

FRET-Enhanced Singlet Oxygen Generation by Nanocomposites Based on Ternary AgInS₂/ZnS Quantum Dots and Porphyrin Derivatives

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Extended Abstract

Recently, ternary I-III-VI chalcopyrite-type quantum dots (QDs), such as CuInS₂, AgInSe₂, and AgInS₂, have attracted considerable interest as a less toxic alternative to conventional Cd- and Pb-based binary semiconductor nanocrystals [1]. Due to their non-toxicity and unique photophysical properties, namely, direct bandgap, high photoluminescence quantum yield in the visible and near-infrared regions, and long photoluminescence lifetimes of hundreds of nanoseconds [2], ternary QDs have emerged as promising materials for a wide range of biomedical applications, including bioimaging, biosensing, and photodynamic therapy (PDT) [3]. For example, ternary QDs can be conjugated with conventional PDT molecular agents to expand their excitation range and increase the efficiency of singlet oxygen (SO) generation [4] through the formation of an additional non-radiative energy relaxation channel associated with Förster resonance energy transfer (FRET) [5]. Detailed analysis of the spectrally-resolved dynamics of FRET between ternary QDs and molecular agents can provide insights into the mechanisms of FRET-assisted SO generation and elucidate the optimized parameters for the formation of novel ternary QD-based nanocomposites for PDT.

In this study, biocompatible water-soluble nanocomposites based on hydrophilic ternary AgInS₂/ZnS QDs and hydrophobic tetraphenylporphyrin (TPP) molecules incorporated into a polymer matrix have been prepared. The analysis of the optical properties of the nanocomposites by steady-state photoluminescence and UV-VIS spectroscopy reveals that an effective sensitization of the TPP emission in the presence of QDs takes place, at the same time, the efficiency of this process decreases with further increase of TPP:QD molar ratio. To explain this phenomenon, we estimate the fraction of non-luminescent aggregates of TPP molecules within the nanocomposite and demonstrate that the TPP of concentration lower than 10⁻⁶ M remains completely in the monomeric form in a part of a nanocomposite, while the increase of concentration to 2.5 · 10⁻⁶ M causes TPP aggregation, reducing the number of molecular monomers to about 88%. It should be noted that the aggregation of porphyrin molecules leads to the loss of their ability to generate SO due to the increase in the non-radiative rate [6]. Therefore, the nanocomposites with optimized TPP:QD molar ratio value have been used for further FRET efficiency analysis. The photoluminescence kinetics of the nanocomposites has been studied by time-correlated single photon counting fluorescence microscopy (PicoQuant, Germany). Bandpass filters with a full width at half maximum of 10 nm were employed to selectively detect the emission in a wavelength range corresponding to the photoluminescence spectrum of the nanocomposites. With this approach, we analyze the spectrally-resolved FRET dynamics within the nanocomposites taking into account the change in the photoluminescence lifetime of QDs in the presence of TPP. It has been shown that the average efficiency of FRET from the QD radiative transition in the short-wavelength region of the photoluminescence spectrum is approximately 25%, while for the transition corresponding to the peak position of the spectrum this value exceeds 35%. To further evaluate the FRET-mediated enhancement of SO generation, we have tested the formed nanocomposites on *Bacillus subtilis* bacteria and observed the improved antibacterial activity as compared to the free TPP molecules.

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