Communication

술폰화 폴리(에테르 술폰)에 의하여 개별 분산된 탄소나노튜브와 은 나노와이어를 이용한 과산화수소 센서 개발

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Debundling of Carbon Nanotube by Sulfonated Poly(ether sulfone) and Silver Nanowire for Hydrogen Peroxide Sensor

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초록: 탄소섬유전극을 기반으로 효소가 불필요한 과산화수소 (H_2O_2) 센서를 분산된 은 나노와이어와 단일벽 탄소나노튜브를 탄소섬유전극 표면에 드롭캐스팅법으로 고정화하여 제작하였다. 센서 제작에 사용된 탄소나노튜브는 고분자 분산제인 술폰화 폴리(에테르 술폰)에 의하여 효과적인 길이/직경의 종횡비를 나타낼 수 있도록 개별 분산되었으며 센서의 성능 향상을 위하여 은 나노와이어와 더불어 컴포지트 형태로 제작되어 새로운 센서 제작법에 활용되었다. 제작된 센서는 H_2O_2에 대하여 높은 전기촉매활성과 재현성, 빠른 분석 시간 및 우수한 감도를 나타냄을 확인하였다(센서 감도: 1.3 μA·mM⁻¹,

검출 한계: 0.69 μM (S/N=3) 및 검출 시간: 3초 미만). 따라서 본 연구에서 개발된 고분자 분산제를 사용한 단일벽 탄소나노튜브의 수용액 내에서의 분산도 향상은 효소가 불필요한 H_2O_2 센서의 설계 및 제작에 활용될 것으로 기대된다.

Abstract: A new non-enzymatic hydrogen peroxide (H_2O_2) sensor based on carbon fiber microelectrodes (CFMEs) has been developed. The CFMEs were modified using a simple drop casting procedure with effectively dispersed silver nanowires (AgNWs) and debundled single-walled carbon nanotubes (SWCNTs). In aqueous solution, the SWCNTs were debundled with a high length/diameter aspect ratio using a synthesized polymer dispersant, sulfonated poly(ether sulfone) (SPES). Enhanced electrocatalytic activity of the sensor for the reduction of H_2O_2 was obtained with the sensor sensitivity of 1.3 μA·mM⁻¹ and the detection limit of 0.69 μM (S/N=3) with a quick turn-around time (less than 3 s). The results clearly reveal that the AgNW-SWCNTs/CFMEs possess high electro-catalytic activity and efficient sensitivity with high reproducibility and fast amperometric response production. Therefore, the proposed debundling approach can be expanded to design and develop non-enzymatic hydrogen peroxide sensors.

Keywords: debundled carbon nanotubes, sulfonated poly(ether sulfone), hydrogen peroxide sensor, non-enzymatic, silver nanowire.

Introduction

Due to the complicated fabrication process of carbon nanotubes (CNT) for the development of electrochemical sensors, single walled carbon nanotubes (SWCNTs) have been widely used as a practical approach for sensor fabrication.[1] The SWCNTs, however, exist as thick bundles in aqueous solutions because of their high surface energies with strong van der Waals forces and commonly show a poor dispersibility. In order to improve the dispersibility, many studies been carried out by debundling the SWCNTs through covalent or non-covalent approaches.[2-4] It has been found that the non-covalent procedure has been an effective method to debundle the SWCNTs with polymeric dispersants and the debundled SWCNTs has exhibited a high aspect ratio and minimal structural defects produced.[5-7]

Microelectrodes (MEs) can be used for rapid and transient electrochemical reaction studies owing to their small inherent time constant.[8] The fast diffusion of substances onto the ME surface allows the measurement of fast-heterogeneous electron transfer kinetics. Owing to these superior properties, the ME has been widely utilized in electrochemistry.[9] Over the past few years, the carbon fiber microelectrodes (CFMEs) have

been gaining more attention for advanced electrochemical sensing applications because of their large surface area and high biocompatibility. The CFMEs also possess high electrochemical applicability with a quicker turnaround time than that with conventional electrodes.[10,11] To enhance the electrochemical performance of CFMEs, they have been modified by integration with many electrode additives such as Nafion,[12] carbon nanotubes,[13,14] polymers,[15,16] and metal nanoparticles.[9]

