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Characterization and Electrocatalytic Activity of Nanocomposites Consisting of Nanosized Cobalt Tetraaminophenoxy Phthalocyanine, Multi-walled Carbon Nanotubes and Gold Nanoparticles

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Abstract: Glassy carbon electrodes were modified with composites containing cobalt tetraaminophenoxy phthalocyanine nanoparticles (CoTAPhPc**NP**), multi-walled carbon nanotubes (MWCNT) and gold nanorods (AuNRs). The modified electrodes were studied for their electrocatalytic behavior towards the reduction of hydrogen peroxide. Phthalocyanine nanoparticles significantly improved electron transfer kinetics as compared to phthalocyanines which are not in the nanoparticle form when alone or in the presence of multiwalled carbon nanotubes (MWCNTs). CoTAPhPc**NP**-MWCNT-GCE proved to be suitable for hydrogen peroxide detection with a catalytic rate constant of 3.45×10^{3} $M^{-1}s^{-1}$ and a detection limit of 1.61×10^{-7} M. Adsorption Gibbs free energy ΔG^{o} was found to be -19.22 kJ mol^{-1} for CoTAPhPc**NP**-MWCNT-GCE.

Keywords: cobalt tetraaminophenoxy phthalocyanine nanoparticles · gold nanoparticles · multi-walled carbon nanotubes · hydrogen peroxide · electrocatalytic reduction

1 Introduction

Modification of the inexpensive electrode material with nanoparticles such as gold nanoparticles (AuNPs) can lead to a large surface area-to-volume ratio [1]. AuNPs enable fast electron-transfer kinetics and decrease overpotentials for electrochemical reactions [2], hence are employed in this work. AuNPs (alone or as composites) have been employed for the detection of a variety of analytes including hydrogen peroxide, hydrazine and nitrite [3–7]. On the other hand, the recent intense interest in the carbon based nanomaterials such as multiwalled carbon nanotubes, MWCNTs) has also made a significant impact in the electrocatalytic detection of a wide range of analytes of environmental [8,9] and biomedical importance [10,11], as well as oxygen reduction reactions [12] among others. Carbon nanotubes promote electron transfer in electrochemical reactions and improve sensitivity [8,9], hence are employed in electrode modification in this work.

Phthalocyanines (Pcs) are well known electrocatalysts [6–8,13–15]. Transforming Pcs into nanoparticles has recently opened a new interest in the electrocatalytic detection of a number of physiologically important molecules [16–19]. Phthalocyanine nanoparticles have been reported [17] to show improved electrocatalytic behaviour compared to their bulk counterparts due to increased surface area.

In this work we explore glassy carbon electrode modification using nanocomposites containing cobalt tetraaminophenoxy phthalocyanine (structure shown in Scheme 1) nanoparticles, multi-walled carbon nanotubes and/or gold nanoparticles. A nanocomposite containing CoPc (not in nanoparticle form), spherical gold nanoparticles and MWCNTs has been reported for the detection of kanamycin [20]. This is the first time that a nanocomposite consisting of MWCNTs, Pc nanoparticles, and rod shaped gold nanoparticles is prepared for electrocatalysis. Goldnanorods (AuNRs) were selected instead of spherical nanoparticles, since the former are known to show better electrocatalysis [21]. Cobalt is employed as a central metal due to the well-known [13] electrocatalytic activity of CoPc derivatives, and converting Pc into nanoparticles improves electrocatalysis as stated above [17]. The phenoxy substituents were employed since they are bulky and may reduce aggregation. Hydrogen peroxide is employed as test analyte since its detection on Pc electrode is known [13,14]. Also hydrogen peroxide is an important physiological and pharmaceutical molecule, hence making its detection of paramount importance [22].

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