



Fluorescence behavior of glutathione capped CdTe@ZnS quantum dots chemically coordinated to zinc octacarboxy phthalocyanines

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ARTICLE INFO

Article history:

Received 2 August 2012

Received in revised form

1 November 2012

Accepted 26 November 2012

Available online 3 December 2012

Keywords:

Glutathione

Zinc octaphthalocyanine

Quantum dots

Fluorescence energy transfer

ABSTRACT

Core-shell CdTe@ZnS quantum dots capped with glutathione (CdTe@ZnS–GSH) were covalently linked to zinc octacarboxy phthalocyanine (ZnPc(COOH)₈). The conjugate was characterized by UV/Vis, infrared and X-Ray photoelectron spectroscopies as well as transmission electron and atomic force microscopies. The fluorescence quantum yields of the core CdTe capped with thioglycolic acid increased upon formation of the core-shell. Upon conjugation with ZnPc(COOH)₈, the fluorescence quantum yield of CdTe@ZnS–GSH decreased due to energy transfer from the latter to the Pc. The average fluorescence lifetime of the CdTe@ZnS–GSH QD also decreased upon conjugation from 26.2 to 13.3 ns.

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1. Introduction

Quantum dots (QDs) are of interest for both research and practical applications because of their high surface-to-volume ratio and their quantum confinement [1]. CdTe quantum dots are relatively easy to synthesize but are toxic due to the presence of Cd. Encapsulating core CdTe QDs into an inorganic shell such as ZnS [2], as used in this work (denoted as CdTe@ZnS) and ZnO [3] have been reported to reduce the toxicity. It has also been indicated that the fluorescence quantum yields improve once the shell is deposited around the core [4]. Peptides such as glutathione (GSH) are reported [5] as excellent ligands for coating the surface of QDs which enables the coordination of other biologically and medically important molecules such as phthalocyanines. Thus in this work we study the photophysical behavior of core: CdTe capped with thioglycolic acid (denoted as CdTe–TGA) and core-shell: CdTe@ZnS capped with L-glutathione (GSH) (represented as CdTe@ZnS–GSH) when linked or mixed with phthalocyanines (Pcs).

Energy transfer from QDs to different phthalocyanine photosensitizers (where the two components are mixed together) has been demonstrated in a number of studies [6–13] through a process called Förster Resonance Energy Transfer (FRET). Conjugating Pcs to QDs results in the production of ¹O₂ via the FRET route. Singlet oxygen is the main species involved in applications

where phthalocyanines are used as photosensitizers for example in photodynamic therapy [14]. In most FRET studies quantum dots have been mixed with phthalocyanines without a covalent bond, only a few studies have been conducted on QDs covalently linked to phthalocyanines. These include the coordination of SiPc with CdSe core QDs through axial ligation [11] and our recent reports of covalent linking of QDs to symmetrically substituted Zn (ZnTAPc) and In (InTAPc) tetraamino phthalocyanines [12]. Linking the QDs to peripherally unsymmetrically ring substituted phthalocyanines has also been reported by our group [13]. All the reported work relating to coordination of QDs to phthalocyanines involved linking carboxy groups on the capping of QDs to the amino groups on the phthalocyanines. The Pc complexes reported for coordination of QDs were not soluble in water. In this work we take advantage of the presence of amino groups on GSH to coordinate the QDs to ZnPc(COOH)₈ via the COOH group of the latter. The ZnPc(COOH)₈ complex (See Scheme 1) is water soluble and not aggregated in aqueous media. The potential application of the conjugates in biological media is made more realistic by the fact that the QDs are also soluble in water. Zn was chosen since ZnPc complexes are good photosensitizers for many applications such as photodynamic therapy [14]. The linking agent N–N'-dicyclohexylcarbodiimide (DCC) was employed for catalyzing the formation of the amide bond between the carboxylic acid of ZnPc(COOH)₈ and the amino group of GSH (represented as CdTe@ZnS–GSH–ZnPc(COOH)₈–linked). Experiments were also performed where QDs were mixed with ZnPc(COOH)₈ without chemical bond formation (represented as CdTe@ZnS–GSH–ZnPc(COOH)₈–mixed).

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