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Luminescence of singlet oxygen generated by fullerene C_{60} — aminopropylsilica nanocomposites

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Immobilization of C_{60} fullerene molecules on silica nanoparticles is a promising way to design nanosystems for X-ray photodynamic therapy. Here, generation of singlet oxygen by C_{60} fullerene aminopropylsilica nanocomposites with and without attached palladium ions, as well as by pristine C_{60} fullerene was studied. Intensive luminescence spectra of singlet oxygen stimulated by 405 nm excitation of C_{60} fullerene solution, as well as suspensions of fullerene aminopropylsilica nanocomposites with and without attached palladium ions in benzene were obtained. It was shown that immobilization of C_{60} fullerene on aminopropylsilica nanoparticles, both in the absence and in the presence of attached palladium ions, does not significantly affect the efficiency of singlet oxygen generation by C_{60} fullerene. Thus, C_{60} fullerene attached to aminopropylsilica nanoparticles could be used for the designing of sensitizer nanosystems for X-ray photodynamic therapy.

Keywords: fullerene C_{60}, silica nanoparticle, singlet oxygen luminescence, X-ray photodynamic therapy.

Люмінесценція синглетного кисню, генерованого нанокомпозитами фулерен C_{60} — амінопропілаеросил. *М.Ю.Лосицький, Р.А.Харченко, Д.В.Гринь, М.А.Доценко, Ю.С.Бойко, О.М.Козачкова, О.М.Самойлов, О.А.Голуб, В.М.Ящук*

Іммобілізація молекул фулерену C_{60} на наночастинках аеросилу є перспективним способом розробки наносистем для рентгенодинамічної терапії. В цій роботі було досліджено генерацію синглетного кисню нанокомпозитами фулерен C_{60} — амінопропілаеросил з приєднаними йонами паладію та без них, а також чистим фулереном C_{60}. Було отримано спектри інтенсивної люмінесценції синглетного кисню, генерованого збудженням на довжині хвилі 405 нм розчину фулерену C_{60}, а також суспензій нанокомпозитів фулерен C_{60} і амінопропілаеросил з приєднаними йонами паладію та без них у бензені. Було показано, що іммобілізація фулерену C_{60} на наночастинках амінопропілаеросилу як за відсутності, так і в присутності приєднаних йонів паладію не впливає істотно на ефективність генерації синглетного кисню фулереном C_{60}. Таким чином, фулерен C_{60}, приєднаний до наночастинок амінопропілаеросилу, може бути використаний для розробки наносистем і сенсибілізаторів для рентгенодинамічної терапії.

1. Introduction

Photodynamic therapy (PDT) is the modern method of cancer treatment, which is based on the destruction of the tumor by reactive oxygen species [1, 2]. These species (singlet oxygen 1O2 being one of them) are generated by the excitation of photosensitizer molecules accumulated in tumor [3–5]. The PDT method is efficient and much less harmful as compared to radiation and chemotherapy [4, 6]. At the same time, due to the low depth of excitation light (generally far-red or NIR) penetration into the tissue, sensitizers to be efficiently excited by deep-penetrating X-rays are being developed since 2006 [7]. For this approach (named X-ray PDT) various sensitizer nanosystems have been proposed, all of them contained the elements absorbing X-rays as well as photosensitizers generating singlet oxygen [8–11]. Besides, to enhance the efficiency of cancer treatment, combination of several methods (such as PDT with radiotherapy [4], or PDT with immunotherapy [12]) based on different mechanisms of tumor destruction is now widely studied. Since heavy elements are known to enhance radiotherapy, their combination with photosensitizers is also studied.

Generation of singlet oxygen by fullerene C_{60} was studied in [13, 14]. Singlet oxygen quantum yield for water-soluble conjugates of fullerene C_{60} with tetraethylene glycol in water was found to reach 0.2 [15]. Thus, C_{60} fullerene could be used for the construction of nanosystems in combination with X-ray absorbing nanoparticles. Earlier C_{60} fullerene — aminopropylsilica nanoparticles were obtained and studied, where C_{60} molecules were attached to silica nanoparticles [16]; in this nanoobject, silica nanoparticle could serve as an X-ray absorber. Luminescent properties of these nanoparticles were studied [16], it was also demonstrated that at low concentrations they do not demonstrate any haemolytic or cytotoxic effects [17]. Efficient generation of singlet oxygen by C_{60} fullerene attached to SiO_2 microparticles (though without comparison to C_{60} alone) was demonstrated in [18].

