Conference Paper

Organic–Inorganic Hybrid Nanosystems for Photodynamic Therapy

Rakovich Yu.P.[1,2]

[1]Materials Physics Center, University of the Basque Country, IKERBASQUE, Donostia-San Sebastián, Spain
[2]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia

Abstract

The purpose of this study is to investigate the possibility of improving the efficiency of a photosensitizer utilizing colloidal semiconductor quantum dots as light-harvesting nanoantenna and reveal the mechanism of this enhancement.

Keywords: quantum dots, photosensitizer, photodynamic therapy, FRET, charge transfer

Corresponding Author:
Rakovich Yu.P.
Yury.Rakovich@gmail.com

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1. Introduction

Photodynamic (PD) therapy takes advantages of light absorption by light-sensitive photosensitizers and the generation of photochemical species such as singlet oxygen ($^1O_2$) or other reactive oxygen species (ROS) linked to apoptosis or necrosis of cancerous cells.[1] One of the necessary conditions for the efficient generation of ROS is wavelength matching of excitation wavelength to optical absorption of a photosensitizer.[2]

Upon last decades, there have been a lot of research activities directed toward the development of PD complexes based on different nanomaterials which are able to expand the excitation spectral region beyond the absorption of a photosensitizer and to enhance the efficiency of ROS generation.[3] Among others, semiconductor quantum dots (QDs) are highly attractive for PD therapy applications. QDs benefit from an extended absorption spectrum and high extinction coefficient both of which make them perfect as highly efficient light harvesting energy donors in complexes with PD molecules.[4, 5]

In this report we focus on recent investigations into the enhancement of photodynamic properties of a photosensitiser using colloidal QDs.

2. Materials and Methods

As a photosensitizer we used organic dye methylene blue (MB) that has been extensively used for a variety of photochemical and medical applications, including PD therapy. Highly absorptive and luminescent CdTe QDs with size of 3.3 nm were utilized as an inorganic constituent of formed hybrid nanosystem. MB and QDs stock solutions were mixed to give solutions with specific QDs:MB ratios (see Figure 1). For every ratio absorption and photoluminescence (PL) spectra, and time-resolved PL decays were measured. Absorption spectra were recorded on a Varian Cary50 spectrophotometer. Steady-state photoluminescence measurements were carried out using a Varian CaryEclipse Spectrophotometer. PL decays were measured using a PicoQuant MicroTime200 set-up.

