THEORETICAL STUDIES OF KINETICS OF PHOTODYNAMIC PROCESSES USING SEMICONDUCTOR NANOMATERIALS QUANTUM DOTS AS PHOTOSENSITIZERS

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Abstract — The present paper concerns the investigations in photodynamic therapy area. Principal photodynamic processes in photodynamic therapy with use of semiconductors quantum dots were described. In this work the mathematic modeling of the kinetics processes of singlet oxygen generation and recording was carried out by means of the method of chemical traps. Graphs of the time dependence generation of singlet oxygen on the concentration of molecular oxygen were obtained.

ТЕОРЕТИЧЕСКОЕ ИЗУЧЕНИЕ КИНЕТИКИ ФОТОДИНАМИЧЕСКИХ ПРОЦЕССОВ С ИСПОЛЬЗОВАНИЕМ В КАЧЕСТВЕ ФОТОСЕНСИБИЛИЗАТОРОВ ПОЛУПРОВОДНИКОВЫХ КВАНТОВЫХ ТОЧЕК

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Аннотация — Данная работа посвящена исследованиям в области фотодинамической терапии. Рассмотрены основные фотодинамические процессы, протекающие при фотодинамической терапии с использованием полупроводниковых квантовых точек. Разработаны математические модели фотодинамических процессов, проведено математическое моделирование кинетики процессов генерации и регистрации синглетного кислорода с помощью метода химических ловушек. Получены графики зависимостей генерации синглетного кислорода от концентрации молекулярного кислорода.

I. Introduction

Nowadays cancer is treated by means of various methods. But these methods are often as toxic for the body as for the tumor. However, now there is the way to destroy tumor cells without toxicity of radiotherapy.

The modern method of directed small-invasive treatment of tumor diseases is photodynamic therapy (PDT) using new nanomaterials such as quantum-confined structures like semiconductor quantum dots (QD's). QD is a small nanoparticle with size about 2 – 10 nm. QD's are applied in photodynamic therapy due to their specific properties. The PDT method is based on physical-chemical processes such as interaction of a photosensitizer (QD's) and light with formation of QD excited state. The latter subsequent reactions with molecular oxygen $^3O_2$ bring to the generation of singlet oxygen $^1O_2$. Singlet oxygen, as a very reaction active form of oxygen, is the main agent which destroys tumor cells *in situ*. On this account the registration of singlet oxygen and its study are important for photodynamic therapy.

II. Main Part

For the registration of singlet oxygen there are many methods. There is a luminescence method of registration of singlet oxygen generation by means of the method of chemical traps. For registration of singlet oxygen we used the method of chemical traps. Histidine was used as chemical traps. The choice of chemical traps depends on special criteria specific for the traps, namely for singlet oxygen, and should not have any side effects. The method is based on the optical bleaching of N,N-dimethyl-4-nitrosoaniline (RNO) at 440 nm caused by the product of $^1O_2$ reaction with histidine.

For these processes the following kinetic equations were developed and calculated.

$$S_0 + h\nu \xrightarrow{k_0} S_1 , \quad (1)$$

$$S_1 \xrightarrow{k_1} T , \quad (2)$$

$$T + {}^3O_2 \xrightarrow{k_3} {}^1O_2 + S_0 , \quad (3)$$

$$ {}^1O_2 + G \xrightarrow{k_5} GO_2 , \quad (4)$$

$$GO_2 + RNO \xrightarrow{k_6} RNO' + P . \quad (5)$$

The above mentioned reactions can be modeled using the following kinetic equations:

$$\frac{d[S_0]}{dt} = -k_0[S_0] + k_3[T][{}^3O_2] , \quad (6)$$

$$\frac{d[S_1]}{dt} = k_0[S_0] - k_1[S_1] , \quad (7)$$

$$\frac{d[T]}{dt} = k_1[S_1] - k_3[T][{}^3O_2] , \quad (8)$$

$$\frac{d[{}^1O_2]}{dt} = k_3[T][{}^3O_2] - k_5[{}^1O_2][G] , \quad (9)$$

$$\frac{d[GO_2]}{dt} = k_5[{}^1O_2][G] - k_6[GO_2][RNO] , \quad (10)$$

Where S_0, S_1, T – ground, excited and triplet states of the photosensitizer (QD), respectively; $^1O_2$, $^3O_2$ – singlet and triplet (ground) state of the oxygen respectively; G – histidine; GO_2 – transannular peroxide; RNO - N,N-dimethyl-4-nitrosoaniline; P – products of reaction.

