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Development of quantum dot-phthalocyanine integrated G-quadruplex /double-stranded DNA biosensor

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ABSTRACT

In the present study, the phthalocyanine (**Pc**) integrated mercaptopropionic acid capped quantum dot (**mpa@QD**) biosensor has been developed for the quantitative determination of G-quadruplex and double-stranded DNA. The working principle of the developed biosensor platform is based on the quenching of the emission signal of the **mpa@QD** in the presence of **Pc** (closed position) and the recovery of the fluorescence signal in the presence of DNA (open position). The parameters affecting biosensor performance, such as **Pc** type and concentration, were optimized. Since the developed biosensor aimed to determine G-quadruplex and double-stranded DNA in biological samples, the effect of common ions (such as Na^{+}, Mg^{2+}) and serum albumin found in many biological matrices on the biosensor performance were examined. The effect of common ions on biosensor signal was negligible, except Zn^{2+}. The analytical properties of the biosensor, such as linear range, calibration sensitivity, relative standard deviation %, the limit of detection, and quantification, were determined. The limit of detection and quantification values were found 0.055 μM and 0.18 μM for **AS1411**, 0.061 μM and 0.20 μM for **Tel21**, 0.038 μM and 0.13 μM for **Tel45** and 0.091 μM and 0.30 μM for **ctDNA**. Several different synthetic samples were prepared. The spiked synthetic samples such as mammalian cell medium were used to evaluate the analytical performance of **Pc-mpa@QD**. All synthetic samples were prepared with polyethylene glycol, which resembles biological samples' crowded environment.

1. Introduction

Quantum dots are often called fluorescent semiconductor nanocrystals consisting of groups II-VI, III – V, or IV metals in the periodic table. These attractive nanocrystals smaller than 10 nm in size were first discovered in a glass matrix by Alexey Ekimov in 1981. Louis Brus synthesized the first colloidal semiconductor nanocrystal solution four years later. QDs have unique structural, electrochemical, and photochemical properties [1]. These zero-size nanomaterials can be easily functionalized through surface modifications [2]. They are conjugated via a bridge or directly electrostatically and covalently. QDs can be dispersible in water by coating with functionalized silica, phospholipid micelles, and binders, such as mercaptoacetic acid, dihydrolipoic acid, or amphiphilic polymers [3,4]. Quantum dots provide several advantages over conventional fluorescent organic dyes in terms of narrow emission spectra, high fluorescence intensity, high quantum efficiency, adjustable excitation spectra, and photo-stability. These unique materials are used in fluorescence probing, imaging, and sensing applications with their size-dependent strong photoluminescence in different areas, such as the production of light-emitting diodes and solar cells [5–9].

QDs are considered promising fluorescent probes for a wide variety of analytes. Adegoke and Nyokong investigated many different QDs decorated with a variety of molecules for the determination of inorganic and organic biologically important analytes such as mercury [10], floride [11], and cysteamine and t-butylhydroperoxide, GSH, $HClO_4$ and ·OH radical [12]; bromide [13], peroxynitrite [14], H_2O_2 [15], superoxide anion [16] and hydroxyl radical [17]. The biomedical imaging applications of quantum dots are also widely employed [18]. QD-based probes were used for the first time in 1998 for *in vitro* biological imaging. Wu et al. have been developed QDs linked to immunoglobulin G (IgG) and streptavidin to label the breast cancer marker Her2 on the surface of fixed and live cancer cells, to stain actin and microtubule fibers in the cytoplasm, and to detect nuclear antigens inside the nucleus [19]. QD-based fluorescent probes are also gaining importance for monitoring the interactions of various cellular proteins. Jaiswal et al. have been developed specific protein tagging approaches based on QD to label

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