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CuInS$_2$ Quantum Dots and Phthalocyanine Hybrid Structure

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A nanoscale hybrid structure based on metallophthalocyanine and colloidal CuInS$_2$ quantum dots is presented in this article. It has been shown that the structure can use dipole-to-dipole energy transfer to form singlet oxygen under irradiation over a wide wavelength range.

Keywords: Quantum Dots, Phthalocyanine, Photocatalysis, Singlet Oxygen.

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Reactive oxygen species (ROS) — including singlet oxygen, hydroxyl/hydroperoxyl/superoxide radicals, and hydrogen peroxide — play crucial role in photocatalytic processes. These reactions typically initiate with the formation of singlet oxygen or superoxide radicals [1]. Due to this fundamental importance, materials capable of generating singlet oxygen find wide applications in photocatalysis, photodynamic therapy, and antimicrobial coatings [2–4]. Among such materials, metal phthalocyanines (MPcs) stand out as efficient singlet oxygen generators. Their activity depends on the central metal cation, with zinc and cobalt complexes being particularly effective [5]. In this study, we focus on zinc phthalocyanine, which produces singlet oxygen through fluorescence upon irradiation within its characteristic absorption bands. These optical transitions include: (1) a broad (B-band) at 350 nm and (2) intense (Q-band) between 600–750 nm, both arising from $\pi-\pi^*$ electronic transitions in the conjugated macrocycle [6].

This study aims to extend MPcs absorption range across the visible spectrum. This can be achieved through energy transfer from a material that actively absorbs energy in the required spectral range to the MPc. One efficient way of energy transfer is the dipole-to-dipole mechanism, wherein a donor is excited at one wavelength and transfers the received energy to an acceptor without the formation of an intermediate photon [7]. This effect is observed at donor–acceptor distances ranging from 10 to 60 Å.

The absorption spectra of the samples were measured using a PE 5400UV spectrophotometer (ECROSKHIM Co., Ltd., St. Petersburg, Russia) with quartz cuvettes.

Photoluminescence (PL) spectra were recorded with a HITACHI F-2700 (Hitachi High-Tech, Tokyo, Japan) spectrofluorometer.

Electron paramagnetic resonance (EPR) spectra were acquired using an SPINSCAN X spectrometer (Advin, Minsk, Belarus) operating at 100 kHz modulation frequency, with a center field of 336 mT and 15 mT sweep width.

We employed colloidal CuInS$_2$ quantum dots (QDs) synthesized according to reference [8] as the donor material. As shown in Figure 1, the photoluminescence (PL) spectrum of the CuInS$_2$ QDs displays a quasi-normal distribution centered at 636 nm with a 75 nm full width at half maximum. The absorption spectrum exhibits characteristic features of I–III–VI ternary chalcogenide QDs (I = Cu, Ag; III = In, Ga, Al; VI = S, Se, Te), presenting a broad, featureless profile with a long absorption tail in the low-energy region and no distinct excitonic peaks [9–11].

The acceptor material was 2(3),9(10),16(17),23(24)-tetra-[4-(2,4-dichlorophenoxy)] zinc (II) phthalocyanine synthesized by the method detailed in [12]. This complementary charge distribution drives the self-assembly of a QD-MPc hybrid system, where each QD (2.97 nm diameter [8]) becomes surrounded by MPc molecules at its periphery. The donor-acceptor distance can be estimated by summing: (1) the MPc molecular length (1.29 nm), and (2) the radius from the QD surface to its geometric center (accounting for uniform copper emission center distribution throughout the CuInS$_2$ QD volume).

The absorption spectra of the obtained system exhibit significant absorption within the transmission window of MPc, suggesting that excitation in the range of 450–550 nm can be utilized to excite acceptor (MPc) through absorption by the donor (CuInS$_2$ QDs).

To verify energy transfer between QDs and MPc, we employed spin-labeling technique. Under 405 nm laser irradiation (within MPc's characteristic absorption bands at 300–450 nm and 580–720 nm), we observed both MPc fluorescence and singlet oxygen generation, confirming successful excitation of the MPc acceptor. EPR spectroscopy enables the detection of singlet oxygen through its reaction with 2,2,6,6-tetramethylpiperidine (TEMP) (J&H CHEM, Hangzhou, China), leading to the formation of a nitroxyl radical ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)) (Fig. 2). The EPR- spectrum of TEMPO is characterized by a triplet with a g-factor of the central peak at 2.0036.

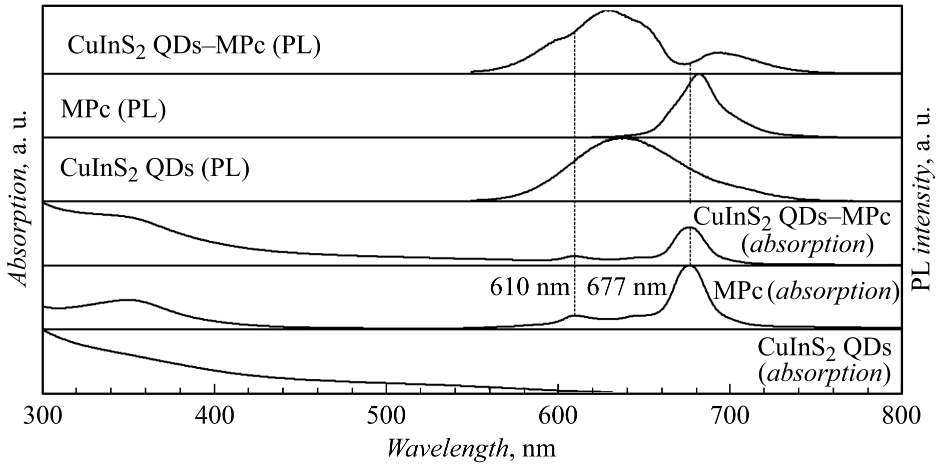

Figure 1. Absorption and PL spectra of $CuInS_2$ QDs, MPc, and their QDs—MPc hybrid ($\lambda_{ex} = 532$ nm).