One of modeling results is shown on Fig. 1-2. Process generation of transannular peroxide occurs

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when singlet oxygen reacts with histidine. When the concentration of oxygen becomes lesser, then generated singlet oxygen is inhibited, also reaction of oxygen and quantum dots lessen (Fig. 1-2).

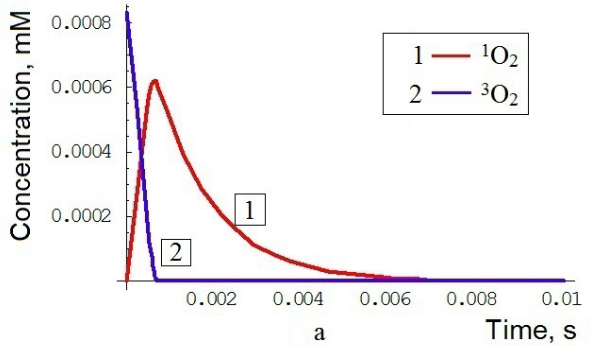

Fig. 1. Graph the time dependence generation of singlet oxygen

Рис. 1. График зависимости генерации синглетного кислорода от времени

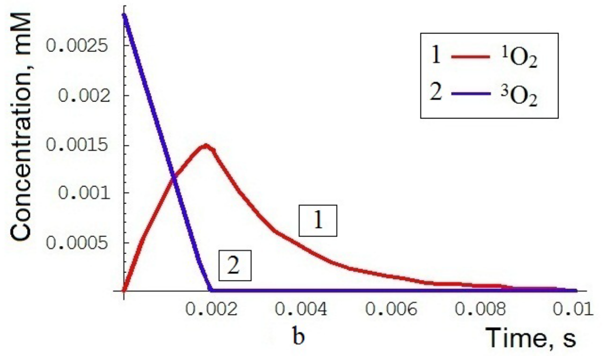

Fig. 2. Process of singlet oxygen generation at increase of molecular oxygen concentration

Рис. 2. Процесс генерации синглетного кислорода при увеличении концентрации молекулярного кислорода

As a result of mathematical simulation the time-dependent singlet oxygen concentration at different levels of triplet oxygen were obtained in order to take into account the effect of perfusion. The variation of processes rate constants and products concentration was included in the obtained results of modeling. Also using the results of modeling the experimental research with registration of generation of singlet oxygen was carried out by method of chemical traps. Obtained results confirmed the generation of singlet oxygen by quantum dots. Spectral characteristics of absorbance quantum dots (Fig. 3) allow exciting them directly for experimental research in photodynamic therapy.

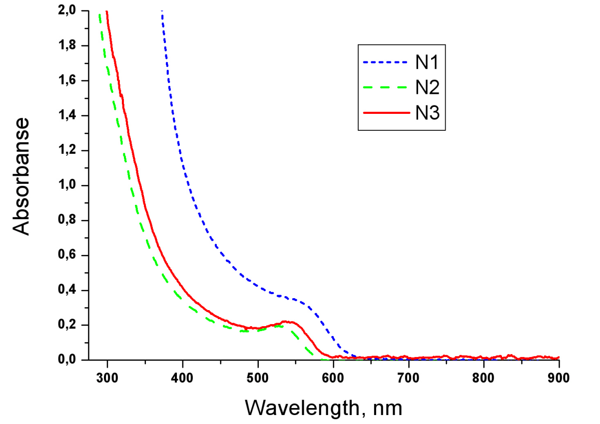

Fig. 3. The absorption spectra of an aqueous solution of CT CdTe/TGA N1 - sample with d = 3.21 nm; N2 - sample with d = 3.1 nm; N3 - sample with d = 3.2 nm

Рис. 3. Спектры поглощения водного раствора КТ CdTe/TGA N1 – образец с d = 3.21 нм; N2 - образец с d = 3.1 нм; N3 – образец с d = 3.2 нм

III. Conclusion

In this work for mentioned processes the kinetic equations were developed and solved. The obtained results of kinetic processes modeling, such as rate constants and products concentration, show the applicability of quantum dots as efficient photosensitizers for PDT.

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