Herein, newly modified CFMEs have been introduced as a non-enzymatic hydrogen peroxide (H_2O_2) sensor. To construct the sensor, the CFMEs were modified by a simple dip-coating method with a silver nanowires (AgNWs) and SWCNTs composite. The composite was prepared in aqueous solution at neutral pH with debundled SWCNTs and AgNWs. The debundling process developed by the authors of the present study, was performed using a polymer dispersant, sulfonated poly(ether sulfone) (SPES).[17] The SPES polymer was able to increase the length/diameter aspect ratio of the dispersed SWCNTs and AgNWs. Therefore, it is suggested that the use of well-dispersed nanomaterials as electrode additives could improve the electrocatalytic activity of the modified CFMEs. The enzyme-mimicking properties of Ag nanomaterials for electrochemical reduction of H_2O_2 have been previously reported[18,19] and Ag nanomaterials could substitute the well-known electrochemically active enzyme, horseradish peroxidase (HRP), as a biological sensing element to construct H_2O_2 biosensors. The synergetic effects from our new debundling process and effective dip-coating method to produce AgNW–SWCNTs composite could improve the performance of H_2O_2 sensors. Schematic representation of the sensor construction is shown in Scheme 1.

Experimental

SWCNTs (1.0-1.2 nm in diameter, 5.0-20 μm in length) were purchased from Nano Solution Co. (Korea) and SPES was synthesized by following the procedure reported previously by the authors of the present study.[17] Aliquots of H_2O_2 were prepared daily by diluting a commercial standard (30 wt%). All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared using deionized water (Milli-Q water purifying system, 18 MΩ·cm^{-1}). SWCNTs (20 mg) were mixed with 20 mL of the SPES (0.1 wt%) solution and dispersed using a bath-type sonicator (WUC-D22H, DAIHAN Scientific Co., 40 kHz, 200 W) for 3 h. The dispersed SWCNT solutions were centrifuged
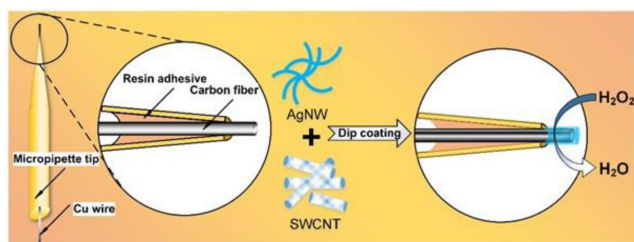
Scheme 1. Schematic representation of the one-step construction of the AgNW-SWCNTs composite modified CFME for the detection of non-enzymatic H_2O_2.

for 10 min at 9425 g (g-force) to remove both the bundled SWCNTs and the metal catalyst.[6,7] The well-dispersed, debundled SWCNT solution was obtained from the supernatant. AgNW dispersion in aqueous solution was obtained from Nanopyxis (Korea)[20] and AgNWs with an average diameter of 25±5 nm and an average length of 25±5 μm were used in the fabrication of the composite.

Carbon fibers were prepared using a procedure reported previously.[11] To prepare MEs, one end of the carbon fiber (1 cm) was connected to a copper wire (diameter: 1 mm; length: 30 mm) using a silver epoxy adhesive. After curing the epoxy adhesive, the fiber was inserted into a micropipette tip and then sealed with resin at both ends. One end of the carbon fiber (diameter: 200 μm; length: 1 mm) was left protruding out and used for further surface modifications. Next, the AgNW-SWCNT composite was prepared by simple mixing of the dispersions of AgNWs (25 μL, 0.3 wt%) and SWCNTs (25 μL, 0.3 wt%). Finally, the prepared AgNW-SWCNT composite was used to modify the surface of the CFMEs by a simple dip-coating procedure: 2 min for dipping and 3 min for drying at room temperature. The dip-coating was repeated 2, 5, or 10 times. AgNW-SPES composites without SWCNTs were also prepared for comparative studies.

Electrochemical measurements were performed using an electrochemical workstation (Compactstat, Ivium Technologies, USA) with a conventional three-electrode cell setup: a CFME as a working electrode, Ag/AgCl (saturated NaCl) as a reference electrode, and a platinum wire as a counter electrode. Cyclic Voltammetry (CV): A 1 mL aliquot of 0.1 M phosphate buffer solution (PBS, pH 7.4) was placed into a disposable 2 mL well and cyclic voltammograms were obtained sweeping from -0.4 to +0.1 V *vs.* Ag/AgCl at a scan rate of 100 mV·s^{-1}.

