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Full Length Article

"Turn on" fluorescence enhancement of Zn octacarboxyphthaloyanine-graphene oxide conjugates by hydrogen peroxide

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ABSTRACT

Zn octacarboxy phthalocyanine-reduced graphene oxide or graphene oxide conjugates were characterized by absorption spectroscopy, transmission electron microscopy, fluorescence spectroscopy, X-ray diffraction, thermo gravimetric analysis and X-ray photon spectroscopy. The presence of reduced graphene oxide or graphene oxide resulted in the quenching (turn on) of Zn octacarboxy phthalocyanine fluorescence which can be explained by photoinduced electron transfer. Zn octacarboxy phthalocyanine-reduced graphene oxide or graphene oxide conjugates "turned on" fluorescence showed a linear response to hydrogen peroxide hence their potential to be used as sensors. The nanoprobe developed showed high selectivity towards hydrogen peroxide in the presence of physiological interferences.

1. Introduction

Phthalocyanines (Pcs) have a wide range of applications. The current and potential applications of phthalocyanines (Pcs) are as a result of their overall stability and exceptional electronic properties [1,2]. These applications include as non-linear optical (NLO) materials [3], dyes and pigments [1,2], photosensitizers in photodynamic therapy [4–6], and components of organic photovoltaic cells [7–9]. Phthalocyanines have also been employed as "turn on" fluorescence sensors in the presence of quantum dots [10,11]. Reduced graphene oxide nanosheets (rGONS) have been employed as fluorescence quenchers of Pcs, with fluorescence being "switched on" in the presence of a gas [12]. However fluorescence sensing of analytes in solution of conjugates of Pcs with graphene oxide has not been reported. Hence this is the aim of this work.

Graphene oxide is a two dimensional sp^2 hybridised nanomaterial which acts as a zero band gap conductor and a highly efficient fluorescence quencher. It quenches fluorescence of molecules such as Pcs as a result of photoinduced electron transfer (PET) where the graphene moiety acts as an electron acceptor and the Pc as an electron donor [13,14] in the excited state and the reverse in the ground state [13]. The quenching though is not permanent and can be restored in the presence of analytes in a fluorescence "turn on" process. This restoration of fluorescence can be exploited for the measurement of different metal ions in environmental samples [14]. Analytes can interact with graphene oxide nanosheets (GONS) functional groups, obstructing the electron transfer between GONS and the Pc, hence restoring the fluorescence of the Pc. The obstruction is as a result of the analyte acting as a spacer between the fluorescent species (Pc) and the quencher (GONS) [13].

In this work we use Zn octacarboxy phthalocyanine (ZnOCPc) which will interact with either rGONS and GONS through π-π stacking. ZnOCPc was chosen due to its lack of aggregation [15] and high solubility. The conjugates are employed for sensing of hydrogen peroxide. H_2O_2 is a reactive oxygen species (ROS) and a by-product of many metabolic reactions. There is need to detect H_2O_2 because excessive production beyond the physiological range often leads to oxidative stress [16]. Several methods have been used for the determination of H_2O_2, these methods include spectrophotometry [17], chromatography [18], chemiluminescence [19] and electrochemistry [18,20,21]. Electrochemistry has been a preferred method due to low detection limits for hydrogen peroxide detection. However electrochemical methods suffer from interference from oxygen reduction and high overpotentials.

An ideal fluorescent probe must show selectivity. Hence, we investigated the selectivity of the proposed ZnOCPc-GONS/rGONS fluorescence sensor towards H_2O_2 in the presence of excess of co-existing biologically active species such as cysteamine (cys), glutathione (GSH), urea, NO_2^-, NO_3^-, L-cysteine (L-cys) and tert-butyl hydroperoxide (TBHP).

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