The initial TEMP solution contained a residual TEMPO concentration of $\sim 1 \cdot 10^{-4}$ mol/L. To reliably confirm singlet oxygen formation, we monitored the kinetics of TEMPO generation. Figure 3, *b* shows the kinetics of TEMPO accumulation in the MPc-TEMP solution under 532 nm laser irradiation.

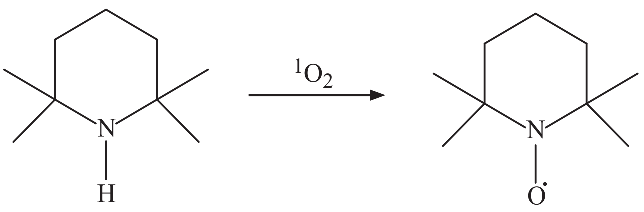

Figure 2. Singlet oxygen ($^1O_2$) detection mechanism. Reaction of TEMP with $^1O_2$ yields the nitroxyl radical TEMPO.

No significant EPR signal changes occurred under 532 nm irradiation, indicating minimal singlet oxygen production. In contrast, 405 nm irradiation triggered a marked increase in EPR peak intensity (Fig. 3, *a*), unambiguously demonstrating TEMPO formation via singlet oxygen-mediated TEMP oxidation.

Irradiation of the $CuInS_2$ QD—TEMP solution at 532 nm produced no significant change in the nitroxyl radical EPR signal intensity. The TEMPO accumulation kinetics (Fig. 3, *b*) confirm this observation, showing minimal concentration variation over irradiation time. In contrast, when exciting the $CuInS_2$ QD—MPc—TEMP hybrid system at 532 nm, we observed a clear increase in TEMPO concentration (Fig. 3, *b*), directly demonstrating efficient singlet oxygen generation through QD-to-MPc energy transfer.

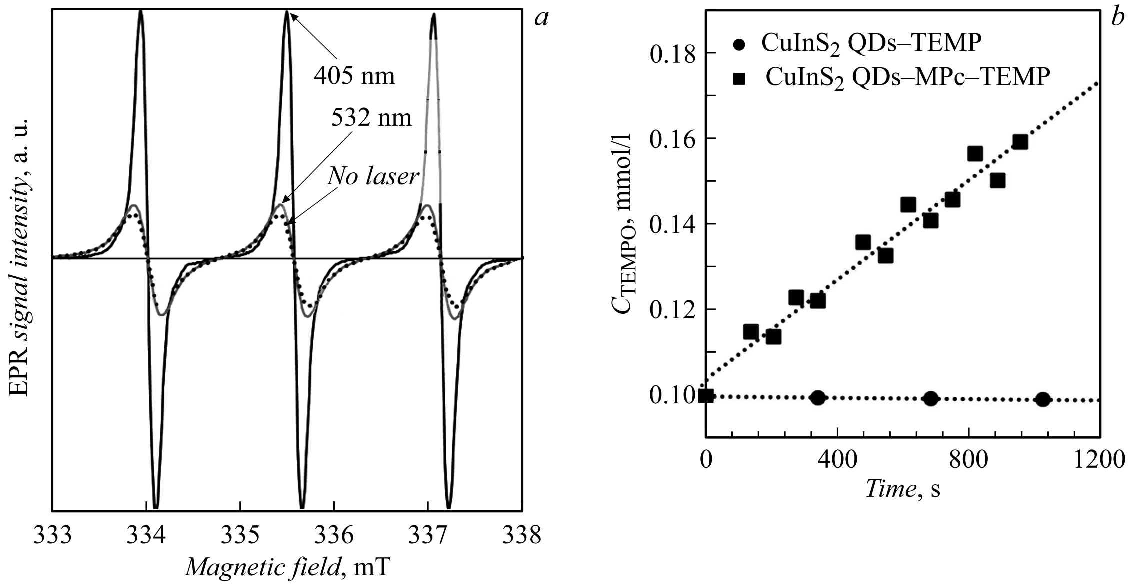

Figure 3. EPR detection of singlet oxygen. (a) TEMPO spectra showing $^1O_2$-dependent signal intensity under 405 nm (strong) and 532 nm (weak) irradiation. (b) TEMPO accumulation kinetics under 532 nm light, proving QD-MPc energy transfer enables $^1O_2$ production.

Thus, the hybrid $CuInS_2$ QD-MPc structure demonstrates dipole-dipole energy transfer, enabling visible-light-driven singlet oxygen generation.

Conflict of interest

The authors declare that they have no conflict of interest.

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