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β-Cyclodextrin Functionalization of Activated Carbon-Carbon Nanotube Composites and Supramolecular Recognition of Ascorbic Acid

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Activated carbon–carbon nanotube (AC-CNT) and β-cyclodextrin–activated carbon–carbon nanotube (βCD-AC-CNT) composites were synthesized successfully by using a simple chemical method and were characterized by using scanning electron microscopy, energy dispersive X-ray spectroscopy and thermogravimetric analyses. The electrochemical supramolecular recognition capability of the two composites was studied by using cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy for ascorbic acid as the biomolecule. More significantly, differential pulse voltammetry showed that the βCD-AC-CNT composite exhibited a high supramolecular recognition and enrichment capability for ascorbic acid and, consequently, displayed an excellent electrochemical response to the probe molecule.

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I. INTRODUCTION

Ascorbic acid (AA), also termed vitamin C, is quite an important bio-component widely present in living organism as antioxidation [1], and cyclodextrins (CDs) are cyclic oligosaccharides containing six (α-CD), seven (β-CD), eight (γ-CD) glucopyranase unit, bound by α-(1-4) linkage forming truncated conical structure [2]. β-CD contains seven primary hydroxyl groups which are free to rotate at the C_6 position and make it diameter narrow, and secondary hydroxyl groups are present at wider side. Cyclic structure is stabilized by intermolecular hydrogen bonding between adjacent hydroxyl group at C_2 and C_3 position. They have a relatively hydrophobic cavity (0.70 nm), while the outer surface is hydrophilic. The most important characteristic of CDs is the formation of inclusion complex with different vitamins like ascorbic acid and with other biomolecules [2–5]. During the formation of the complex between β-cyclodextrin and ascorbic acid, hydrophobic interaction as well as Van der Waal's interaction plays very important role [4–7].

Carbon material, such as carbon nanotube (CNT) and activated carbon, has been used by the researchers, and they found that it enhances the formation of inclusion complex between β-cyclodextrin and biomolecule [5–7] because CNT could be easily functionalized by cyclodextrin. The CD modification of carbon nanotube is simple and effective. CD groups were found to be possibly adsorbed at the surface of the nanotubes walls [8,9]. In addition, activated carbon (AC) which has relatively high surface area and high pores is very useful for various applications, such as supercapacitors, catalysis and adsorption applications, and batteries, and it can also be functionalized by using β-CD easily [10].

In this work, we synthesized AC-CNT and it was used for supramolecular recognition of ascorbic acid in presence and absence of β-CD by using cyclic voltammetry, differential pulse voltammetry, and impedance spectroscopy. We believed that the synergistic effect of larger surface area and high conductivity of CNT and highly porous and good adsorbent activity of AC together makes larger surface area [11–13] as well as provides available sites for the functionalization of β-CD. β-CD loading on AC and CNT of high conductivity and larger surface area [4–6] could be expected

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to increase the sensitivity towards a biomolecule. At the same time, properties of the activated carbon-carbon nanotube (AC-CNT) composites without β-CD are characterized as a biomolecule sensor. As a result we found that the functionalization of AC-CNT by β-CD enhanced the supramolecular capability significantly.

II. EXPERIMENTAL

Activated carbon (MSP-20, Kansai Coke and Chemicals, Japan) was purified as follows: 1 g of activated carbon was mixed with 20 ml of nitric acid in room temperature for 24 h and followed by washing and drying to get clean powder sample. The sample obtained was named as AC. Multi-walled CNT (MWCNT, CM-150, 87 - 93% purity, Hanwha Chemical Ltd.) was also purified as follows: 1 g of CNT was mixed with 50 ml of the nitric acid in a round vial and then stirred in the reflux condition at 500°C for 5 h followed by washing several times with deionized (DI) water. The obtained CNT was dried at a vacuum oven for overnight. Ascorbic acid was purchased from Sigma-Aldrich and it was used without further treatment.

The βCD-AC-CNT composite was synthesized by mixing 10 mg of AC, 20 mg of CNT, and 200 mg of βCD in 40 ml of DI water, and then the mixture was sonicated for 180 min at room temperature. After sonication, the mixture was filtered by using a cellulose paper. The obtained βCD-AC-CNT composite was dried at 60°C in a vacuum oven for overnight and was used for the characterization. A free-standing film of βCD-AC-CNT was finally obtained. AC-CNT composite was also synthesized by the similar process with same weight of AC and CNT except for βCD absence.