Here we have studied the generation of singlet oxygen by C_{60} fullerene — aminopropylsilica nanoparticles, as well as by C_{60} fullerene — aminopropylsilica nanoparticles with attached palladium ions (suggested to enhance X-ray absorption), in comparison to pristine C_{60} fullerene.

2. Experimental

Materials

Fullerene — aminopropylsilica nanoparticles (SiO_2–C_{60}) as well as fullerene — aminopropylsilica silica nanoparticles with attached palladium ions (SiO_2–C_{60}–Pd) were synthesized as described in [16]. SiO_2–C_{60} contain 0.15 mmol C_{60} per 1 g SiO_2, while SiO_2–C_{60}–Pd contain 0.25mmol Pd and 0.1065 mmol C_{60} per 1 g SiO_2. Palladium ions forms preferably square planar di(aminopropyl)dichloridopalladium(II) complexes on aminopropylsilica surface located next to immobilized fullerenes. C_{60} fullerene was purchased from SES Research Inc. (USA). Benzene was used as a solvent.

Preparation of solutions

Stock solution of C_{60} fullerene (10^{-3} M) was prepared in benzene, and further dissolved for the measurements in benzene to 10^{-5} M. Suspensions of SiO_2–C_{60} and SiO_2–C_{60}–Pd were prepared by adding weighted amount of the compounds to benzene (0.5 mg/mL) and further treatment by ultrasound. Directly before measurements, suspensions were subject to ultrasound and upper fraction was used for the measurements.

Spectral measurements

Absorption spectra were registered with the UV1900PC spectrophotometer (China). Fluorescence excitation and emission spectra were measured with the help of Cary Eclipse fluorescence spectrophotometer (Varian, Australia). For measurements, solutions and suspensions were placed into 1 cm·1 cm quartz cell. All measurements were performed at room temperature.

Singlet oxygen luminescence measurements

Luminescence spectra of the molecular oxygen were registered with the help of the laboratory-designed spectral station based on MDR-24 monochromator (wavelength range 400–1400 nm) and Hamamatsu PMT cooled module in the range 1200–1300 nm. Excitation was performed with 405 nm diode laser.

3. Results and discussion

Absorption spectra of C_{60} fullerene solution (10^{-5} M) and SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions in benzene are presented in the Fig. 1. The spectrum of fullerene C_{60} in benzene contains characteristic bands of C_{60} at 335, 407, 540 and 598 nm; similar bands were observed in other solvents e.g. in cyclohexane [19]. The low-intensive fluores-

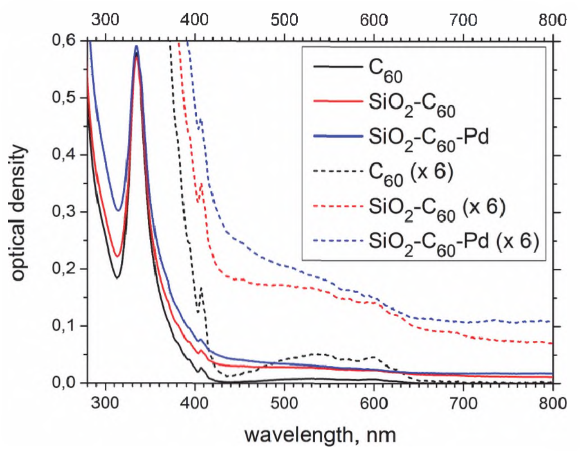

Fig. 1. Absorption spectra of C_{60} solution as well as SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions in benzene (for the region > 390 nm, same spectra enhanced in 6 times are also provided).

cence emission with maximum near 720 nm was observed for this sample, that is also close to the spectrum of fullerene C_{60} solution in cyclohexane observed in [19]. The excitation spectrum of this emission is similar to the absorption spectrum of C_{60}; this means that the fluorescence (and thus, possibly, also generation of singlet oxygen) of this fullerene could be obtained by excitation at the wide wavelength range from UV till about 650 nm (Fig. 2).

