Glucose detection based on CN_x/Co_3O_4 composite electrode fabricated by a hybrid non-thermal plasma/sol-gel deposition technique

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Abstract: In the present study, the electrochemical performance of CN_x/Co_3O_4 nano-composite electrodes toward applications in the non-enzymatic glucose detection is reported. The multilayer electrodes were nano-engineered by a novel hybrid non-thermal plasma/sol-gel deposition process combining low-pressure dielectric barrier discharge plasma and sol-gel spin-coating methods. The results indicated that the synergistic effects arising from interleaving redox active Co_3O_4 interlayers between CN_x layers involving numerous nano-pores lead to the remarkable electrochemical activity of the composite electrodes.

Keywords: Multilayer electrode, a-C:H:N, Co_3O_4, non-thermal plasma, glucose detection.

1. Introduction

Nowadays, due to the low power requirement, high sensitivity, simplicity and high accuracy, glucose sensors based on the electrochemical detection process are widely used in the areas of clinical diagnosis especially in measurement of glucose level in the blood of diabetic patients, biotechnology, and food analysis [1,2] . The glucose sensors supported by electrochemical techniques can be classified as the enzymatic glucose sensors and the non-enzymatic glucose sensors, respectively. For a correct functioning of amperometric glucose sensors, having a reference electrode (RE), which is both stable and precise in the physiological environment, is a crucial requirement. It is well-known that the stability of enzymatic glucose sensors is strongly affected by environmental humidity, pH, and temperature[1,3], which hinder the feasibility of in-situ monitoring of glucose concentration. Hence to avoid such issues, non-enzymatic sensing with direct oxidation of glucose on the electrode has emerged as a new approach but is still in its infancy. Much effort has been devoted to investigate enzyme-free electrode materials including various metal nanoparticles, as well as transition metal oxides (TMOs) [4–6]. In particular, Co_3O_4 exhibits intriguing electronic, electrochemical, and electro-catalytic properties compared to other metal oxides. Nevertheless, some serious drawbacks of Co_3O_4 electrodes lie in a poor electrical conductivity, short active site density, and the dissolution or agglomeration during electrochemical processes. These restrictions can be suppressed by an effective nano-engineering of the compounding Co_3O_4 with carbon materials due to their high abundance, high electrical conductivity, wide potential window, excellent chemical stability, and good biocompatibility. Notably, N-doped hydrogenated amorphous carbon (a-C:H:N or N-DLC) as a valuable alternative to the boron-doped diamond (BDD) electrode has received considerable attention as attractive electrode material for electrochemical applications due to its exceptional physicochemical properties. Among various methods employed for nitrogen doping in DLC structure [7–12], Dielectric Barrier Discharge (DBD) plasma technique is a promising approach due to its ability to modify the structure and morphology of nanomaterials during their synthesis by tuning the amount of chemical functionalities and active species in the non-thermal plasma medium. Therefore, within the present study, the electrochemical performance of a-C:H:N/Co_3O_4 multilayer composite film as a promising electrode material in the non-enzymatic glucose detection has been evaluated. Our innovative approach to a-C:H:N/Co_3O_4 multilayer film fabrication offers an excellent control on the thickness and crystallinity of TMO interlayers. In addition, it improves the accessing of ions to metal centers by introducing more pores as well as enhancing conductivity induced by plasma deposition of a-C:H:N layer by the DBD method.

2. Experimental section

A novel hybrid process is conducted to fabricate the CN_x/Co_3O_4 composite films: (1) deposition of a-C:H:N (CN_x) layer by a low-pressure and non-thermal DBD plasma method using C_2H_4/N_2 gas mixture followed by (2) sol-gel spin-coating of nanostructured Co_3O_4 interlayer via cobalt acetate tetrahydrate $[Co(C_2H_3O_2)_2(H_2O)_4]$ sol as Co precursor. Corning glass and FTO substrates were used for analytical and electrochemical testing, respectively. Moreover, in order to compare the characteristics of a-C:H:N/Co_3O_4 multilayer electrode with the pristine Co_3O_4, pure Co_3O_4 electrode was also fabricated using spin-coating technique, separately.

