

Designing Microbial Sensors based on Synthesis, Characterization and Sensing Application of Nanocomposite Prepared using Nanoparticles and Conducting Polymer

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Abstract—Many types of microbial sensors have been developed as analytical tools. Such a microbial sensor consists of a transducer and a microbe as the sensing element. Originally the microbial sensors lacked in specificity as compared to enzyme sensors or immunosensors, which are highly specific for the substrates of interest, but with advancement of research the specificity of the microbial sensor has been improved significantly by genetic modifications of the microbe used as the sensing element. Microbial sensors have the added advantages of a tolerance to the measuring conditions, a long lifetime, and cost performance. Since their discovery in the mid-1970s, research on conducting polymers (CPs) has become an ever-growing research area in polymer chemistry. The redox behaviour and an unusual combination of the properties of metals and plastics make conducting polymers a preferred class of materials for composite formation. We herein report the synthesis of nanoparticles decorated- graphene oxide sheets by a one-pot solution-based method. Further, polymer was introduced into this nanoparticle decorated graphene oxide sheets to prepare a nanocomposite by electropolymerization using potentiodynamic mode on indium tin oxide electrode. The synthesized nanocomposite was characterized by different techniques such as transmission electron microscopy, scanning electron microscopy, cyclic voltammetry etc. The surface morphology studies show that after introduction of polymers the morphology of prepared material changes. The prepared nanocomposite electrode was further used as genosensor.

Keywords: Sensors, nanoparticles, polymer.

1. INTRODUCTION

Conducting polymers (CPs), have received much from a long period of time due to their strong electrical properties, ease of preparation and good environmental stability, enabling wider application in electronic devices, electrodes for rechargeable batteries and supercapacitors, solid electrolytes for capacitors, sensors and corrosion protection materials [1-5]. In spite, of the several interesting properties, the major drawback is the insolubility of the CPs in common solvents and infusibility

which make them poorly processable either via a solution technique or by melt-processing methods. These material properties can be improved by forming composites or blends with commercially available polymers or inorganic materials, which offer better mechanical and optical properties as well as stability and processability. In this context, graphene oxide (GO) due to its excellent inplane mechanical and thermal properties, outstanding electrical conductivity and cost effectiveness has been widely explored. The presence of oxygen-containing functional groups, such as hydroxyl, epoxide, carbonyl, carboxyl, etc., makes GO hydrophilic in nature which helps it to interact with solvents. Although, GO possesses above mentioned properties, they are electrically insulating in nature due to presence of these functional groups and in order to obtain high electrical conductivity it is necessary to reduce graphene oxide. However, CPs have been reported to be able to act as reducing agents to reduce GO to graphene, thus it eliminates the need for pre or post electrochemical reducing step and decreases the possibility to deal with hazardous chemicals like hydrazine which is normally reported to reduce GO [3]. Hence, being cost effective nanomaterial graphene and their derivatives can act as better substitute as reinforcement or filler material for the preparation of polymer based nanocomposite replacing carbon nanotubes[3].

2. RESULTS AND DISCUSSION

2.1 Methodology for nanocomposite preparation

Graphene oxide (GO) was prepared from natural flake graphite powder by the modified Hummers method [6]. For exfoliation of GO, ultrasonication was performed till the solution appears translucent with no visible particulate [7,8] and then it was heated to 100 °C using condenser. In the typical experiment, 4 mL GO aqueous dispersion containing

0.5 M various CPs prepared in KNO_3 (0.1 M) ultrasonicated to form uniform mixture. Potentiodynamic deposition of GO-CPs, was performed by CV scanning in the potential range of 0-1.2 V vs. Ag/AgCl.

2.2 Growth of conducting polymers on electrode

The CPs nanostructures formation by potentiodynamic method depends on the scan rates of deposition as already reported [9]. Taking this phenomena into consideration, CPs nanostructures formation was first studied by CV cycling from a fixed potential range depending upon the precursor without the addition of GO. Fig. 1 shows the SEM images of pure CPs thin films deposited on ITO at different scan rates, (a) 20 mV/s, (b) 50 mV/s, (c) 100 mV/s, (d) 200 mV/s. From the micrographs, it was observed that the surface morphology of CPs changes from agglomerated nanoflowers to nanostars and then to nanosheets with increase in the scan rate. The surface of polymer films deposited at 20 mV/s scan rates [Fig.1 (a)] shows some agglomerated regularly arranged hexagonal structures giving appearance of some flowers along with some nanocubes. At 50 mV/s scan rates, the polymer film looks much clearer with shapes becoming more clear and bigger and giving appearance of some nanostar type structures [Fig. 1 (b)]. Further on increasing the scan rates upto 100 mV/s [Fig.1 (c)] the formation of stars and cubes appear to disappear and it is observed that long striations appear which further. The surface appears more uniform and the morphology changes to nanosheets. As the scan rate is increased from 100 to 200 mV/s the surface becomes completely smooth [Fig. 1 (d)]. The most probable reason behind gross variation of the structure as the scan rates progresses might be the deposition time. The time for deposition and dissolution of polymer becomes shorter at higher scan rates leading to the formation of nanosheets like structure with much uniformity while the slow scan rates provides more time for deposition, hence dense and packed structures are formed [9].