Amperometric Measurements: One of the AgNW-SWCNTs/ CFMEs was inserted into the electrochemical cell and con-

nected to the workstation. A 900 μL aliquot of 0.1 M PBS was added to the cell and the electrode was polarized at -0.1 V *vs.* Ag/AgCl. After achieving a stable baseline response with 0.1 M PBS, 100 μL of H_2O_2 solution was added to the cell and the amperometric current response was recoded as a function of time. The measurements were then repeated to construct calibration curves. A series of CV scans were performed to determine the electrocatalytic activity of the AgNW–SWCNTs/CFMEs for the reduction of H_2O_2.

Results and Discussion

Figure 1(A) shows comparative voltammograms of H_2O_2 on the CFMEs with AgNWs, AgNW-SPES, and AgNW-SWCNT modifications. The CV results showed that the cathodic peak current (i_{pc}) increased and became higher on the AgNW-SWCNTs/CFMEs than that with the AgNW-SPES/CFMEs (by a factor of 16) and AgNW/CFMEs (by a factor of 2). The i_{pc} value of each CFME was measured at -0.2 V, and the values of i_{pc} are plotted in Figure 1(B). The reduction of H_2O_2 on the surface of AgNW-SWCNTs/CFMEs involves a simple electrochemical mechanism[19,21] and the i_{pc} value increases owing to the synergistic effect of the modified AgNW-SWCNT composite. H_2O_2 present in an electrolyte can be reduced by AgNW to form an oxygen intermediate, and the multistep electrochemical reduction of the intermediate oxygen was observed on the AgNW-SWCNTs/CFMEs.

To obtain the optimum operating conditions, the effects of dip-coating cycles, pH, and applied potential were investigated. As described in the experimental section, amperometric measurements of H_2O_2 were performed using the AgNW-
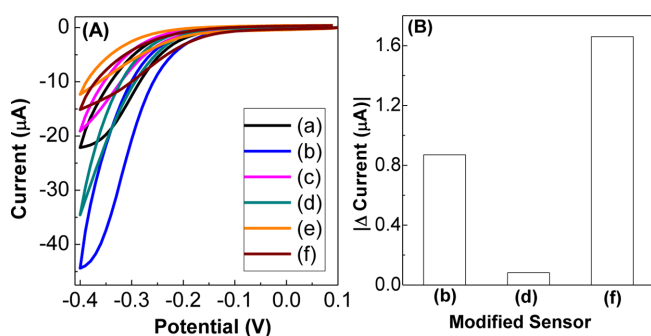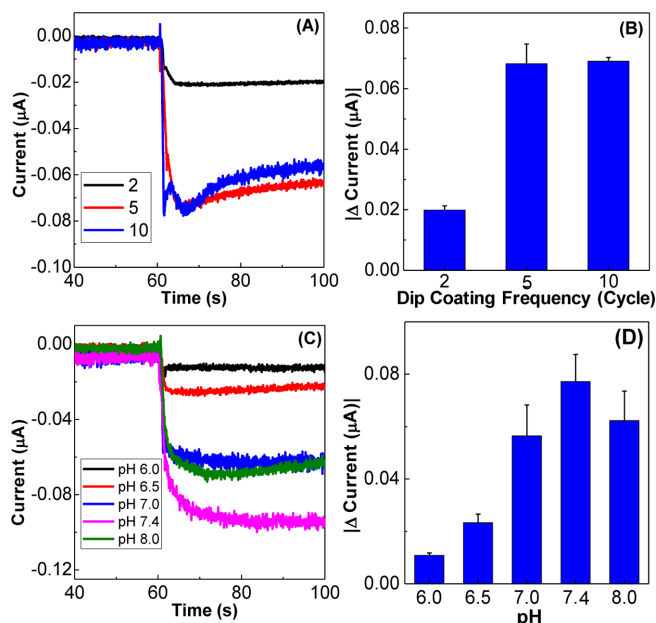

Figure 2. (A) Amperometric response of the AgNW-SWCNTs/CFMEs with different numbers of dip-coating cycles in 0.1 M PBS (pH 7.4) containing 50 μM H_2O_2; (B) corresponding peak current plots; (C) different pH values; (D) pH *vs.* peak current plot.

SWCNTs/CFMEs prepared by three dip-coating cycles. A representative result is shown in Figure 2(A); the measurements were carried out five times. The average i_{pc} values from the five and ten dip-coating cycle electrodes were increased 3.3 times compared to the electrodes with two coating cycles (Figure 2(B)). It was found that the five times coating was almost covered the surface of the CFME and additional coating cycles were not effectively adsorbed on the surface of CFME. Because of these considerations, five dip-coating cycle was used in all subsequent experiments.

