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# Electrode modification using nanocomposites of boron or nitrogen doped graphene oxide and cobalt (II) tetra aminophenoxy phthalocyanine nanoparticles

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Reduced graphene oxide nanosheets (rGONS), reduced boron doped graphene oxide nanosheets (rBDGONS) and reduced nitrogen doped graphene oxide nanosheets (rNDGONS) and their composites with cobalt tetra aminophenoxy phthalocyanine nanoparticles (CoTAPhPc**NP**) were employed towards the detection of hydrogen peroxide. The nanomaterials were characterized by absorption spectroscopy, transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, linear sweep voltammetry and cyclic voltammetry. rNDGONS showed excellent electrooxidation and electroreduction of hydrogen peroxide supported by superior surface coverage values. The inclusion of nanosized Pc significantly lowered the reduction overpotential. CoTAPhPc**NP**-rNDGONS-GCE gave a sensitivity of 39.30 mA/M, catalytic rate constant of $1 \times 10^3$ $M^{-1}$ $s^{-1}$ and a detection limit of 8.2 nM. An adsorption equilibrium constant and Gibbs free energy of $1.26 \times 10^3$ $M^{-1}$ and $-17.69$ kJ $mol^{-1}$ respectively were observed.





## 1. Introduction

Research into carbon based materials is increasing due to their potential applications in areas including as sensors, in electrocatalysis, fuel cells, photovoltaic cells and supercapacitors [1–7]. These applications are as a result of easy tunability of the carbon based materials [8,9], hence control of their electronic, chemical and optical properties [10,11]. Graphene is a two dimensional material consisting of $sp^2$ hybridised carbons [10,12,13] hence rich in delocalised electrons which can be exploited for electrical conduction. Graphene has been considered one of the most promising materials for a variety of applications [13]. Heterogeneous atoms such as sulphur, boron and nitrogen can be chemically doped into graphene with relative ease, enabling the change of the chemical behaviour of the material to suit the intended and more diverse applications [10,13–15]. While doping graphene oxide with either boron or nitrogen has been reported, and reduction is said to occur concurrently, this work is the first report where further reduction after doping is undertaken. Nitrogen doping of graphene is important for electrocatalysis since nitrogen atoms can donate electrons to the conjugated system of graphene, making electrocatalysis more favourable [3]. Even though N-doped graphene has attracted most of the attention and research, more recently, B-doped graphene has also been reported to efficiently catalyze reactions such as oxygen reduction [16]. Hence, the comparative effects of B and N doped graphene systems on the electrocatalytic detection of hydrogen peroxide by a phthalocyanine are reported in this work.

Metallophthalocyanines (MPcs) are well known electrocatalysts especially when the central metal is electro active [17]. In this work we describe for the first time the electrocatalytic behaviour of composites of reduced nitrogen (rNDGONS) or reduced boron ( rBDGONS) doped graphene oxide nanosheets with nanosized cobalt tetra amminophenoxy phthalocyanine (CoTAPhPcNP) towards the oxidation of hydrogen peroxide, and compared to the effects of reduced graphene nanosheets (rGONS) which are not doped. It has been previously shown that nanosized MPc molecules have better electrocatalytic properties [18] than their bulk counterparts hence our choice in this work. Co is chosen as a central metal due to the well known electrocatalytic activity of CoPc derivatives. Aminophenoxy substituent was chosen due to its bulky nature which will prevent aggregation. Even though

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