Quenching Effect of Quantum Dots on Bovine Serum Albumin

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Abstract
Due to their unique optical properties, quantum dots (QDs) are rapidly revolutionizing many areas of medicine and biology. Despite the remarkable speed of development of nanoscience, relatively little is known about the interaction of nanoscale objects with organism. In this paper, the interaction between bovine serum albumin (BSA) and water soluble CdTe quantum dots modified with different ligands (3-mercaptoacetic acid (MPA), thioglycolic acid (TGA) and glutathione (GSH)) was studied using the fluorescence (FL) spectroscopy.

Fluorescence (FL) quenching efficiency and the aspect of quenching mechanism of the BSA by QDs were studied. CdTe QDs were prepared in aqueous phase using MPA, GSH or TGA as a stabilizer [1], resulting in the linkage of the thiol groups to the surface of CdTe QDs by SH-Cd coordination, while the functional carboxylic group is free, which can be easily coupled to biomolecules with amino groups, such as proteins, peptides or amino acids [2]. BSA absorption spectrum shows absorption peak in UV region at 280 nm, and FL peak at 328 nm. The fluorescence intensity of BSA was quenched accompanied by a slight blue shift of the maximum emission wavelength with increasing concentration of CdTe QDs as can be seen in Figure 1 – Figure 3. These figures represent the emission spectra of MPA-QDs conjugation (GSH-QDs, TGA-QDs, respectively) with BSA via covalent interaction (EDC and NHS were used as coupling agents). The blue shift here indicated that tryptophan residue (BSA component) was in more hydrophobic environment due to the tertiary structural change of albumin. The intrinsic reason for this change might lie in the more flexible conformation of albumin adsorbed on the NPs surface, which favored the access of tryptophan residues to the bulk surface of QDs [3].

The FL quenching is known to occur due to excited state reactions, energy transfer, collisional quenching (dynamic quenching) and complex formation (static quenching). The last two processes are mainly considered. Both dynamic quenching and static quenching reveal the connection of linearity between relative FL intensity (F₀/F) and QDs concentration [4]. The quenching of BSA FL by QDs can be described by Stern-Volmer equation:

\[
\frac{F_0}{F} = 1 + K_{SV}[Q]
\]

where \(F_0\) and \(F\) are FL intensity of BSA in the absence and presence of QDs, respectively, \([Q]\) is QDs concentration and \(K_{SV}\) is the Stern-Volmer quenching constant. The \(F_0/F\) ratios were calculated and plotted against quencher concentration. After linear fit, \(K_{SV}\) were calculated from the slope of the plots [5]. The results show that the quenching constant \(K_{SV}\) is variant with different type of QDs and the higher \(K_{SV}\) is, the higher is the quenching effect [6].

The FL intensity decreased more significantly in the case of GSH-QDs than in the case of MPA-QDs or TGA-QDs. These results indicated that QDs can effectively quench the FL of BSA in a ligand-dependent manner. Structurally, this is due to the presence of NH₂ and COOH groups in the QDs capping agent, namely MPA (1 × COOH group); GSH (3 × NH₂ and 2 × COOH groups) and TGA (1 × COOH group). Therefore hydrogen bonds can be easily formed between GSH-QDs and BSA. In other words, the number of amino-groups can strongly influence the interactions between BSA and QDs capped with GSH. Therefore, the order of interactions between BSA and QDs is as follows: TGA-QDs < MPA-QDs < GSH-QDs.

References

Figures

Figure 1. Emission spectra of BSA capped MPA-CdTe QDs (a), GSH-CdTe QDs (b) and TGA-CdTe QDs (c) via covalent interaction at various QDs concentration.

Figure 2. Stern-Volmer plot of BSA FL quenching effect caused by CdTe QDs covalently conjugated with BSA.

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