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Cyclodextrin-Graphite Oxide-Carbon Nanotube Composites for Electrochemical Supramolecular Recognition

Hien Thi Ngoc Le, Hae Kyung Jeong*

Department of Physics, Institute of Basic Science, Daegu University, Gyeongsan, 712-714, Republic of Korea

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ABSTRACT

Three different cyclodextrins (α, β, and γCD) are used in a synthesis of free-standing cyclodextrin-graphite oxide-carbon nanotube (CD-GO-CNT) composite films and compared for the electrochemical supramolecular recognition. All composites show very good electrochemical response to three biomolecules (dopamine, ascorbic acid, and thioridazine), and the response of the electrical current is linearly proportional to the concentration of the biomolecules. The γCD-GO-CNT composite gives the best electrochemical supramolecular recognition performance among the other composites (αCD-GO-CNT and βCD-GO-CNT) because of the biggest cavity of γCD (0.95 nm of diameter) compared to αCD (0.57 nm of diameter) and βCD (0.78 nm of diameter). The composite of bigger size CD is more sensitive, resulting that αCD-, βCD-, and γCD-GO-CNT composites are in the order of the increasing sensitivity, to the response, and detail results will be discussed.

1. Introduction

The β cyclodextrin-graphite oxide-carbon nanotube (βCD-GO-CNT) composite has been investigated and showed the excellent supramolecular recognition capability to three biomolecules (dopamine, ascorbic acid, and thioridazine) compared to CNT itself and βCD-CNT [1]. The hydrophilic and planar GO [2] could immobilize βCD molecules effectively on the hydrophobic CNT matrix, providing a synergistic effect of high electric conductivity from CNT and high supramolecular recognition capability from βCD for biosensor applications. However, the supramolecular recognition capability of the composite depending on the concentration of the biomolecules was not investigated yet. Furthermore, there has been no report on the other CDs, such as αCD and γCD, for the supramolecular recognition.

Three different CD, such as α, β, and γCD, exists depending on the number of the glucose unit: six, seven, and eight glucose for α, β, and γCD, respectively [3]. They have a hydrophobic inner cavity and a hydrophilic exterior, and size of the inner cavity is 0.57, 0.78, and 0.95 nm for α, β, and γCD, respectively [4]. Only βCD-GO-CNT composite has been investigated up to now [5] so that the other CD composites need to be investigated further.

In this report, three kinds of the free-standing CD-GO-CNT composite films are synthesized using α, β and γCD and compared for the electrochemical supramolecular recognition. The same biomolecules, such as dopamine, ascorbic acid, and thioridazine, used in the previous study of βCD-GO-CNT composite [1] are applied for the supramolecular recognition study. The three guest molecules are very important in human nervous system. Excess of lack introduces serious problems in our body, such as schizophrenia, Parkinson's disease, psychosis, abnormal immune system, and scurvy. The γCD-GO-CNT composite which has the biggest cavity of CD shows the best performance of the supramolecular recognition compared to the other composites, indicating easier capture of the biomolecules inside the bigger cavity. Concentration dependent response of the biomolecules demonstrates that the electrical response of all composites is linearly proportional to the concentration, and especially the γCD-GO-CNT composite is more than five times sensitive to the concentration compared to the others.

We also investigate and compare the electrochemical supramolecular behaviors of α, β, γCD-CNT composites with α, β, γCD-GO-CNT composites. Three kinds of CD-GO-CNT composites display the higher oxidation peak currents compared to the other three CD-CNT composites which has no GO component, indicating that more CD molecules could be immobilized in GO-CNT matrix rather than in CNT matrix only and resulting in higher supramolecular recognition capability which is corresponds to the previous result of βCD composites [1].

* Corresponding author. Tel.: +82 53 850 6483.
E-mail address: outron@gmail.com (H.K. Jeong).

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2. Experimental

Graphite (200 mesh) and multiwalled CNT (20 μm of length, 10 nm of diameter) were purchased from Alfa Aesar and Hanwha Nanotech, respectively, and three kinds of CD (α, β, and γCD) and biomolecules (dopamine, ascorbic acid, and thioridazine) were purchased from Sigma-Aldrich and used without any pretreatment.

The composites of α, β, and γCD-CNT were synthesized by mixing of each CD (200 mg) and CNT (20 mg) in deionized (DI) water of 20 mL. Then the mixture was sonicated for 180 min at room temperature, followed by a vacuum filtration using a cellulose paper. Obtained α, β, and γCD-CNT composite films were dried at 60 °C in a vacuum oven for overnight and used for the characterization.

The composites of α, β, and γCD-GO-CNT were also synthesized through the similar processes as described above except for adding GO into the solution. GO was first synthesized by the modified Brodie method from graphite, as described elsewhere [2,6,7], and then GO of 10 mg was mixed with DI water of 20 mL followed by the sonication for 2 h to form well dispersed GO solution. The GO solution was mixed with CNT (20 mg) and α, β, or γ-CD (200 mg) followed by the same procedure described above. The final free-standing composite films were shown in Fig. S1.

X-ray diffraction (XRD, Rigaku Rotaflex D/MAX System, Rigaku, Japan) at 40 kV with Cu Kα (1.54 Å) was used to characterize the crystal structure of the composites, and thermogravimetric analysis (TGA, TGA Instruments, Q600, Ramp 10 °Cmin^{-1} to 900 °C, N_2 gas) was performed to measure components and its weight. The surface morphology of the composites was investigated by using scanning electron microscopy (SEM, Ltd., S-4300, JEOL, Japan) at different magnifications.