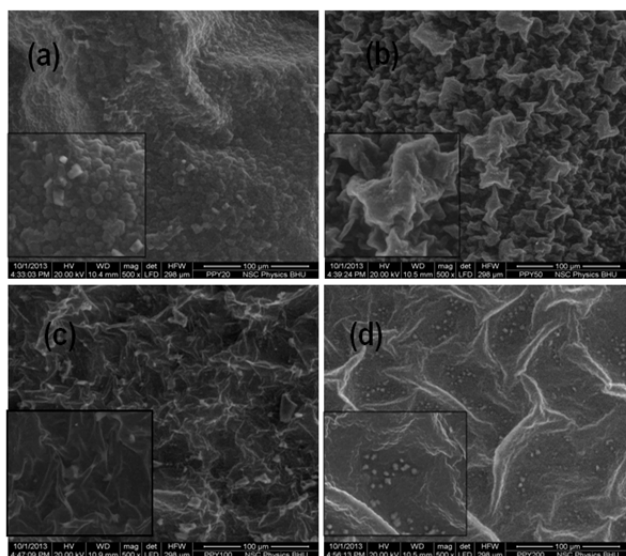


Fig. 1: The SEM image of CP at different scan rates.

2.3 Sensing on prepared nanocomposite films

When GO was added to polymer then sharp increase in peak currents was observed clearly indicating that, the addition of GO acts as a catalyst to promote electron transfer across the electrode and finally results in increased current density. For studying microbial response the pDNA was immobilized on the nanocomposite modified electrode. On immobilization of pDNA, there was a sharp decrease in the peak current with the increase in peak potentials with respect to that of the GO/CPs/ITO electrode. This probably is due to the repeating structure of phosphate backbone which makes the DNA molecules electronegative and thus repulse the $[\text{Fe}(\text{CN})_6]^{3-}$. The other reason behind this phenomenon may be attributed to the long polymer chain of DNA which may experience steric hindrance, and further reduces the electron transport rate resulting in the sluggish electron transport across the bioelectrode. The results on this issue are still under investigation and will be communicated shortly.

3. CONCLUSION

Nanocomposite based sensors employing conducting polymers hold a lot of promise for miniaturization of sensors and preparation of technology which would be cheap. Unlike in larger sensors we find that under normal operating conditions the signal increases with the sensor diameter rather than its volume. This interesting dependence partially negates the signal loss due to the sensor miniaturization. These sensors are capable of detecting very low analyte concentrations for microbes especially pathogens in food and water samples. Further development into technology will reduce the cost of individual sensors and sensors will be more easy to use for the end-users.

4. ACKNOWLEDGEMENT

The author is grateful for financial support from UGC and DBT, India.

REFERENCES

- [1] S. Bose, T. Kuila, M. E. Uddin, N. H. Kim, A. K. T. Lau, J. H. Lee, *Polymer* 2010, **51**, 5921-5928.
- [2] D. G. Shchukin, K. Köhler, H. Möhwald, *J. Am. Chem. Soc.* 2006, **128**, 4560-4561.
- [3] Y. S. Lim, Y. P. Tan, H. N. Lim, W. T. Tan, M. A. Mahnaz, Z. A. Talib, N. M. Huang, A. Kassim, M. A. Yarmo, *J. Appl. Polym. Sci.* 2013, **128**, 224-229.
- [4] N. Attarzadeh, K. Raeissi, M. A. Golozar, *Progress in Org. Coat.* 2008, **63**, 167-174.
- [5] G. J. Li, L. H. Liu, X. W. Qi, Y. Q. Guo, W. Sun, X. I. Li, *Electrochim. Acta* 2012, **63**, 312-317.
- [6] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339-1339.
- [7] I. Tiwari, M. Singh, C. M. Pandey, G. Sumana, *Sens. Actuators, B*, 2015, **206**, 276-283.
- [8] C. Zhu, J. Zhai, D. Wen, S. Dong, *J. Mater. Chem.* 2012, **22**, 6300-6306.
- [9] D. P. Dubal, S. H. Lee, J. G. Kim, W. B. Kim, C. D. Lokhande, *J. Mater. Chem.* 2012, **22**, 3044-3052.