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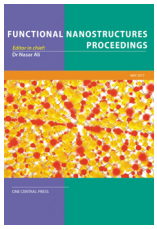

Effect of nanocomposite MnO_2/Ppy/rGO on electrochemical sensing of methyl parathion

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ABSTRACT

In the present work, we report the synthesis of a new hybrid nanocomposite MnO_2/Polypyrrole (Ppy)/ reduced grapheneoxide (rGO)/GCE for high performance electrochemical detection of methyl parathion (MP). A novel single step process by chemical polymerization method was employed for the synthesis of MnO_2/Ppy/rGO nanohybrid. The sensitivity of the electrode was greatly enhanced by the influence of inducted polymer, Ppy encapsulated with MnO_2 nanoparticles. The structural, morphological and electrochemical properties of MnO_2, MnO_2/Ppy and MnO_2/Ppy/rGO were investigated by FE-SEM, HR-TEM with EDX, XRD and FTIR spectroscopy. The crystallographic properties revealed the tetragonal and rhombohedral crystal structure for MnO_2 and rGO, respectively. The combined characteristic peaks of MnO_2 and rGO were observed in the XRD patten of nanohybrid composite. The appearance of broad characteristic peak at 23.6° confirmed the distortion of crystal structure of MnO_2 and rGO nanocomposite and the transformation of amorphous phase during the oxidation process of polymerization. SEM and TEM images revealed that the pure MnO_2 and Ppy nanoparticles show porous morphology with high surface area compared to rGO. The diameter of the MnO_2 and rGO particles was found to be in the range of 30-50 nm and 50-150 nm, respectively. The EDX result of the composite confirmed the effective doping of MnO_2, Ppy and rGO. The electrocatalysis of organophosphorus pesticide methyl parathion (MP) was investigated by Cyclicvoltammetric (CV) measurement. Further the effect of pH and concentration on the electrochemical behavior of MP was examined. The composite exhibited excellent electrocatalytic activity with enhanced peak current of 34.8 µA and reduction potential of 0.067 V. The improvement of electrocatalytic ability was exhibited with peak current value at 11.3 µA, 24.4 µA and -34.8 µA, corresponding to modified MnO_2, MnO_2/Ppy and MnO_2/Ppy/rGO, respectively. From the experimental data, it was evident that the current response of the modified electrode towards MP was linear in the range from 0.5 µM – 10 µM, with detection limit (LOD) of 81 nM and the sensitivity 8.22 µA μM^{-1} cm^{-2}. The synergistic catalytic effect of the composite was more effective and hence enhanced the electrosensing ability of the electrode. The present work successfully demonstrated a simple, rapid, effective, economical and sensitive method for the detection of MP. The proposed method was furthermore employed for the determination of MP in fruits and vegetables samples.

I. INTRODUCTION

Pesticides are widely used in agricultural field to enhance the production and quality of agriculture yields. In the physiological function of human MP is converted into active metabolites methyl paraoxon by *invivo* which can act as an acetylcholinesterace inhibitor leading to harmful diseases like nausea, dizziness, confusion, disrupts normal neural transmission, which leads to a state of hyperarousal and even respiratory paralysis and death. The present study provides a promising method to develop electrochemical sensor to detect MP. As the composite exhibited unique morphology, elemental composition long term stability and excellent conductivity, the present study revealed the synergistic effect of electrocatalytic activity and excellent conductivity of MnO_2, Polypyrrole and reduced graphene oxide on the performance of modified electrode for the detection of MP.

II. EXPERIMENTAL METHODS

Preparation of MnO_2/Ppy/rGO

Nanohybrid composite of MnO_2/Ppy/rGO was prepared by in situ chemical oxidative polymerization method. Firstly, 100 ml of 0.5 M HCl solution containing 0.005 M CTAB surfactant was added slowly to 50 mg of newly synthesized rGO nanoparticle with constant stirring for 5 h under ice cold condition. Then 0.54 µl of pyrrole monomer was added to the mixture, followed by the addition of 0.79g $KMnO_4$ which act as oxidant. The reaction mixture was stirred vigorously in ice cold condition for 3 days and it was filtered and washed. The dark brown MnO_2/Ppy/rGO precipitate was finally dried under vacuum oven at 60 ºC for 12 h.

