



The interaction between graphene quantum dots grafted with polyethyleneimine and Au@Ag nanoparticles: Application as a fluorescence “turn-on” nanoprobe



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ABSTRACT

Graphene quantum dots grafted with polyethyleneimine (GQDs-PEI) and Au@Ag core-shell nanoparticles blend was demonstrated to be a novel biosensing nanoprobe for the rapid and highly sensitive detection of biothiols such as cysteine (Cys), homocysteine (Hcys) and glutathione (GSH). The fluorescence emission of GQDs-PEI was quenched efficiently upon interaction with Au@Ag core-shell nanoparticles. The quenched fluorescence emission of the GQDs-PEI was restored in the presence of the biothiols. The fluorimetric sensing is based on the strong affinity between the mercapto (SH) groups of the biothiols and the Au@Ag core-shell nanoparticles by which the interaction between GQDs-PEI and Au@Ag core-shell nanoparticles was disrupted with a consequent modulation (‘turn-on’) of the quenched GQDs-PEI emission. Thus, a new, simple, rapid and highly sensitive fluorescence nanoprobe for detecting biothiols has been developed in this work.

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1. Introduction

Graphene quantum dots (GQDs) are carbon-based nanomaterials with excellent photoluminescence properties [1], hence have drawn a lot of attention for use as optical and fluorescence nanoprobe [2]. The photoluminescence properties of GQDs are determined by physical and chemical interactions taking place at their surfaces and edges. Such interactions may lead to either fluorescence quenching or enhancement [3–5].

The interactions of GQDs with biomolecules such as DNA, amino acids, cytochrome c, biothiols and melamine have been reported [6–10]. Also, GQDs have been grafted with polymers such as polyethylene glycol (PEG) and polyethyleneimine (PEI) to modify their surface and edge states in order to introduce desired functionality [11,12]. PEI is an organic polymer that has a high density of amino groups that can be protonated to give polycations [13]. The grafting of GQDs with PEI introduces positive charges on the surface of GQDs [11] and is an excellent surface passivation agent; hence it is employed in this work. However, to date the fabrication of a nanosensor based on GQDs grafted with polymers has not been reported. In this study, we report for the first time on the fabrication of a fluorescence “turn-on” nanoprobe composing

of GQDs-PEI and Au@Ag core-shell nanoparticles for sensing. The fluorescence of the grafted GQDs is “turned off” by Au@Ag nanoparticles (NPs), and “turned on” by analytes. In this work we use biothiols as test analytes due to the presence of thiol groups. Strong metal-thiol (Ag-S and Au-S) bonds are expected to be formed between the biothiols and the Au@Ag nanoparticles.

Core-shell and alloy bimetallic nanoparticles are interesting because they provide opportunities to tune the optical properties of individual metal nanoparticles [14,15]. The bimetallic core-shell nanoparticles with combined properties of individual metallic elements are more interesting than single metallic nanoparticles [16].

The design and synthesis of nanoensembles or nanoprobe capable of binding and sensing biological molecules (biomolecules) selectively has attracted much attention in recent years because of the fundamental roles played by biomolecules in human systems and in chemical and environmental processes [17]. Among the biologically important molecules, biothiols are of particular interest due to the fact that biothiols (such as L-cysteine (Cys), DL-homocysteine (Hcys) and glutathione (GSH)) (which are used as examples in this work) are key players in cellular functions and take part in various redox reactions reversibly. The optical and fluorescence techniques developed so far for the detection of biothiols include; bovine serum albumin (BSA)-Ag nanoclusters, graphene oxide-Ru-DNA complex, GQDs-Hg²⁺ blend (not suitable for bio-applications due to Hg²⁺), G-quadruplex, carbon nanodots,

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