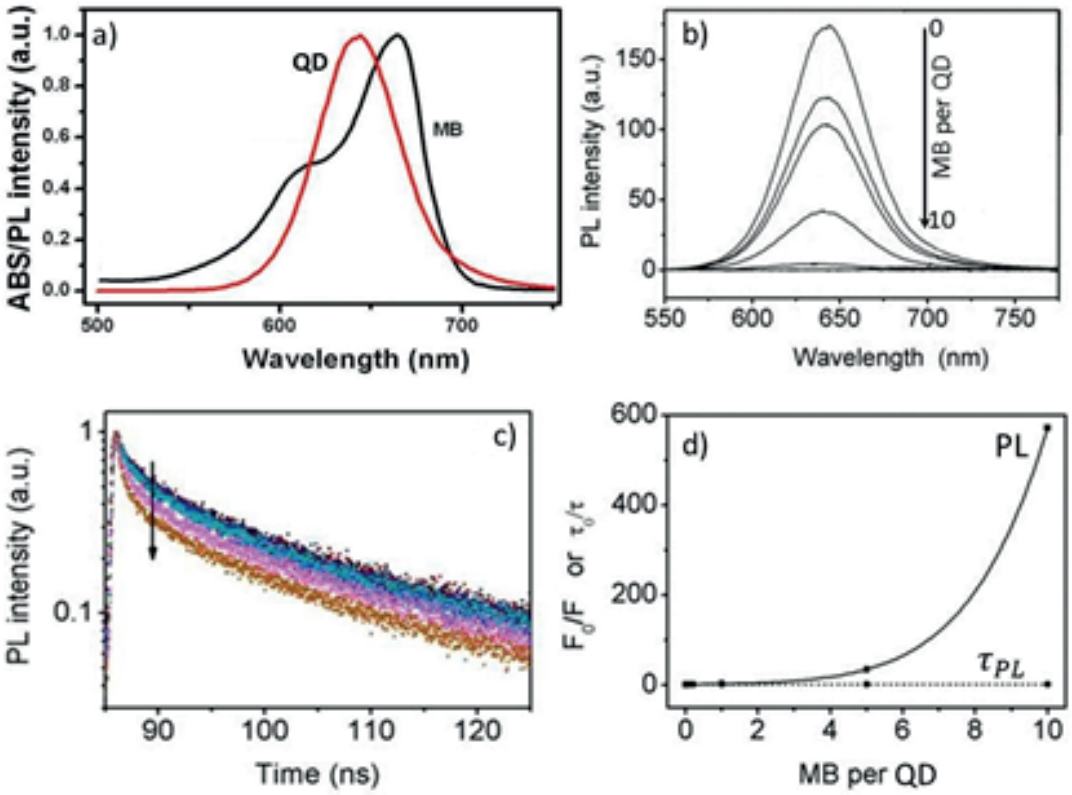

Figure 1: PL (red) and absorption (black) spectra of QDs and MB, respectively (a), changes in PL spectra of QDs solution (b) and PL decay (c) at increased dye concentration, PL lifetime and PL intensity Stern–Volmer plots (d).

3. Discussion

Figure 1a shows PL spectrum of QDs and absorption spectrum of MB with strong overlap of PL and absorption bands. Figure 2b demonstrate strong quenching of QDs

PL with increased QDs:MB ratios which is accompanied by reduction of PL decay times (Figure 2c).

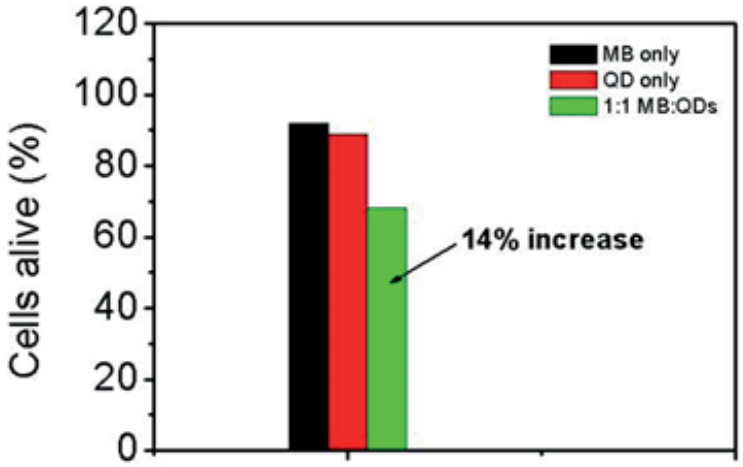

Figure 2: Observed a decrease in the number of HeLa cancerous cells after a 30 hour incubation and after after excitation with UV light during 30 seconds.

At first glance all these data are consistent with highly efficient Förster resonant energy transfer (FRET) from QDs to MB molecules which supposed to be main mechanism of enhancing photodynamic properties of various photosensitizers using this approach.[6-8]

However, upon the inspection of extends of PL quenching and reduction of PL lifetime we have concluded that, for this system, photoinduced charge transfer is the most likely mechanism of PL quenching. The evidence for the photoinduction can be derived through the comparison of lifetime and PL intensity Stern–Volmer plots, which shows orders of magnitude difference (Figure 2d).

This clearly indicates that the dye quenches the QDs PL primarily via charge transfer, however, we cannot completely exclude FRET from consideration because of sufficient overlap between PL emission of QDs and MB absorption.

Nevertheless, in order to demonstrate improvement of the efficiency of a photosensitizer utilizing QDs in vitro studies on the growth and viability of HeLa cancerous cells incubated in MB/QDs-containing mixtures of various concentrations were carried out. These studies point toward an improvement in the cell kill efficiency for the developed organic-inorganic hybrid nanosystem (Figure 2).

4. Conclusions

All these results suggest the possibility of improving the efficiency of any generic photosensitizer utilizing colloidal semiconductor QDs as light-harvesting nanoantenna

regardless exact mechanism of energy transfer. The broad absorption bands of QDs imply that the necessity of the expensive monochromatic light sources for PD therapy can be strongly reduced.

Acknowledgements

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