MnO_2 Nanoflowers Array/ Graphene Composite on Carbon Cloth as Flexible Electrode for Non-Enzymatic Hydrogen Peroxide Sensing

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Abstract: In this work, 3D MnO_2 nanoflowers (MnO_2 NFs) array supported on the graphene oxide (GO) modified carbon cloth (CC) was successfully fabricated via a hydrothermal method. MnO_2 NFs act as the catalysts for hydrogen peroxide (H_2O_2) electroreduction were directly grown on conductive CC without use of polymer binders and additives for active materials immobilization. The experimental results show that the flexible electrode demonstrates large linear range, excellent selectivity and a satisfactory stability for H_2O_2 detection, making that it is a promising electrochemical sensor in field of food analysis, environment protection and medicine.

1 INTRODUCTION

Flexible electronics have attracted a great deal of attention owing to their extraordinary potential application in wearable devices and smart electronics(Dong et al., 2016; Yousaf et al., 2016). The design of flexible biosensors creates special needs for freestanding substrates with superior mechanical strength and flexibility. Among various electronic devices, flexible electrochemical biosensors have been considered to be one of the most promising candidates for monitoring molecule in clinical diagnostics and environmental monitoring. In order to realize the high-performance of flexible electrodes, the interfacial properties of high conductive and surface area could be developed. Carbon cloth (CC) is a new flexible free-standing films with a three-dimensional structure, high conductivity and good chemical stability, which have been widely attracted attention in the fields of flexible solid state supercapacitors(Yu et al., 2015). The fabrication of such flexible electrode by directly grow electroactive nanostructures on CC surface is benefit for exposing more active site. Moreover, the CC is interwoven by bundles of carbon fibers that can provide multiple porous channels for liquid diffusion, leading to the enhanced activity.

In recent years, The CC have been research as a promising supporting material for flexible electrochemical biosensors. For example, Wang et al. constructed nickel borate nanoarray on carbon cloth (Ni@Bi/CC) for H_2O_2 electro-reduction in neutral media(Wang et al., 2017). Xu et al. synthesized MnOOH nanorod arrays on CC substrate by hydrothermal route(Xu et al., 2016). The MnOOH nanorods are uniformly distributed on the CC substrate with a 3D porous network structure. In comparison with the rigid graphite supported electrode, the MnOOH/CC electrode exhibits a higher sensitivity and a wider linear range for H_2O_2 detection. Until now, due to the low cost, relatively high stability, and excellent electrical-activity behavior of transition metal oxides, numerous non-enzymatic biosensors have been constructed based on those transition metal oxides(Wang et al., 2018; Xie et al., 2018). Graphene and carbon nanotubes, which possess excellent properties of high conductivity and high surface area, are employed as supporting materials combining with transition metal to improve the sensitivity of the biosensor(Jeong et al., 2018). However, In comparison with graphene or carbon

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nanotube hybrid nanocomposites modified common rigid electrodes, use of CC as a flexible electrode substrate can provide multiple porous channels and numerous electroactive sites for rapid liquid diffusion, which is benefit to the diffusion between the electrolyte and electrode material.

Herein, 3D MnO_2 nanoflowers array, vertically grown on the graphene oxide (GO) modified CC, were synthesized via a facile hydrothermal method. The CC films were treatment with GO to present hydrophilic with amounts of reactive oxygen functional groups. Moreover, the conductivity of CC can be further improved after GO reduced at high temperature. MnO_2 NFs array were directly grown on conductive CC without use of polymer binders and additives for active materials immobilization, in which MnO_2 nanoflowers act as the catalysts for hydrogen peroxide (H_2O_2) electroreduction. The constructed MnO_2 NFs /reduced graphene oxide/CC (MnO_2 NFs /rGO/CC) binder-less electrode demonstrates high sensitivity, large linear range and excellent selectivity for H_2O_2 detection.

2 EXPERIMENTAL SECTION

2.1 Reagents and Materials

The CC (W0S1002) purchased from Taiwan CeTech with the thickness of 360 μm and basis weight of 125 g m^{-2}. Graphene oxide (GO) was obtained from Nanjing XFNANO Materials Tech CO.Ltd(China).Ethanol, acetone, $KMnO_4$, H_2O_2, (30%) and glucose were purchased from Chongqing Chuan Dong Chemical Group (China). Cystine (Cys), Tryptophan (Trp) were purchased from Cheng Du Ke Long (China). Glutataione (GSH) and uric acid (UA) were purchased from Sigma-Aldrich (Shanghai, China).