Micro-Raman spectrometer (Senterra II Bruker Optik GmbH) with a laser excitation wavelength at 532 nm was used for structural characterization. The cross-sectional micrographs of the films as well as their thicknesses were analyzed by a field emission gun scanning electron microscope (FEG-SEM, Hitachi SU8020) operating at 3 kV. The cyclic voltammetry (CV) of the electrodes were investigated using an electrochemical analyzer (Biologic SP-300) at room temperature in a three-electrode system where synthesized electrode, Ag/AgCl and platinum wire served as working, reference and counter electrodes, respectively. The glucose detecting tests were performed using 0.1 M NaOH as blank electrolyte containing D-glucose $C_6H_{12}O_6$ (Sigma Aldrich).

3. Results and discussion

Fig. 1 shows the cross-sectional FEG-SEM micrographs of pure Co_3O_4 (hereafter named Co), and multilayer composite a-C:H:N/Co_3O_4 (hereafter named MCNCo) films, respectively. The uniform nano-layer of Co_3O_4 incorporated by the hybrid process and the excellent topological interconnection of Co_3O_4 interlayers and a-C:H:N layers is clearly apparent from cross-section view of MCNCo image. The obtained porous structure of a-C:H:N layer in depth promotes both the active surface area and ion diffusion process. Therefore, the access to the metal sites and current density in the electrode material will be enhanced and will consequently result in high electrochemical electrode activities .

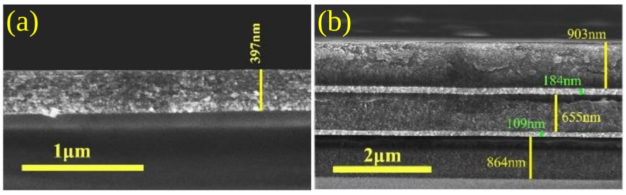

Fig. 1. FEG-SEM cross-section images of (a) Co and (b) multilayer composite MCNCo films.

The formation of a hybrid structure of MCNCo consisting of Co_3O_4 and a-C:H:N is confirmed by Raman spectrum (see Fig. 2). The characteristic peaks observed at 193.5, 478 , 520, and 685.5 cm^{-1} correspond to B_{1g}, E_g, F_{2g}, A_{1g} crystalline Co_3O_4 modes, respectively, while two dominating features around 1341 and 1590 cm^{-1} are attributed to D- and G bands in disordered carbon materials. The D band associated with defects and disorders is the result of breathing mode of A_{1g} symmetry mode of carbon whereas the G band is ascribed to the E_{2g} mode of sp^2 C-C bond, implying on partial graphitized carbon in amorphous carbon matrix [12–16].

Fig. 3 represents the CV voltammograms of the Co, and MCNCo electrodes, respectively, measured in 0.1 M NaOH containing 1 mM $C_6H_{12}O_6$ (glucose) at different scan rates (10-50 mVs^{-1}). A significant increase in the current densities was observed for the MCNCo composite electrode compared to the Co ones. These results reveal the synergistic effects of the presence of sp^2 hybridized carbon as well as graphitic nitrogen in MCNCo electrode leading to a promising increase in its electrochemical performance suitable for glucose detection [17]. In fact, Co_3O_4 interlayers in the MCNCo composite electrode provide active centers for electrochemical reactions. Subsequently, the electrons that produce by electrochemical reactions timely transfer by CN and graphitized carbon, which are beneficial to the collection of electrical signals along with the electrocatalytic oxidation of glucose [2]. Note that the conductive and chemically inert CN_x layers not only are favorable to the high-speed electron transfer, but also can protect the Co_3O_4 active sites from agglomeration and/or dissolution during electrochemical processes.

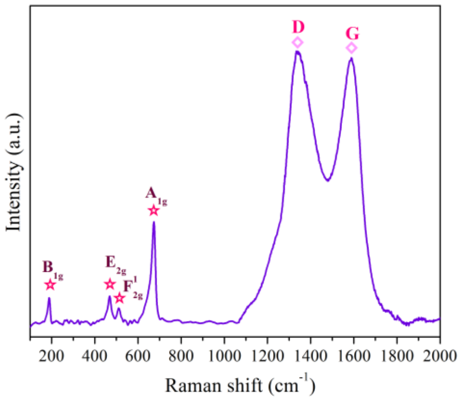

Fig. 2. Raman spectra of MCNCo.