Electrochemical properties of samples were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) by using EC-Lab (Bio-Logic, sp-150, France) in a three-electrode cell. An Ag/AgCl electrode was used as the reference electrode, and a platinum wire was employed as the counter electrode. The working electrode was prepared as follows. Each sample of 0.5 mg was dispersed well in 1 mL of 2-propanol and then the mixture of 10 μg was dropped onto the glassy carbon electrode (GCE) and dried completely. CV was performed at the scanning rate of 50 mVs^{-1}, and DPV was measured in the potential ranges between −0.2 and 0.5 V, −0.5 and 0.5 V, and 0.4 and 0.85 V, respectively. The pulse amplitude of 2.5 mV, pulse width of 100 ms, and scan rate of 10 mVs^{-1} were applied for DPV measurement. Each biomolecule of 0.25 mL was mixed with 0.1 M phosphate buffer solution (PBS, $[H_2PO_4]^-/[HPO_4]^{2-}$, pH = 7.5) of 10 mL for the supramolecular recognition detection.

3. Results and discussion

Fig. 1 shows XRD and TGA results of samples. The three kinds of CD have similar XRD spectra in which a broad background between 10 and 25 degrees indicates an amorphous structure of CD with low undistinguished peaks (inset of Fig. 1a), but CNT and GO show their unique XRD spectra (Fig. 1a). GO has the typical (002) peak near 13 degrees [6], and CNT has typical peaks at 26 and 13 degrees, corresponding to the first and second order of (002) diffraction of the graphite structure [8] with interlayer distance of 3.4 Å and 6.8 Å. The maghemite Fe_2O_3 phase near 17 degrees was shown [9] and indicated the existence of metal oxide catalyst used for the synthesis of CNT. The CD-CNT composites present XRD peaks originated from each CD and CNT in Fig. 1b, and the CD-GO-CNT composites also show XRD peaks originated from not only each CD

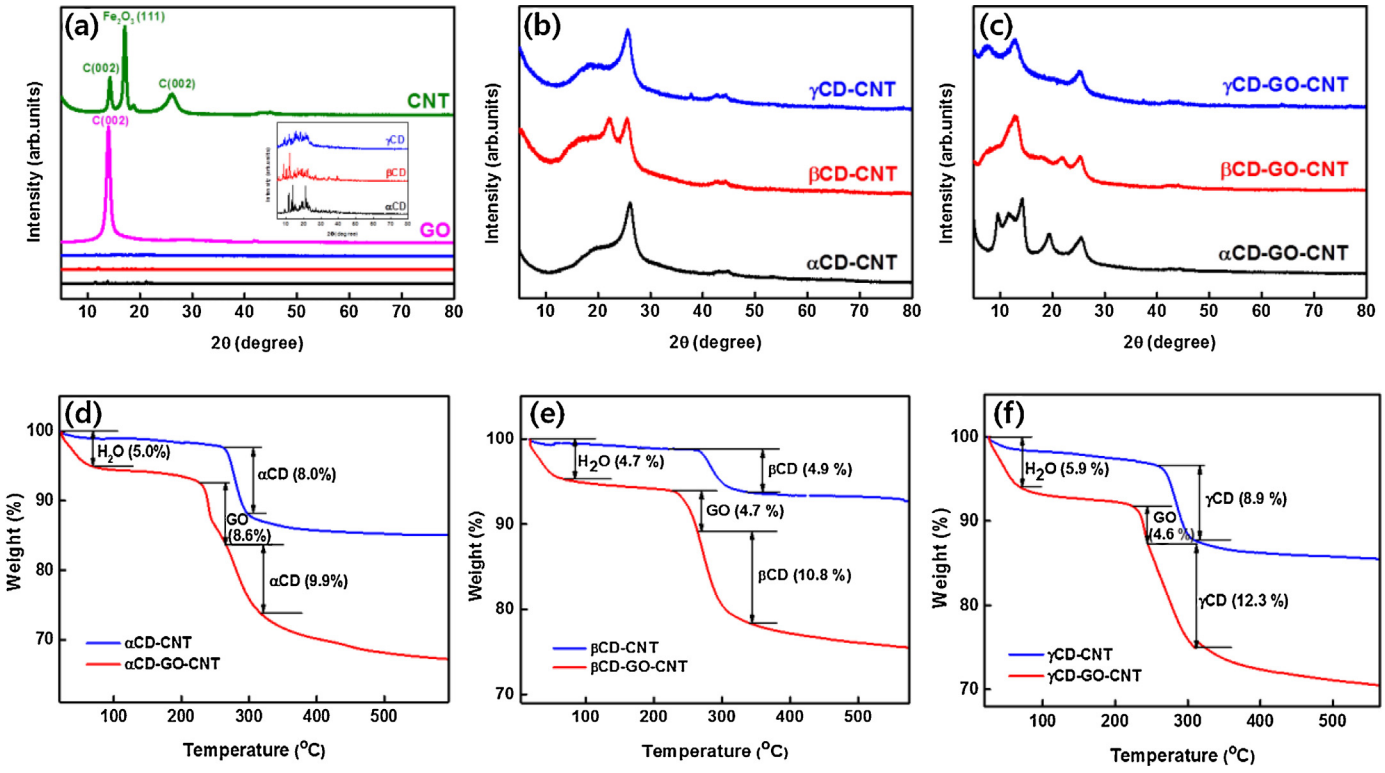

Fig. 1. XRD spectra of (a) CNT, GO, CDs, (b) the CD-CNT composites, and (c) the CD-GO-CNT composites. TGA results of (d) αCD-(GO)-CNT, (e) βCD-(GO)-CNT, and (f) γCD-(GO)-CNT.