X-ray diffractometer (XRD, CuK_α radiation, $\lambda = 1.54A^0$, D/Max-2500/PC, Rigaku, Japan) was used to confirm the successful synthesis of AC-CNT composites. Thermogravimetric analysis (TGA, Q 600) was carried out to confirm the functionalization of βCD over AC-CNT. Scanning electron microscopy (SEM, Ltd., S-4300, JEOL, and Japan) was used to study the morphology of the composites, and electron dispersive X-ray spectroscopy (EDS) was used for elemental analysis of samples. Electrochemical properties of the composites were studied by using the cyclic voltammetry (CV), impedance spectroscopy, differential pulse voltammetry (DPV), using EC-Lab (Bio-logic, sp-150, France) in a three electrode cell. Ag/AgCl and platinum electrodes were used as the reference and counter electrodes. Working electrode was made as follows: 0.5 mg of each composite in 2 ml of isopropyl alcohol (IPA) solution, after proper sonication, was dropped onto a glassy carbon electrode (GCE), and it was dried completely for measurement. CV was performed at the scanning rate of 50 mVs^{-1}, and DPV was measured in the potential ranges between -0.2 to 0.5 V. Pulse amplitude of 2.5 mV, pulse width of 100 ms, and the scan rate of 10 mVs^{-1} are applied for DPV measurement. 30 mmol/L of ascorbic acid was used, prepared by weighing of 0.105672 g of ascorbic acid in 20 ml of DI water.

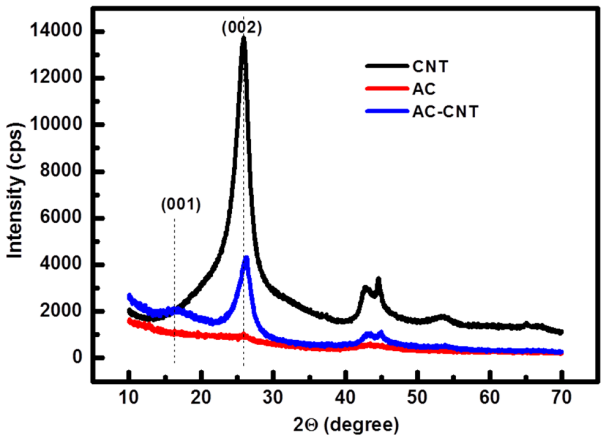

Fig. 1. (Color online) XRD results of the samples.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD results of CNT, AC, and AC-CNT. Before the functionalization of β-cyclodextrin, XRD was measured to confirm the successful synthesis of the AC-CNT composite. AC displayed an amorphous pattern because of its low crystallinity while CNT and AC-CNT show the typical (001) and (002) diffraction peaks of CNT. This implies that, the composite was successfully formed.

To confirm the functionalization of βCD over AC-CNT, thermogravimetric analysis (TGA) was performed. Fig. 2(a) shows the TGA results of two composites with and without βCD. The βCD-AC-CNT composite shows