2.2 Synthesis of MnO_2 NFs /rGO/CC

CC was cleaned with 1M hydrochloric acid, acetone, deionized (DI) water, and ethanol, respectively, under sonifcation. Then the cleaned CC was soaked in 1 mg mL^{-1} GO solution for one week and dried at 70 °C. MnO_2 NFs arrays were synthesized by a facile hydrothermal method. In a typical experiment, pieces of CC were immersed in 30 mL 5 mM $KMnO_4$ and the whole solution with CC was further transferred into Teflon-lined autoclave, then it maintained at 140 °C for 12 h. During the hydrothermal process, the GO was reduced at high temperature. After that, the obtained MnO_2 NFs /rGO/CC was rinsed with DI water and dried at 70 °C.

2.3 Characterization and Electrochemical Measurements

The morphologies were analyzed by field-emission scanning electron microscope (SEM JEOL-6300F). The crystal structures were investigated by powder X-ray diffraction (XRD, Maxima-X XRD-7000). Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Shanghai CH Instrument, China) with a three-electrode system including MnO_2 NFs /rGO/CC (active area 0.5 cm × 1.0 cm) as working electrode, a silver/silver chloride (Ag/AgCl) reference electrode and a platinum wire counter electrode. 0.01 M phosphate buffered saline (PBS, pH 7.4) solution as electrolyte was ventilated with high-purity nitrogen for 20 min to remove dissolved oxygen before all electrochemical measurements.

3 RESULTS AND DISCUSSION

3.1 Morphology and Structure

The MnO_2 nanostructure was synthesized by the hydrothermal method. $KMnO_4$ can decompose to form MnO_2 nuclei at high reaction temperature as the following reaction mechanism: $4KMnO_4 + 2H_2O = 4MnO_2 + 4KOH + 3O_2$, and the MnO_2 nuclei on the surface of carbon cloth further growth by Ostwald ripening mechanism(Shinde et al., 2017). Figure 1 shows the SEM of the GO/CC and MnO_2 /rGO/CC films at different magnifications. It can be seen in the Figure 1B that a few wrinkles coated on the surface of carbon cloth after modifed by GO. The SEM images of MnO_2 /rGO/CC (Figure 1 C-J) show that the vertically aligned MnO_2 nanoarray uniformly covered on the surface of carbon fibers, and the surface morphology of MnO_2 changes from acicular structure (100°C) to dense flower-like structure (140°C) with the rise of the hydrothermal temperature. At low reaction temperature, the low reaction rate leads to the isotropic growth of crystals, while at high reaction rate, MnO_2 crystals aggregated on the surface of carbon cloth by the manner of anisotropic growth.

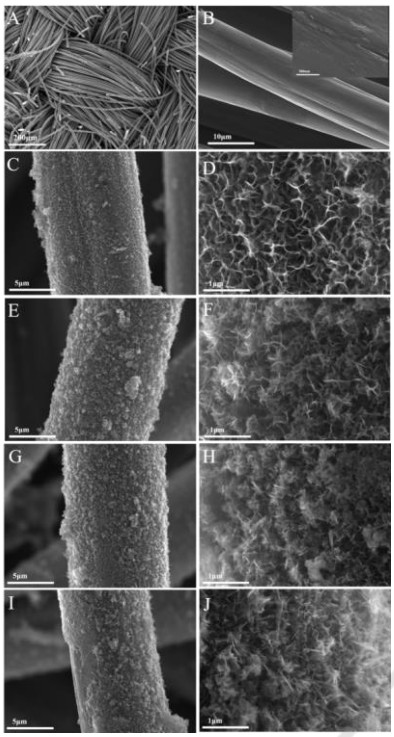

Figure 1 : FESEM images of MnO_2 /rGO/CC films deposited at different hydrothermal temperature.(A, B) /rGO/CC; (C, D) 100°C; (E, F) 120°C; (G, H) 140°C, (I,J) 160°C.