Additional amperometric measurements were performed in PBS at different pH values (pH 6.0-8.0), and the measurements were repeated five times at each pH (Figure 2(C)). As can be seen in Figure 2(D), the maximum response was obtained at pH 7.4 and it was chosen as the optimum pH and used for further experiments. To determine the optimum operating potential, measurements were repeated with varying potentials (Figure 3(A)).

Hydrodynamic plots at potentials ranging from 0.0 to -0.3 V can be seen in Figure 3(B), with more negative potentials leading to the increase of i_{pc}. However, -0.1 V was chosen as the optimum condition for all subsequent experiments to avoid possible interference from the dissolved oxygen.
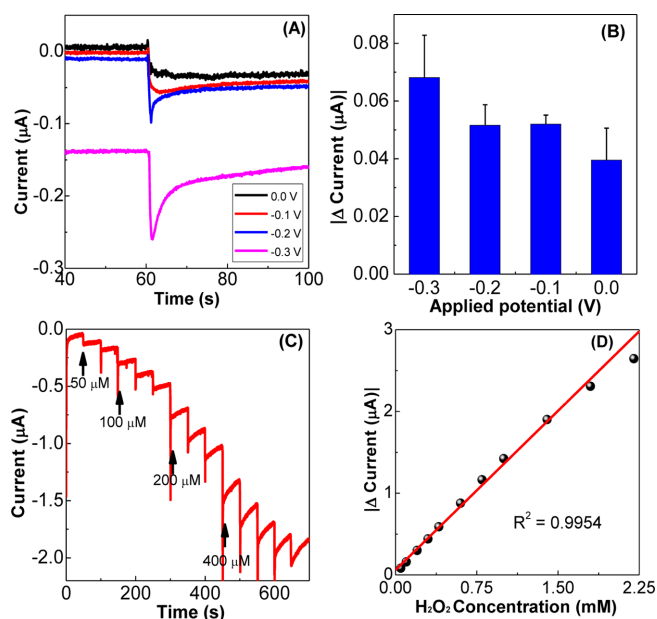
To construct a calibration curve for H_2O_2 on the AgNW-

Figure 1. (A) Cyclic voltammograms of AgNWs (a, b), AgNW-SPES (c, d), AgNW-SWCNTs (e, f) coated CFMEs with (b, d, f) and without (a, c, e) 500 μM H_2O_2 in 0.1 M PBS (pH 7.4) at scan rate of 100 mV·s^{-1}; (B) the corresponding cathodic peak current plots.

Figure 3. (A) Amperometric response of the AgNW-SWCNTs/ CFMEs in 0.1 M PBS (pH 7.4) containing 50 μM H_2O_2, at different applied potentials; (B) corresponding peak current plots; (C) different concentrations of H_2O_2 in 0.1 M PBS (pH 7.4), applied potential -0.1 V; (D) the corresponding calibration curve.

SWCNTs/CFMEs, amperometric measurements were repeated under the optimum conditions (Figure 3(C)). Using the obtained calibration curve (Figure 3(D)), the linear dynamic range was determined to range from 50 μM to 1.8 mM (R^2= 0.996), the sensor sensitivity was calculated to be 1.3 μA·mM^{-1}, the detection limit was 0.69 μM (S/N=3), and the sensor turn-around time was less than 3 s. Additionally, the selectivity and inter-electrode reproducibility of the sensor were evaluated. Undetectable interfering responses were observed after adding biological concentrations of ascorbic acid, uric acid, and acetaminophen.[18] The relative standard deviation (RSD) as the inter-electrode reproducibility was calculated to be 15% (*n*=5).

Conclusions

We have fabricated a new non-enzymatic H_2O_2 sensor based on CFMEs coated with a debundled SWCNT-AgNW composite. The sensor system clearly demonstrated that the SWCNTs were effectively dispersed in a neutral aqueous solution by using a unique polymer dispersant, SPES. The debundling process produced high aspect ratios of AgNWs and SWCNTs, and improved the electrocatalytic activity of the sensor with regard to its linear dynamic range and highly

enhanced sensitivity. The sensor also demonstrated enzyme (HRP)-mimicking properties with high selectivity and reproducibility. The AgNW-SWCNTs/CFMEs were operated at a low applied potential of -0.1 V to avoid any interferences commonly present in real biological or clinical samples. Therefore, the sensor system developed herein can be applied to *in vitro* or *in vivo* H_2O_2 sensing applications.

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