Electrochemical measurement

A suspension was prepared by adding 10 mg of the nanohybrid composite MnO_2/Ppy/rGO to 0.1 ml 5% Nafion solution and dispersed homogeneously by ultrasonication. The suspension of 0.7 µl of the ink-like nanocomposite was dropped by on a well- polished GC electrode surface by drop-dry-method. The electrode was dried in air for 30 min at room temperature. The electrochemical behavior of the bare GC and MnO_2/Ppy/rGO modified GC electrode was studied by cyclic voltammetry (CV) and Difference pulse voltammograms using 0.1 M phosphate buffer solution (PBS) with pH 7.00 as the supporting electrolyte. The electrochemical response of the MP sensor was tested by cyclic voltammetry in the potential range of -1.0 V to +0.2 V.

III. RESULTS AND DISCUSSION

Structural characterization of MnO_2/Ppy/rGOnanocomposite

The surface morphology of pure MnO_2/Ppy/rGO nanocomposite was studied by FE-SEM, HR-TEM with EDX, FT-IR and XRD respectively. The structural morphology obtained from the SEM images (Fig. 1a) revealed that MnO_2 and Ppy show porous morphology over rGO with high surface area and it fulfills the key requirement of the modified electrode for effective redox reaction. The TEM image of the nanohybrid MnO_2/Ppy/rGO shown in (Fig. 1b) clearly indicates the crystalline nature of nanoparticles with well-defined lattice. It can be seen that rGO sheets have been exfoliated and deurated randomly with MnO_2 and Ppy. Fig. 1c shows the FTIR sepctra of MnO_2/Ppy/rGO nanocomposite displayed the absorption peaks at 721 cm^{-1} and 575 cm^{-1} corresponding to (Mn-O) and (O-Mn-O) vibrations, absorption peaks of Polypyrrole at 3146 cm^{-1}, 1596 cm^{-1}, 1128 cm^{-1} and 787 cm^{-1} represents N-H, C=C, C-N and C-H stretching vibration and bending vibration and 1729 cm^{-1}, 1585 cm^{-1}, 1223 cm^{-1} corresponding to rGO for C=O carboxylic, C=C for aromatic ring C=O alkoxy groups respectively. The XRD patterns of MnO_2/Ppy/rGOin Fig 1d shows the characteristic peaks centered at 32.46º, 37.74º, 54.72º, 65.26º and 25.94º which can be indexed to (101), (121), (530), (002) and (009) crystal planes of MnO_2, rGO respectively. Ppy in which a broad peak centered at at 23.26º can be assigned to the repeated unit of pyrrole ring, inferring that the polypyrrole chain is highly oriented and in amorphous state.

