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Morphology control of 3D-networked boron-doped diamond nanowires and its electrochemical properties

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ABSTRACT

3D-networked boron-doped diamond (BDD) nanowire was synthesized using an electrostatic self-assembly technique and a chemical vapor deposition process. This BDD nanowire was a BDD-CNT core-shell hybrid nanostructure and applied as an active electrode material on electrochemical sensor. Because electrochemical sensing performance is generally affected by its surface structure and interface characteristics, the deposition time was controlled to identify the optimal morphology. As the deposition time increased, the BDD-CNT nanostructures became thicker, while their porosity and electron transfer resistance were smaller. The electrochemical properties of the BDD based electrodes were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The BDD-CNT electrodes had the significantly higher sensitivity and wider linear range than the BDD electrode due to large surface area and low electron transfer resistance. The BDD-CNT 40 electrode exhibited a highest sensitivity (275.27 μA/mM·cm^2). Therefore, the 3D-networked BDD nanostructures can be applied for electrochemical detection of various analytes as a promising electrode material.

1. Introduction

Boron-doped diamond (BDD) has attracted considerable attention as a potential candidate for next-generation electrochemical sensor platforms due to their unique properties such as wide potential window (ca. 3.5 V), high electrical conductivity, low background current, good chemical stability, enhanced signal-to-noise ratio and quasi-metallic conductivity according to the boron doping condition [1–3]. Owing to these properties, the electrochemical sensors based on a BDD electrode exhibit a high sensitivity, a low detection limit, reversible or quasi-reversible electron transfer kinetics and long-term stability [4–7]. Many researchers have tried to develop high-performance electrochemical sensors using the nanostructured BDD electrodes. Especially, the 3D-networked BDD-CNT core-shell hybrid nanomaterials provided excellent sensing performance including enhanced electron transport efficiency and large effective surface area, resulting in significantly high sensitivity, very wide linear range and remarkably low detection limit [8]. Generally, the electrochemical performance is affected by its surface structure and interface characteristics. So, it is necessary to identify the effect of morphology and electrochemical property of the BDD-CNT hybrid nanostructures on electrochemical performance.

In this study, we fabricated the BDD-CNT hybrid electrodes using an electrostatic self-assembly (ESA) technique under various deposition times and investigated their electrochemical sensing performances. The surface characteristics and electrochemical properties of the BDD-CNT hybrid nanomaterials were analyzed by field emission scanning electron microscopy (FE-SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).The nanostructured electrode with the larger effective surface area and smaller electron transfer resistance are expected to exhibit enhanced electrochemical performances.

2. Material and methods

2.1. Reagents

Stainless steel 316L (SUS316L) nanoparticles (average particle size = 100 nm) and nanodiamond powder (average size = 5 nm) were obtained from Nanotechnology Co. LTD (Daejeon, Korea) and JinGangYuan New Material Development Co. LTD (Guangdong, China), respectively. Here, SUS316L nanoparticles were used as a catalyst-support for the MWCNTs synthesis. Potassium ferricyanide ($K_4Fe(CN)_6$), potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) and potassium chloride (KCl) were purchased from Samchun Chemicals (Gyenggi-do,