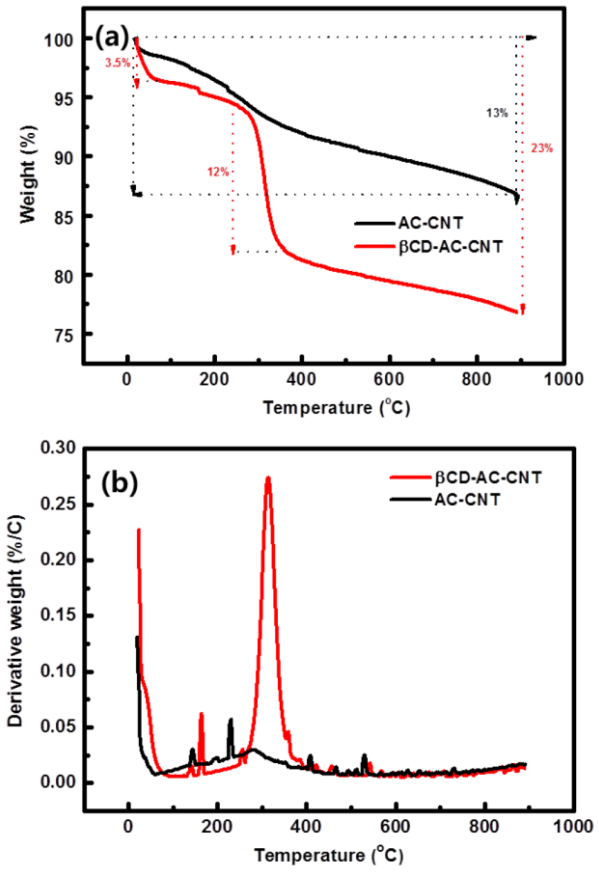

Fig. 2. (Color online) (a) TGA and (b) derivative weight results of AC-CNT and βCD-AC-CNT.

significant weight loss (total of 23%) with different steps due to initial evaporation of water (∼3.5%) and decomposition of βCD (∼12%), indicating that βCD is well functionalized over the surface of AC-CNT [4, 5, 9, 10]. Whereas AC-CNT only shows the 13% of weight loss due to initial evaporation of water and slow decomposition of residues. It confirmed that 12% of βCD is loaded over the surface of AC-CNT. Fig. 2(b) displays derivative weight as a function of temperature, confirming again the existence of βCD in the βCD-AC-CNT composite clearly near 300°C.

Fig. 3 shows SEM images of βCD-AC-CNT and AC-CNT. Both exhibit CNT, which has one dimensional thread like structure and scattered along the surface of composites and AC, which possess three dimensional bulk structure. The activated carbon and carbon nanotubes are covered by βCD in βCD-AC-CNT, so that βCD makes smooth surface and larger surface area in βCD-AC-CNT. However, in case of AC-CNT, surface

Table 1. EDS results of AC-CNT and βCD-AC-CNT.

Sample	Element	Weight %	Atomic %	Weight % ratio of O/C
AC-CNT	C	86	89	0.16
	O	14	11	
βCD-AC-CNT	C	80	84	0.25
	O	20	16	

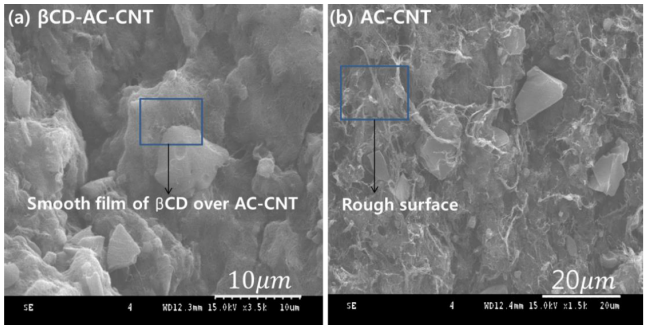

Fig. 3. (Color online) SEM results of (a) βCD-AC-CNT and (b) AC-CNT.

seems to be rough. This result indicates that the presence of βCD over AC-CNT makes the smooth and large surface, which is very important for the incoming analyte biomolecule.

Table 1 shows EDS results of both composites, and it was found that oxygen to carbon ratio in βCD-AC-CNT is larger than that of AC-CNT due to the addition of βCD. The oxygen percentage also increased because of the existence of βCD in βCD-AC-CNT.

Fig. 4(a) shows the results of cyclic voltammetry (CV) performed in phosphate buffer solution (PBS) $[H_2PO_4]^-/[HPO_4]^{2-}$ (PH = 7.5). Both composite shows the typical double layer capacitor behavior, having rectangular shape of CV. The current intensity of βCD-AC-CNT is significantly higher than that of AC-CNT, indicating that the presence of βCD on the surface of AC-CNT increases the rate of electron transfer from the electrolytic solution to the working electrode because of good conductivity and larger surface of βCD [4–6, 9, 10]. Electrochemical impedance spectroscopy (EIS) results are consistent with the CV results. EIS results in Fig. 4(b) shows that the impedance of βCD-AC-CNT is lower than that of AC-CNT when measured frequency from 100 mHz to 100 kHz. It is concluded that the functionalization of βCD over AC-CNT cause enhancement

