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Inkjet-printed graphene-PEDOT:PSS modified on screen printed carbon electrode for sensing applications

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Abstract

In this work, a novel method for electrode modification based on inkjet-printing of electrochemically synthesized graphene-PEDOT:PSS (GP-PEDOT:PSS) nanocomposite is reported for the first time. GP-PEDOT:PSS dispersed solution is prepared for use as an ink by one-step electrolytic exfoliation from a graphite electrode. GP-PEDOT:PSS layers are then printed on screen printed carbon electrodes (SPCEs) by a commercial inkjet material printer and their electrochemical behaviors are characterized towards three most common electroactive analytes including hydrogen peroxide (H_2O_2), nicotinamide adenine dinucleotide (NAD^+/NADH) and ferri/ferro cyanide ($Fe(CN)_6^{3-/4-}$) redox couples. It is found that the oxidation signals for H_2O_2, NADH and $K_2Fe(CN)_6$ of PEDOT:PSS modified and GP-PEDOT:PSS modified SPCEs are ~2-4 and ~3-13 times higher than those of unmodified SPCE, respectively. In addition, excellent analytical features with relatively wide dynamic ranges, high sensitivities and low detection limits have been achieved. Therefore, the inkjet-printed GP-PEDOT:PSS electrode is a promising candidate for advanced electrochemical sensing applications.

Key words: Graphene, PEDOT:PSS, Inkjet print, Biosensor

Introduction

Graphene is an ideal material for electrochemistry because of its very large two-dimensional electrical conductivity, excellent electron transfer rate, huge specific surface area and low cost. In addition, it is considered a more practical electrode material than carbon nanotubes (CNTs) counterpart because it can be cheaply produced from low cost graphite with no metallic impurity [1-2]. In this work, a electrochemically synthesized graphene-PEDOT:PSS (GP-PEDOT:PSS) is presented as a new electroactive material that is utilized for the first time to modify screen printed carbon paste electrode (SPCE) by inkjet printing technique.

Experimental

The electrochemical characteristics of the inkjet printed SPCE electrode is characterized by cyclic voltammetry (CV) for detection of salbutamol. Two graphite rods were placed in an electrolysis cell filled with the PEDOT:PSS electrolyte and a constant potential of 8 V was applied between electrodes for 5 hours to obtain stable GP-PEDOT:PSS dispersion with intended graphene concentrations [3]. The dispersed product was centrifuged at 1200 rpm to separate large agglomerates and supernatant portion of the dispersion was then decanted. The GP-PEDOT:PSS solution was used as an ink for inkjet printing on SPCE by the commercial Dimatrix material inkjet printer. Five layers of GP-PEDOT:PSS material were coated over 3x5 mm^2 electrode area.

Results and Discussion

The surface morphologies of fabricated electrochemical electrodes were examined by SEM (Figure. 1). It is seen that uncoated SPCE electrode has rough surface with large grain size of several microns and surface becomes smoothen after inkjet printing with PEDOT:PSS or GP-PEDOT:PSS.

The electrochemical characteristics of inkjet-printed GP-PEDOT:PSS modified SPCE were measured by CV using the commercial electrochemical work station and home-made electrochemical cell. H_2O_2, NADH and $K_4Fe(CN)_6$ solutions with different concentrations were then prepared for concentration study by proper dilution of the stock solutions in buffer solutions. Working electrode was immersed in tested solutions and CV scans were run at several scan rates for different concentrations of analytes. The selected voltage windows for H_2O_2, NADH and $K_4Fe(CN)_6$ were -0.4 to +1.2 V, 0 to 1.0 V and -0.2 to 0.8, respectively because their redox peaks appeared within these potential ranges. The electrochemical efficacy of GP-PEDOT:PSS electrode is evaluated from CV responses and compared to those of PEDOT:PSS modified and unmodified SPCEs as shown in Figures 2, respectively. It should be noted that the repeatability of all responses in Figures 2 is within 5% from twenty successive measurements. The analyte concentrations used for comparative study are selected from the highest concentrations in linear dynamic ranges, which are subsequently demonstrated in Figure 3. It is evident that GP-PEDOT:PSS modified SPCE exhibits much larger current responses towards three analytes than PEDOT:PSS modified and unmodified SPCE respectively. In addition, it can be seen that PEDOT:PSS considerably enhances the electrochemical activity of SPCE to H_2O_2, NADH and $K_4Fe(CN)_6$ and the addition of graphene substantially increases the response further.

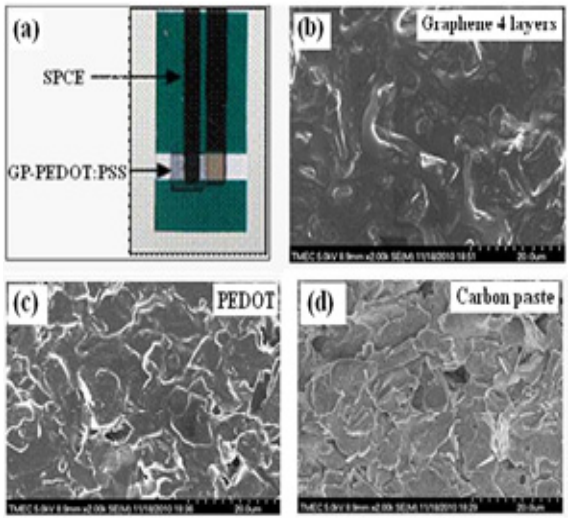

Fig. 1. (a) Typical photograph of inkjet-printed GP-PEDOT:PSS SPCE and SEM micrographs of (b) inkjet-printed GP-PEDOT:PSS SPCE, (c) inkjet-printed PEDOT:PSS SPCE and (d) SPC

