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Graphene Supported Metal Oxide for Non-Enzymatic H_2O_2 Sensing

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The discovery of two-dimensional carbonaceous crystal by Andre Geim and Konstatin Novoselov in 2004 at the University of Manchester opened new paths in various fields around the world [1]. Graphene attracted the researchers around the globe owing to its unique features such as high surface area, high electric conductivity, high flexibility and many more which lead to the announcement of Noble prize in 2010 to its discovers [1]. Graphene serves as an excellent support to host various metal oxides. Graphene offers its massive surface to anchor metal oxides along with preventing the agglomeration of the metal oxide nanoparticles during their assembly in the process of forming the composite [2]. Even the small deviation on the surface of the graphene layer causes significant change in electric conductivity which makes the developed material extremely sensitive to their environment and thus elevating the electrochemical performance of the prepared composites [3]. These two properties make graphene a highly dependable candidate as a support for the active materials in the H_2O_2 sensing.

Iron oxides have gained huge attention in the field of graphene based electrochemical sensors because of the lower cost, recyclability and better catalytic activities. Karimi et al. [4] synthesized Fe_2O_3-rGO composite through self-redox assembly process in the basic medium. The composite displayed linear range of 0.05-9.0mmolL^{-1}, LoD of 6.0μmolL^{-1} with long term stability. Fe_2O_3-rGO is claimed to have better stability and electrochemical activity due to its higher electric conductivity over only Fe_2O_3 without support [5-7]. Ye et al. [8] showed that the size of Fe_3O_4 NPs could be controlled and maintained within 35-45nm with the use of graphene support to anchor Fe_2O_3 NPs. Researchers found that iron oxide displays one of the best synergistic effects with GO as a result better electrochemical output are achievable [9,10].

The increase in the usage of transition metal oxides as the electrode material gained remarkable attention in the scientific community due to their abundance, biocompatibility and low costs. Kong et al. [11] synthesized Co_3O_4-rGO composite through hydrothermal method. The morphology of Co_3O_4 were found to be nano wires which formed web like structure over the graphene surfaces due to the intercalation of nano wires by hydrothermal method. The composite displayed a comparative electrochemical performance against H_2O_2 with a linear range of 0.015-0.675 mM, sensitivity of 1.14mA mM^{-1} cm^{-2}, LoD of 2.4μM. Li et al. [12] synthesized CoOx-rGO composite through electrodeposition technique by electrodepositing CoOx over electrochemically reduced GO. This method provided the homogenous distribution of CoOx NPs over the surface of graphene. The sensitivity of 148.6mA mM^{-1} cm^{-2} and the LoD of 0.2μM were achieved. The enhancement in the electrochemical performance is attributed to the presence of graphene. Electro-deposition technique was found more appropriate for the production of homogenous composites.

The ease of synthesis and handling the researches started synthesizing more composites based on zinc oxides. Salih et al. [13] synthesized ZnO-rGO nanocomposite through simple solution mixing. The microscopic studies revealed the morphology of pieces of leaf ranging from nm-μm. The conjugation between the ZnO and the GO enhanced the electron transfer promoting the electrochemical performance. They also studied the effect of pH on the working condition. The electrochemical studies showed the linear range of 1-15mM and the LoD of 0.8mM with higher sensitivity and long term stability. Palanisamy et al. [14] synthesized ZnO-rGO composite through electrochemical reduction method following 30 successive cyclic voltammetry cycles. Firstly, GO was drop casted onto the glassy carbon electrode and allowed to dry then was immersed into Zn^{2+} solution for electrodeposition. The flower like morphology was obtained for the composite. The linear range of 0.2-8.8μM and sensitivity of 8.50μAμ$M^{-1}$$cm^{-2}$ were obtained.

The use of copper oxide as electro-catalyst for hydrogen peroxide detection is very common as reported in the literature [15-17]. Liu et al. [15] synthesized graphene wrapped Cu_2O nanocubes by chemical reduction method at low temperatures. The composite showed the linear range of 0.3-7.8mM with the LoD being 20.8μM. Kumar et al. [16] synthesized Cu_2O-rGO composite through bio-reduction using mango bark extract. The method showed simultaneous reduction of GO along with the formation of Cu_2O NPs in one pot. They reported the linear range of 0.2 to 400mM, LoD of 42.35nM and sensitivity of 7.435mA mM^{-1}. The improvements in the electrochemical results were mainly attributed to the presence of graphene. Kumar et al. [17] in another work synthesized Cu_2O-rGO composite through two-step electrochemical deposition technique. In the synthetic technique followed they first deposited graphene on the stainless steel substrate over which Cu_2O were anchored. This technique allowed distribution of Cu_2O NPs homogenously over the graphene surface without much agglomeration which greatly enhanced the electrochemical performance. The composite showed the sensitivity and limit of detection of 52.8595μAμ$M^{-1}cm^{-2}$ and 34.32nM, respectively.

Conclusion

In the above discussion various composites where graphene was used as a support for metal oxides was discussed in detail. Various strategies undertaken by researchers for achieving better electrochemical performance were also highlighted in brief. Researchers around the globe affirmed the importance of graphene as a support for metal oxides in enhancing electro-catalysis and achieving homogeneity in the composition.

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