Figure 2 shows the XRD patterns of GO/CC and MnO_2/rGO/CC, respectively. The diffraction peaks of carbon cloth at 25.9° is corresponding to reflection peak (002) of graphite 2H. The characteristic diffraction peaks at 37.3°, 43.7° and 65.3° correspond to the (021), (230) and (002) planes, which coincides well with the standard data of the tetragonal phase of MnO_2 (JCPDS card no. 44-0141)(Wang et al., 2015). The XRD spectrum illustrates that the successful synthesis of MnO_2 on the surface of carbon cloth.

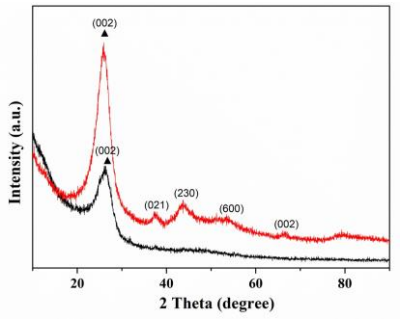

Figure 2 : XRD patterns of as-prepared rGO/CC (black line) and MnO_2 NFs/rGO/CC (red line).

3.2 Electrochemical Properties of the MnO_2 /rGO/CC Films

The electrochemical properties were investigated by Cyclic voltammetry (CV) in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1mol L^{-1} KCl at scan rate of 0.05 V s^{-1}. As shown in Figure 3A, the rGO-CC exhibited increased redox peaks, indicating the enhanced conductivity of rGO-CC films compared with the CC films. After further functionalization with MnO_2 NFs, a larger CV curve was displayed due to the MnO_2 nanocrystal synergistic with rGO contributes the high capacitance of MnO_2 NFs/rGO/CC films. In addition, the CV at different scan rates from 10 to 310 $mV \cdot s^{-1}$ of the MnO_2 NFs/rGO/CC films were recorded in Figure 3B. It can be seen that the peak current and the scan rate presents a good linear relationship, which illustrated that the mass transfer process is mainly adsorption-controlled process at the modified electrode surface.

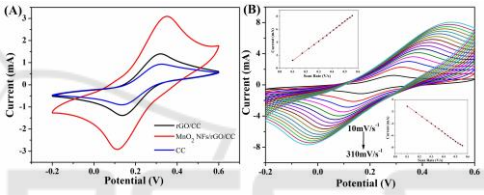

Figure 3 : (A) Cyclic voltammogram of CC, rGO/CC and MnO_2 NFs/rGO/CC at a scan rate of 0.05 V s^{-1}. (B) CVs of the MnO_2 NFs/rGO/CC at different scan rates (10–310 mVs^{-1}) (inset: the plot of peak current against the scan rate) in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1mol L^{-1} KCl .

3.3 Electrochemical Behavior of MnO_2 /rGO/CC Films towards H_2O_2

To investigated the electrocatalytic behaviors toward H_2O_2 of MnO_2 /rGO/CC films, CV was performed in the absence and presence of H_2O_2 in 0.01 M PBS (pH 7.4). As shown in the Figure 4A, the modified carbon cloth show an obvious reduction peak around -0.4V in CV curve, and the reduction current is dramatically enhanced with the increased H_2O_2 concentration. The result indicated the MnO_2 /rGO/CC films has excellent catalytic activity for hydrogen peroxide reduction.

The typical current-time (i-t) curves were recorded with the successive addition of 200 μM H_2O_2 into the stirred 0.01 M PBS solution at an applied potential of -0.4V to compare the catalytic activity of different modified carbon cloth (Figure 4B). It can be seen that the detection sensitivity of H_2O_2 reaches a maximum value at the hydrothermal

temperature risen to 140℃ and then the sensitivity declines. The reason for the difference detection sensitivity is probably due to the form of different morphologies under difference hydrothermal temperature, which provide different surface areas result in different electrochemical properties. Therefore, the MnO_2 /rGO/CC film, which is prepared under hydrothermal temperature of 140℃, was employed in the following experiments to investigate the detection linear range, sensitivity and detection limit of the flexible sensor.