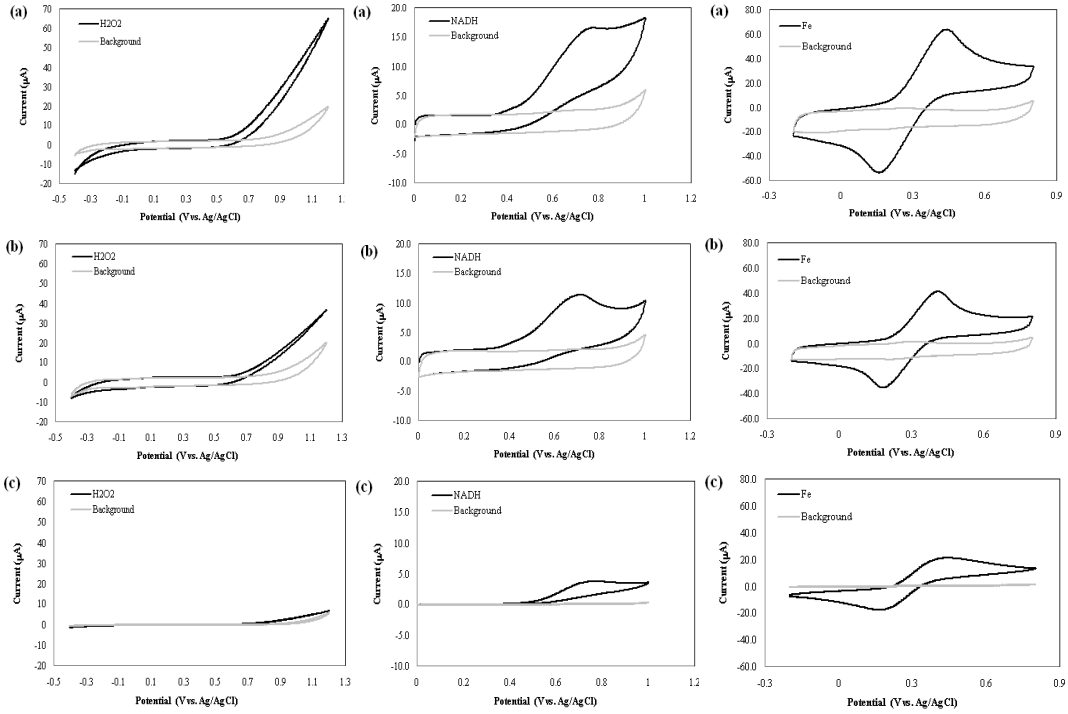

Fig. 2: CV responses to H2O2, NADH and K4Fe(CN)6 solution of (a) GP-PEDOT:PSS and (b) PEDOT electrode and (c) SPCE electrode. Scan rate was 100 mVs-1

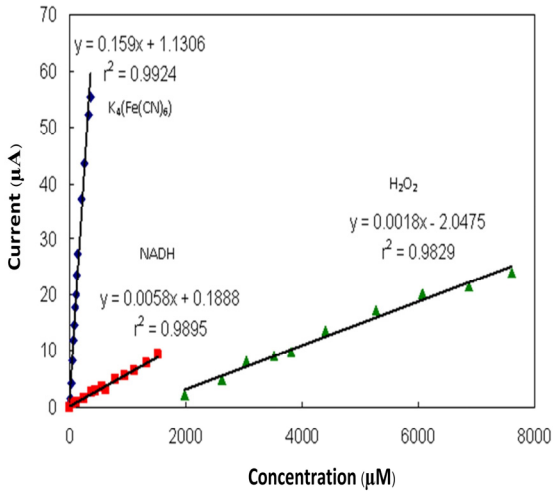

Fig. 3: Oxidation currents at a moderate potential (0.9 V) for H2O2 and at oxidation peaks for NADH and K4Fe(CN)6 vs. concentration. Scan rate was 100 mVs-1.

The dramatic enhancement can be attributed to huge reactive surface area, high electronic mobility, high sensitivities, low detection limits and excellent electron transfer rate of GP-PEDOT:PSS composite. Therefore, inkjet-printed GP-PEDOT:PSS on SPCE is highly promising for advanced electrochemical detection.

Conclusion

In conclusion, this report presents the first utilization of inkjet-printed GP-PEDOT:PSS modified SPCE electrode for electrochemical detection of H_2O_2, NAD^+/NADH and $(Fe(CN)_6^{3-/4-})$ redox couples. GP-PEDOT: PSS ink is synthesized by one-step electrolytic exfoliation method and inkjet printed on SPCE. SEM image indicates that SPCE surface is smoothen after successive GP-PEDOT:PSS printing. From CV measurement, the oxidation signals for H_2O_2, NADH and $K_4Fe(CN)_6$ of PEDOT:PSS modified and GP-PEDOT:PSS modified SPCEs are found to be ~2-4 and ~3-13 times higher than that of unmodified SPCE, respectively. In addition, the method provides excellent analytical features with relatively wide dynamic ranges, high sensitivities and low detection limits. Therefore, inkjet-printed GP-PEDOT:PSS on SPCE is highly promising for advanced electrochemical detection.

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