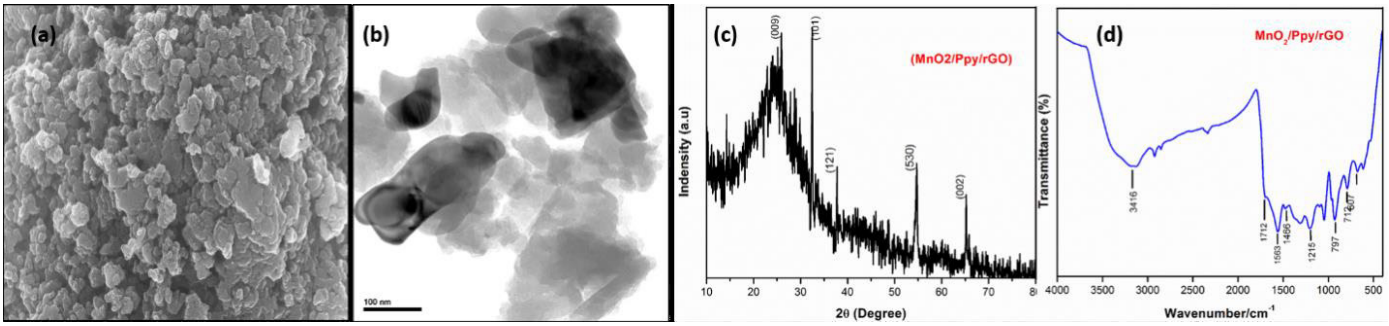

Figure 1 a) and b) FE-SEM and HR-TEM image of MnO_2/Ppy/rGO nanocomposite. c) and d) XRD pattern and FTIR spectrum of MnO_2/Ppy/rGO nanocomposite.

Electrochemical behavior of Methyl parathion

The Cyclic Voltammograms (CVs) of modified MnO_2/Ppy/rGO towards 200 µM MP were shown in Fig. 2a. Fig. 2b represent as difference concentration and scan rate of MP. The catalytic effect of the composite towards MP was investigated though DPV (Fig. 2c) showed a linear enhancement in the peak current for each addition of MP. From the DPV experimental result it is found that the sensitivity of the electrode is 8.229 (± 0.011) µA Mm^{-1} cm^{-2} over the range of 0.5- 10 µM concentration and the Limit of detection (LOD) is 81 nM.

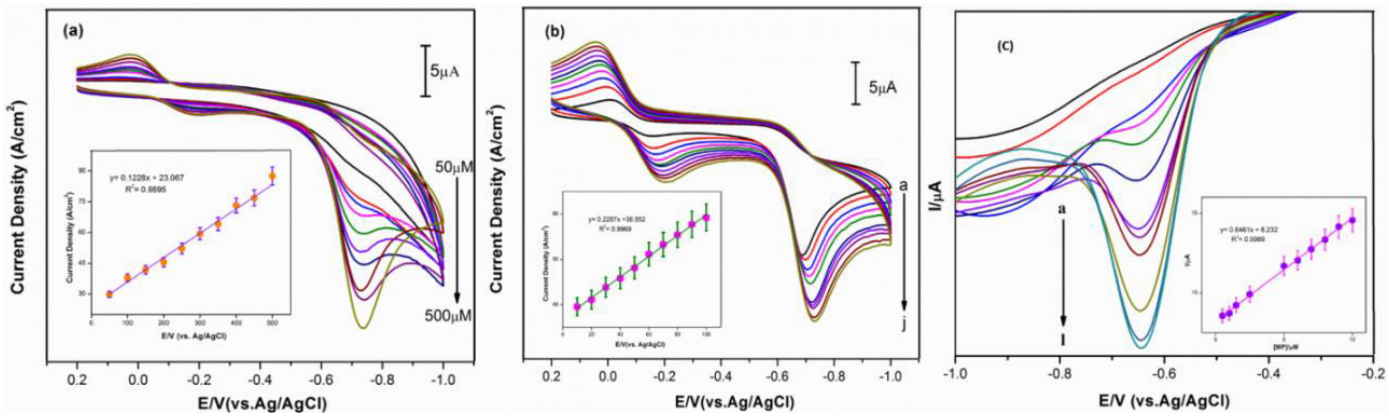

Figure 2 a) and b) CV of MnO_2/Ppy/rGO nanocomposite of different concentration and scan rate of methyl parathion. c) DPV responses of increasing MP concentration.

IV. CONCLUSION

The synergistic effect of nano MnO_2, Ppy and rGO operating on the performance of modified electrode for the detection of MP with control electrode was compared and it is found that the synergistic effect greatly facilitated and the efficiency of the modified electrode MnO_2-/Ppy/rGO was excellent compared to bare GC. The present work will provide lot of insights in the fabrication of sensors leading to wide range of applications to socially relevant problems.

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