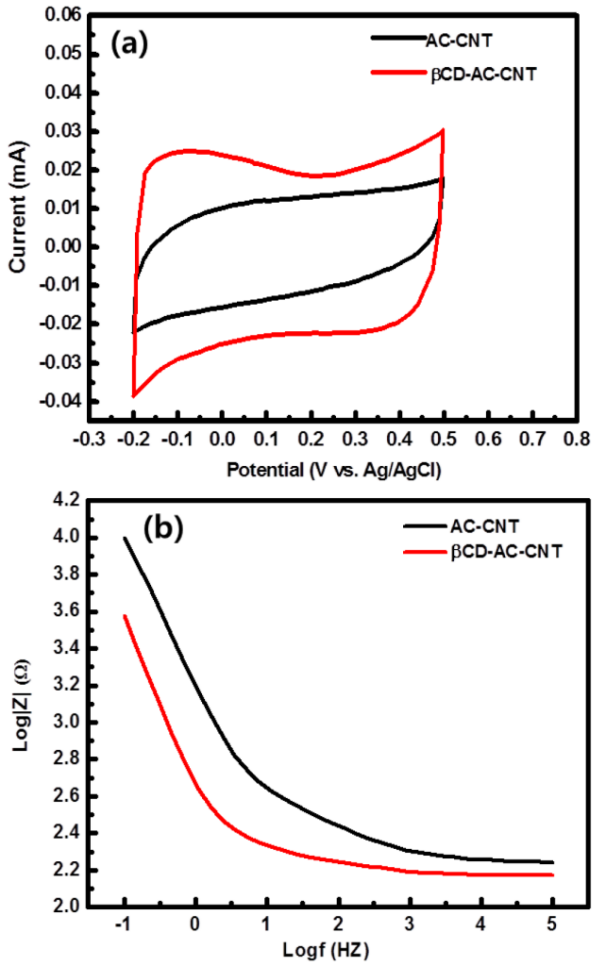

Fig. 4. (Color online) (a) CV and (b) EIS results of AC-CNT and βCD-AC-CNT.

of the electron transfer so that it decrease impedance of βCD-AC-CNT.

Fig. 5 shows DPV results of the samples with 30 mM of ascorbic acid. DPV typically measures redox properties of the analyte that occurs at the working electrode. The oxidation peaks is at +0.005 V due to the oxidation of ascorbic acid. The βCD-AC-CNT composite shows the higher oxidation current, demonstrating efficient electron transfer from the biomolecule towards the working electrode. Therefore, functionalization of βCD on the surface of AC-CNT makes the inclusion complex between βCD and ascorbic acid effectively [1,7], resulting in the increase of the electron transfer reaction at the working electrode by the oxidation. Consequently, sensitivity of the electrode increases [4–6]. The modified AC-CNT composite with βCD displayed better electrochemical performance as well as high detection of ascorbic acid as an electrode for biosensors.

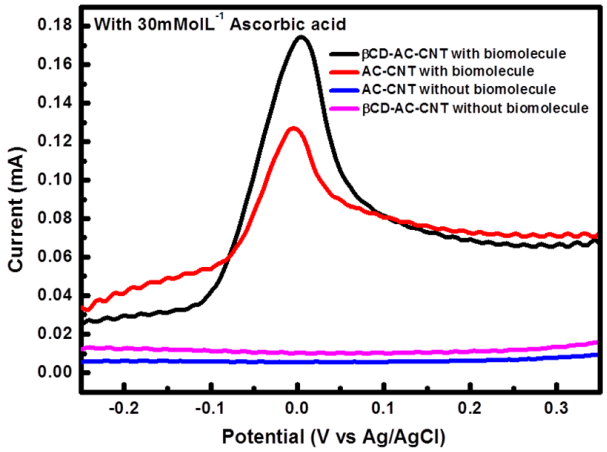

Fig. 5. (Color online) DPV results of AC-CNT and βCD-AC-CNT with and without biomolecule (ascorbic acid).

IV. CONCLUSIONS

βCD-AC-CNT and AC-CNT composites were synthesized by the simple chemical method. The βCD was successfully functionalized over AC-CNT, and the functionalized composite was used for the supramolecular recognition of ascorbic acid by using electrochemical measurements. The electrochemical activity of AC-CNT was also studied and compared. The result showed that presence of βCD in the composite AC-CNT enhanced effective electron transfer and lowered the electrochemical impedance. Therefore, βCD-AC-CNT could be the good biosensor electrode for supramolecular recognition of ascorbic acid.

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