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Nanocomposites of sulphur-nitrogen co-doped graphene oxide nanosheets and cobalt mono carboxyphenoxy phthalocyanines for facile electrocatalysis

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ABSTRACT

Nanocomposites consisting of cobalt mono carboxyphenoxy phthalocyanine (CoMCPhPc) either covalently linked to graphene oxide nanosheets (GONS), sulphur doped graphene oxide nanosheets (SDGONS), nitrogen doped graphene oxide nanosheets (NDGONS) or sulphur/nitrogen co-doped graphene oxide nanosheets (SNDGONS) or sequentially added were used to modify glassy carbon electrode. The modified electrodes were characterised using several techniques: voltammetry, X-ray photon spectroscopy and scanning electron spectroscopy before testing their activity on the detection of hydrogen peroxide at pH 7. The presence of SNDGONS had a significant improvement on the currents as compared to CoMCPhPc modification alone in both sequentially added or covalently linked to MPcs. CoMCPhPc-SNDGONS(seq)-GCE and CoMCPhPc-SDGONS(linked)-GCE resulted in impressive limits of detection and catalytic rate constant values of 1.58 nM and 5.44 nM, 3.07×10^5 M^{-1} s^{-1} and 3.01×10^3 M^{-1} s^{-1} respectively. Gibbs energy value was determined to be -21.22 kJ mol^{-1} for CoMCPhPc-SNDGONS(linked)-GCE indicative of a facile spontaneous electroreduction reaction on the surface of this electrode.

1. Introduction

Graphene oxide nanosheets (GONS) are quasi-two dimensional sp^2 carbon skeleton characterised by basal oxygen moieties (hydroxyl, carboxylates, epoxy) [1–3]. The carboxylate groups located on GONS are used in this work to form covalent bonds with established electrocatalysts (metallophthalocyanines, MPcs) and applied towards electrocatalytic sensing of hydrogen peroxide. The incorporation of guest atoms with different electronegativities into GONS improves their electronic and electrocatalytic properties [4,5]. Boron, sulphur, nitrogen and phosphorus have been successfully incorporated into GONS [4–8]. It has been reported that co-doped (with hetero atoms) graphene oxide gives higher current densities [9,10].

On the other hand, MPcs are well documented for their excellent electrocatalytic activity towards the detection of a myriad of analytes including nitrites [11], hydrogen peroxide [6,12,13] and hydrazine [14,15] among others. In our recent work we have shown that the sequential modification of glassy carbon electrodes by heteroatom doped graphene oxide nanosheets and phthalocyanines results in enhanced detection of hydrogen peroxide [8,16,17]. In the reported work, phthalocyanines were adsorbed onto GONS for electrocatalysis. Also reduced GONS with less oxygen functionalities were employed. Reduced GONS show improved electrocatalytic activity compared to when they are not reduced. In the current work, GONS (not reduced, hence having higher oxygen functionalities) are chemically linked to an MPc for the first time. The effect of linking the MPc to GONS is evaluated compared to when adsorbed without linking. S/N co-doped GONS are employed in this work. Individual graphene nanosheets highly agglomerate, limiting their electrochemical utilization. The presence of MPcs in the GONS structure may reduce aggregation.

Chen and co-workers reported that platinum functionalization of GONS resulted in a three dimensional channel [1], brought forth by the disruption of the stacking between the GONS, as postulated by Qin and co-workers [18]. This led to improved electrocatalytic activity. Phthalocyanine functionalization reported in the current work, may therefore result in three dimensional graphene nanosheets that have open channels for the electrolyte hence exposing more catalytic centres for electrocatalysis on the modified glassy carbon electrode. This work therefore aims at demonstrating the effect of co-doping and covalent linkage of GONS to an MPc on the overall detection protocol for hydrogen peroxide.

A monosubstituted CoPc derivative is employed due to specificity to the binding site [19,20]. Hydrogen peroxide is used as a test analyte due to its physiological and environmental significance [21,22]. Probes of this nature have potential application as indirect glucose sensors.

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