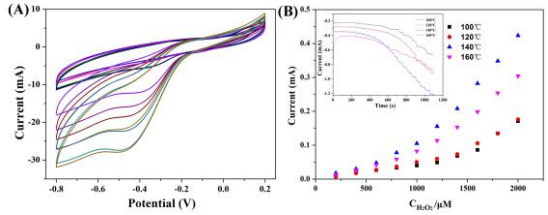

Figure 4 : (A) CV curves of MnO_2 NFs/rGO/CC in 0.01 M PBS solutions (pH 7.0) containing 0-24 mM H_2O_2; (B) the comparison of the electrochemical properties for H_2O_2 reduction at different deposited hydrothermal temperature of the MnO_2 /rGO/CC.

3.4 Amperometric Detection of H_2O_2 the MnO_2 NFs/rGO/CC Films

Figure 5A displays the amperometric response of the MnO_2 /rGO/CC film with successive additions of varying concentrations H_2O_2 in 0.01 M PBS solution (pH=7.4) at −0.4 V. A stepwise current response was observed after addition of H_2O_2. The reduction current of the flexible electrode has two segments linear relation with the H_2O_2 concentrations in a range of 20μM-1mM and 1mM-5mM with a correlation coefficient of 0.991 and 0.999, respectively (Figure 5B and C). The sensitivity was calculated to be 68μA·M^{-1}·cm^{-2} and the detection limit was 17.9μM (S/N=3). Therefore, these results indicated that the excellent performance of the MnO_2 /rGO/CC film for H_2O_2 detection.

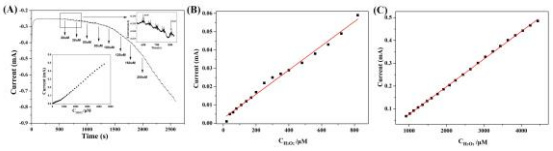

Figure 5 : (A) Amperometric response of MnO_2 NFs/rGO/CC to successive additions of H_2O_2 at -0.4V in 0.01 M PBS. (B, C) Linear relation between the amperometric response and H_2O_2 concentration.

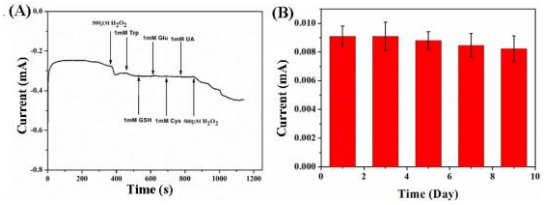

Figure 6 : The interference studies (A) and reproducibility test of the MnO_2 NFs/rGO/CC (B).

The interference studies were performed to evaluate the selectivity of MnO_2 /rGO/CC film toward H_2O_2 reduction (Figure 6). The addition of 1 mM tryptophan (Trp), 1 mM glutathione(GSH), 1 mM glucose(Glu), 1 mM cysteine (Cys) and 1 mM uric acid (UA) result in negligible current responses, and the 500μM H_2O_2 produced an obvious current change, demonstrating that the flexible sensor have an excellent specificity for H_2O_2 detection. In addition, the stability of the MnO_2 /rGO/CC film was also examined by measuring the response to 500 μM H_2O_2 for every two days. It retained 90.47% of its initial response after nine days when the sensors were stored at room temperature, indicating the good stability of the present sensor.

To further evaluate the applicability, real water sample from Jia Ling River (Chongqing, China) is collected and analyzed by our developed electrode. The water sample was filtered, diluted and detected by the standard addition method. In the case of water sample spiked with 500 μM and 2 mM H_2O_2, the results showed that the recoveries were 92.6 and 96.2% with relative standard deviations of 3.1% and 2.4%, indicating the appreciable practicality of the non-enzymatic sensor for the determination of H_2O_2 in real samples.

4 CONCLUSIONS

In summary, we developed a novel analytical device for non-enzymatic detection of H_2O_2 based on 3D MnO_2 nanoflowers array on rGO modified carbon cloth. The flexible carbon cloth as a freestanding electrode plays a significant role in electrochemical sensor because of its multiple porous channels for liquid diffusion. The 3D MnO_2 nanoflowers array growing on the surface of carbon cloth via one-step hydrothermal method leads to the enhanced activity because of the increased active surface areas. Electrochemical measurement results show that the as-prepared carbon cloth-supported 3D MnO_2 nanoflowers array exhibit excellent catalytic activity

toward H_2O_2 with high selectivity and sensitivity, which is a promising candidate for the design of flexible non-enzymatic sensors for H_2O_2 detection in food analysis, environment protection and medicine.

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