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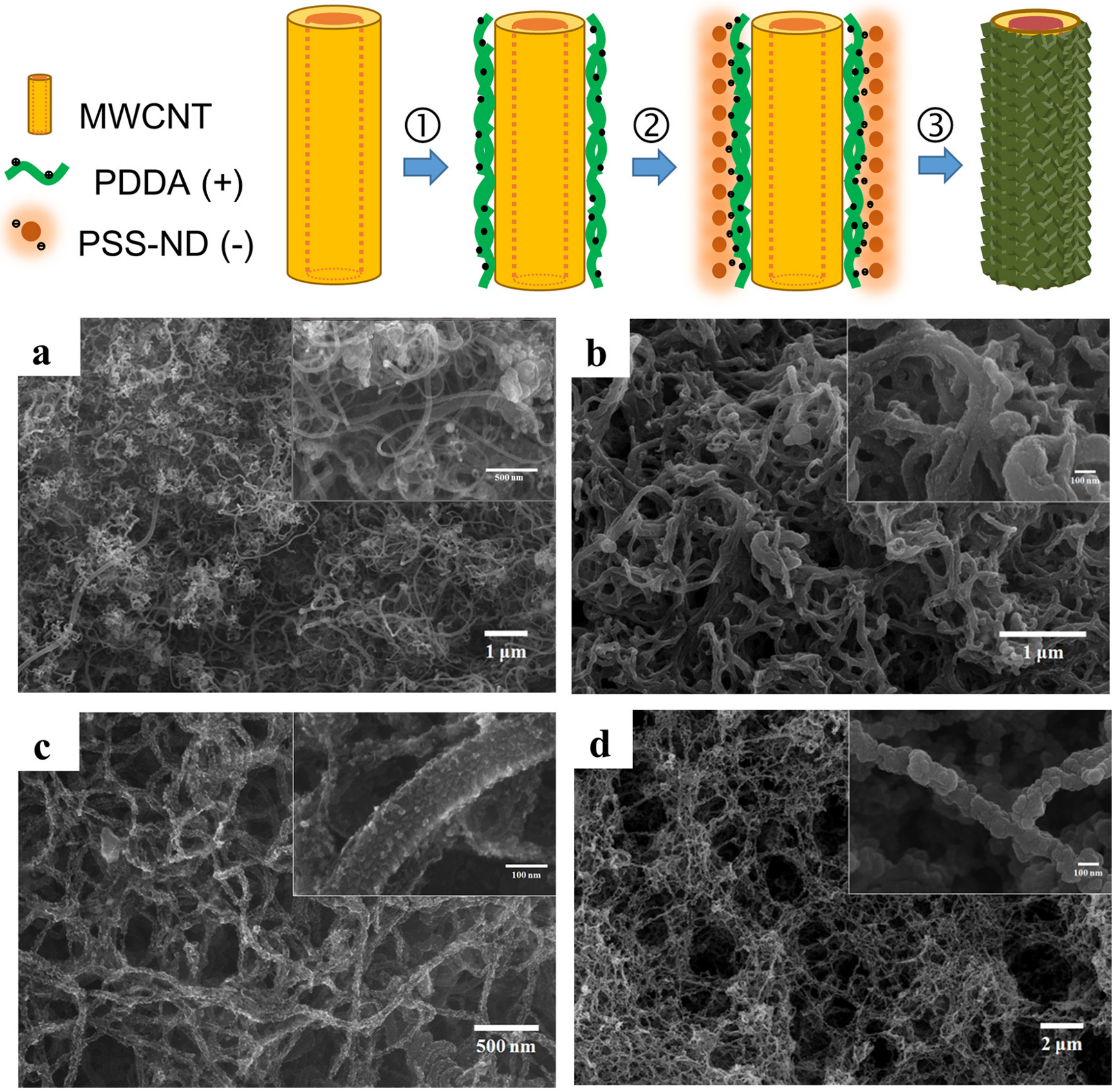

Fig. 1. Schematic representation for synthesis of the BDD-CNT hybrid nanomaterial and SEM images for each step process: (a) as-grown MWCNTs, (b) cationic PDDA coated MWCNTs, (c) PSS-NDs seeded MWCNTs, (d) BDD-CNT hybrid nanomaterial.

Korea). Glutaraldehyde (GA) solution (25% in water) was obtained from Kanto Chemical (Tokyo, Japan). Poly diallyldimethyl ammonium chloride (PDDA; MW: 400,000–500,000), poly sodium 4-styrene sulfonate (PSS; MW: 70,000), 3-Aminopropyltriethoxysilane (APTES), D-glucose and glucose oxidase (GOx; E.C. 1.1.3.4, 200 U/mg) from *Aspergillus niger* were purchased from Sigma-Aldrich (St. Louis, U.S.A.). The stock solutions of glucose were dissolved in a 0.05 M phosphate buffer solution (PBS; pH 7.0) and its diluted solutions were prepared from the stock solution immediately before use.

2.2. *Instruments*

The growth morphologies of the 3D-networked BDD-CNT hybrid material were investigated using field emission scanning electron microscopy (FE-SEM; JSM-7500F, JEOL, Japan). All electrochemical measurements were performed using a CompacStat instrument (Ivium technologies, Eindhoven, Netherlands) connected to a three-electrode cell. The three-electrode system consisted of a platinum (Pt) wire as a counter electrode, an Ag/AgCl reference electrode, and the BDD-CNT hybrid electrodes (diameter = 1 cm) as the working electrode.

2.3. *Preparation of the BDD-CNT hybrid electrodes*

The BDD-CNT hybrid electrodes were fabricated by an electrostatic self-assembly (ESA) technique and thermal chemical vapor deposition (CVD) process [8]. Because the MWCNTs were acted as frameworks for synthesizing the BDD-CNT hybrid electrode, MWCNTs were grown firstly on the SiO_2 substrate using the SUS316L nanoparticles and then the BDD shell layer was deposited on MWCNT surface. Fig. 1 shows the schematic representation for the modified electrode and their SEM images according to surface treatment steps. The MWCNTs electrode was treated with cationic PDDA (step 1) and an anodic PSS-coated nanodiamond (PSS-ND) particles were attached to surface of the cationic MWCNTs (step 2). The BDD was deposited by a hot-filament chemical CVD under 850 °C at various deposition times (20 min, 40 min and 60 min) (step 3). The obtained samples were noted to BDD-CNT 20,