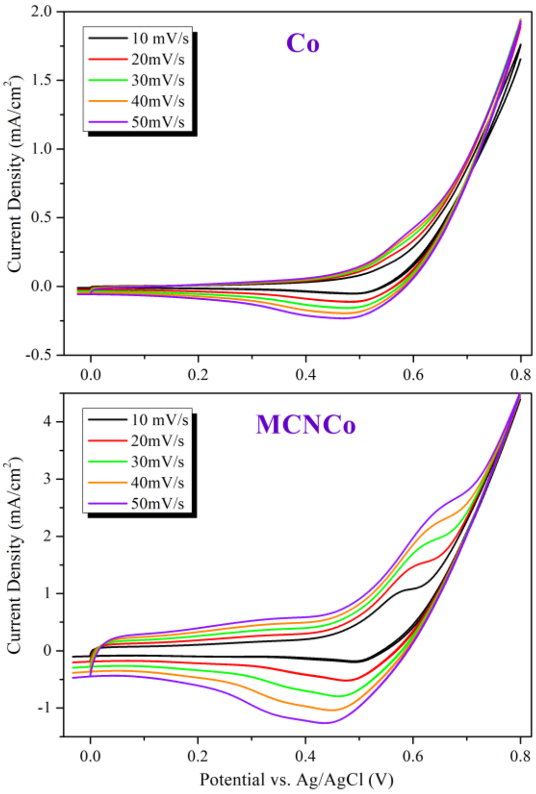

Fig. 3. Cyclic voltammograms of Co, and MCNCo electrodes in 0.1M NaOH containing 1 mM $C_6H_{12}O_6$ electrolyte at various scan rates.

The CVs of MCNCo composite electrode towards the different concentrations of glucose are presented in Fig. 4. The oxidation current peak gradually increases with enhancying the concentration of glucose, further revealing the excellent performance of MCNCo in the detection of glucose. This measured glucose concentration range is corresponded to human blood ones demonstrating feasible application of the fabricated composite electrode in non-enzymatic glucose detection.

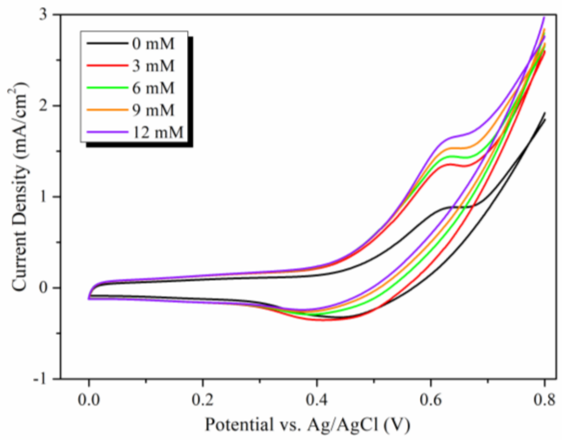

Fig. 4. Cyclic voltammograms of MCNCo electrode in 0.1M NaOH with different concentration of glucose (scan rate: 10 mV s^{-1}).

4. Conclusions

In summary, a multilayer CN_x/Co_3O_4 composite electrode was successfully fabricated by a novel hybrid plasma/sol-gel deposition process for non-enzymatic glucose detection. The results significantly revealed that the highest performance attained by the a-C:H:N/Co_3O_4 as a electrocatalyst for glucose detection is based on synergistic effects between Co_3O_4 and CN_x. Indeed, Co_3O_4 provides a large number of active sites, while CN_x layers serve as well-structured diffusion channels to deliver high electron transfer rate. Moreover, chemically inert a-C:H:N (CN_x) layer supports Co_3O_4 thin interlayer from dissolution/agglomeration during electrochemical processes. The present study demonstrates that the a-C:H:N/Co_3O_4 thin film electrode can be a prosperous candidate for the electrochemical-based glucose sensors.

5. References

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