As it could be seen from the Fig. 1, the same characteristic bands at 335 and 407 nm are also clearly present in absorption spectra of fullerene-containing nanosilica samples SiO_2–C_{60} and SiO_2–C_{60}–Pd. At the same time, the bands at 540 nm and 598 nm are manifested less clearly, but still could be observed. Thus the system of electronic energy levels of the fullerene molecules does not significantly change when bound to silica nanoparticle (both in the case of SiO_2–C_{60} and SiO_2–C_{60}–Pd, i.e. in the absence and in the presence of Pd ions attached to silica nanoparticles). Besides, based on the comparable absorption intensities at 335 and 407 nm for the three samples studied (Fig. 1), we could conclude that the concentrations of fullerene in the studied SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions are close to that of C_{60} solution (i.e. about 10^{-5} M). Further, luminescence spectra of singlet oxygen stimulated by 405 nm excitation of C_{60} fullerene solution (10^{-5} M) and SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions in benzene were measured (Fig. 3). It is seen from the Fig. 3 that all three mentioned samples demon-

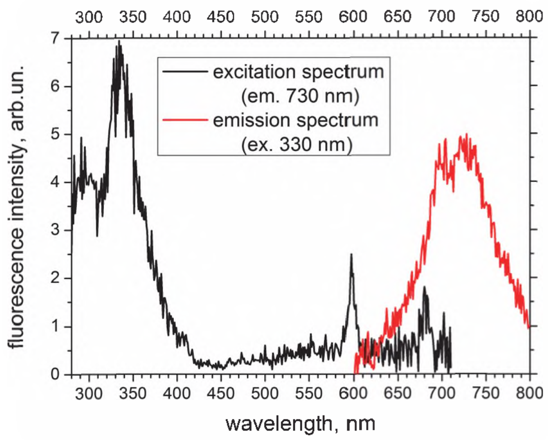

Fig. 2. Fluorescence excitation (emission wavelength 730 nm) and emission (excitation wavelength 330 nm) spectra of C_{60} solution (10^{-5} M) in benzene.

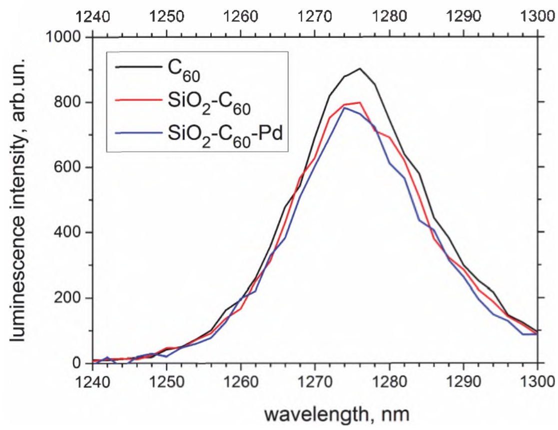

Fig. 3. Luminescence spectra of $^1O_2$ obtained by excitation (at 405 nm) of C_{60} solution as well as SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions in benzene.

strate a band at 1275 nm of nearly the same intensity that corresponds to the emission of singlet oxygen. Since the concentration of C_{60} fullerene is close in all the studied samples, close intensity of $^1O_2$ luminescence in all three samples (C_{60} fullerene solution, and SiO_2–C_{60} and SiO_2–C_{60}–Pd suspensions) implies that the efficiency of singlet oxygen generation by fullerene attached to aminopropylsilica nanoparticles (both with and without Pd ions) is close to that of free fullerene solution. In other words, attaching C_{60} fullerene to aminopropylsilica nanoparticles does not make strong effect on the ability of C_{60} fullerene to generate singlet oxygen. Hence, attaching C_{60} fullerene to aminopropylsilica nanoparticles could be used for the designing of sensitizer nanosystems for PDT (and particularly X-ray PDT).

Besides, interaction of C_{60}/DNA, SiO_2–C_{60}/DNA and SiO_2–C_{60}–Pd/DNA systems and their components with the model phospholipid membrane was studied by differential scanning calorimetry using salmon testes DNA as well as low molecular weight salmon sperm DNA (LmwDNA). Efficient interaction of LmwDNA with the membrane was demonstrated; the obtained results suggest that LmwDNA can be used to promote the interaction of nanoparticles with cell membranes [20].

4. Conclusions

Intensive luminescence spectra of singlet oxygen generated by 405 nm excitation of C_{60} fullerene solution as well as suspensions of fullerene-aminopropylsilica nanoparticles and fullerene-aminopropylsilica nanoparticles with attached palladium ions in benzene were obtained. It was demonstrated that attaching C_{60} fullerene to aminopropylsilica nanoparticles does not significantly affect the efficiency of singlet oxygen generation by C_{60} fullerene. Thus, aminopropylsilica nanoparticles with attached C_{60} fullerene could be used for the designing of sensitizer nanosystems for PDT (and particularly X-ray PDT).

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