually attributed to the (Mn–O) stretching vibration in the basal plane of MnO_6 sheet. Fig. 3 shows that all the reaction products have the Raman spectra of the birnessite-type MnO_2. Comparison of the Raman spectra of MnO_2 synthesized by using bare and acid-treated CNT indicates that acid-treatment of CNT had no influence on the phase and the short range ordering of MnO_2.
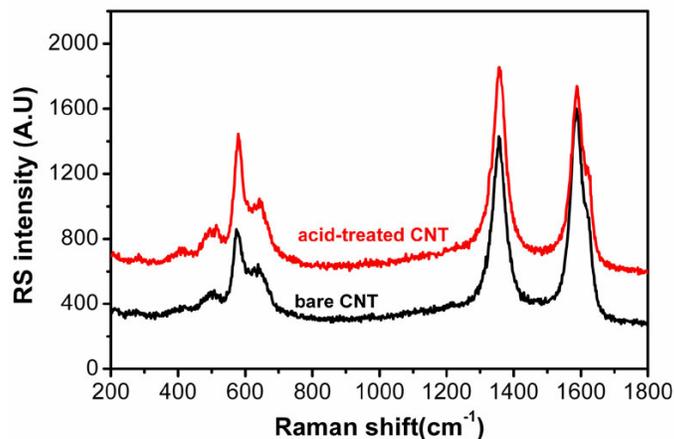

Figure 3. Raman spectra of MnO_2/CNT nanocomposite prepared in the 200 ml aqueous solution of 0.1 M $KMnO_4$ containing 1.0 g of bare CNT and acid-treated CNT

Conclusion

Birnessite-type MnO_2 was spontaneously deposited on CNTs via simple immersion of the CNTs into an aqueous $KMnO_4$ solution. Through in situ monitoring of the reduction potential and pH of the solution, the CNTs were found to act as a reducing agent and substrate for the heterogeneous nucleation of MnO_2 in an aqueous $KMnO_4$ solution. This process is the simplest method for synthesizing MnO_2 on CNTs. Reduction times were measured from the potential plateau in a plot of the reduction potential vs. reaction time. Through the acid–treatment of CNT, the reaction time for complete reduction of MnO_4^- ions to MnO_2 was shortened and the morphology of MnO_2 roughened, while the phase of MnO_2 on the CNTs was fixed to birnessite.

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