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Generation of Singlet Oxygen via the Composites of Water-Soluble Thiol-Capped CdTe Quantum Dots—Sulfonated Aluminum Phthalocyanines

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Singlet oxygen ($^1\text{O}_2$), one of the reactive oxygen species, plays an important role in many biomedical applications. The various compounds including the phthalocyanines, quantum dots (QDs) and QD complex, which may have potential to produce $^1\text{O}_2$, thus received more and more attentions in recent years. By means of the direct detection of near-infrared 1270 nm, we found that the water-soluble thiol-capped CdTe QDs can photoproduce $^1\text{O}_2$ in deuterated water with a low quantum yield (QY) of 1%. When sulfonated aluminum phthalocyanines (AlSPc's) were connected to these QDs, forming water-soluble QD–Pc composites, the $^1\text{O}_2$ QY of the composites increased to 15% under the excitation of 532 nm, while little $^1\text{O}_2$ production can be found for AlSPc alone at the same excitation because of the poor absorption of AlSPc in this region. The results of indirect measurements of $^1\text{O}_2$, obtained from the photodegradation of the $^1\text{O}_2$ chemical trap anthracene-9,10-diyl-bis-methylmalonate (ADMA), confirmed $^1\text{O}_2$ yields in both QD and QD–Pc composite solutions. The QD–Pc composites have the advantage of extending the excitation region to 400–600 nm with remarkably enhanced extinction coefficients as compared with that of AlSPc. Therefore QD–Pc composites can fully utilize visible region light excitation to effectively produce $^1\text{O}_2$, which may facilitate the applications of QD–Pc composites in broad areas.

1. Introduction

Photodynamic therapy (PDT) has been established as a new modality for some medical indications during the last two decades. The principle of this modality is that the photosensitizing drugs preferably accumulate in a lesion and produce active oxygen species such as singlet oxygen ($^1\text{O}_2$) when excited with the appropriate wavelength light to destroy the lesion.¹ Among the popularly used photosensitizers, the metallo-phthalocyanines are a family of promising photosensitizers for PDT used in both preclinical and clinical studies.^{2–4} The characteristics of the strong Q-band absorption at 600–700 nm and high $^1\text{O}_2$ quantum yield have made them outstanding candidates for cancer PDT treatments. The phthalocyanines (Pc's) were also used in photoinactivations of viruses such as HIV⁵ and bacteria⁶ as well as in photocatalytic reactions,^{7,8} but Pc's have no absorption bands in the visible region of 400–600 nm that limits their efficiency in these applications. How to harvest more light in the visible region is thus a challenge for widening the applications of Pc's.

Recently, the semiconductor quantum dots (QDs) have attracted widespread attention from various fields including

physics, chemistry, biology and medicine,^{9–11} based on their unique photoluminescence (PL) properties such as the wide region absorption with high extinction coefficients, size-dependent tunable narrow PL band and extreme photostability.¹² QDs have been successfully used as the fluorescence probes in various biological applications.¹³ Samia et al. first conjugated QDs to phthalocyanine (Pc4) in organic solution, fulfilling the fluorescence resonance energy transfer (FRET) from QDs to Pc4.¹⁴ This work opened a new way to broaden the absorption region of Pc's by conjugating QDs with Pc's for producing $^1\text{O}_2$ via the FRET route. Although the $^1\text{O}_2$ quantum yield of conjugates is probably not so high, the high extinction coefficients of QDs, which are an order of magnitude larger than those of most dyes,^{15,16} could ensure the high production of $^1\text{O}_2$. However, this conjugate is not water-soluble, so that it is unmatched to the biological environments. With respect to biomedical applications, Shi et al. connected the water-soluble QDs with a photosensitizer of porphine dihydrochloride (TSPP), achieving a $^1\text{O}_2$ quantum yield (QY) of 0.43,¹⁷ and Tsay et al. synthesized peptide-coated QD photosensitizer (Rose Bengal or chloin e6) conjugates in water solution obtaining a $^1\text{O}_2$ QY of 0.1–0.3.¹⁸ The combination of QDs with photosensitizers, particularly with the Pc's, seems a promising modality to effectively produce $^1\text{O}_2$ via the FRET route under excitations of any wavelength in the visible region, which would be very valuable for Pc applications. The search for more simple and convenient combination pairs of QDs and Pc's in water solution is thus of necessity and importance.

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An efficient way to directly harvest the water-soluble QDs, called the hydrothermal route, has been developed recently.¹⁹ The thioglycolic acid (TGA) and the 3-mercaptopropionic acid (MPA) were found to be the best surface stabilizers, and were commonly used in the synthesis to form thiol-capped QDs.²⁰ In the present study, these water-soluble thiol-capped CdTe QDs were connected to the sulfonated aluminum phthalocyanines (AlSPc's), forming water-soluble QD–Pc composites to establish a new model of FRET QD–Pc pairs. The $^1\text{O}_2$ luminescence of QD–Pc composites under the visible region excitation, where the AlSPc's have no or poor absorption, was directly measured in water solution at a wavelength of 1270 nm, and compared with that of thiol-capped CdTe QDs alone.

2. Experimental Section

Synthesis of CdTe QDs and QD–AlSPc Composites. Thiol-capped CdTe QDs were prepared in our lab by a modified hydrothermal route. The details of the synthesis procedure can be found in ref 21. Briefly, with a molar ratio of 2:1, sodium borohydride was used to react with tellurium in water to prepare the sodium hydrogen telluride (NaHTe , 1 mM). Freshly prepared NaHTe solution was added to N_2 -saturated CdCl_2 solution in the presence of 3-mercaptopropionic acid (MPA) at pH 9.0 in the ice–water bath. The molar ratio (i.e., $[\text{Cd}^{2+}]/[\text{MPA}]/[\text{Te}^{2-}]$) was fixed at 1:1.5:0.5. Then, the CdTe precursor solution (40 mL) was put into a Teflon-lined stainless steel autoclave with a volume of 50 mL. The autoclave was maintained at 180 °C for 30 min and then cooled to room temperature by the hydrocooling process. After cooling, the thiol-capped CdTe QDs dispersed in water were obtained. The PL band of obtained QDs with a size of 3.6 nm centered at 650 nm.

Aluminum tetrasulfophthalocyanine (AlSPc) was synthesized, purified and characterized according to the Weber and Busch method.²² AlSPc (1×10^{-4} M) was mixed with the 3×10^{-6} M QD in aqueous solution for 1 h to form the QD–Pc composites. To separate the QD–Pc composites and unbound AlSPc, ethanol was added into the sample solution to precipitate the composites and then the solution was centrifuged at a high speed of 15000 rpm for 1 h to collect the pellet of QD–Pc composites in the bottom of the centrifuging tube by removing the unloaded AlSPc supernatant. The harvested composite pellet was resuspended in water with the concentration the same as that before mixing, and the fluorescence of the sample solution was excited by 630 nm in a spectrophotometer (Hitachi, F-2500), since the 630 nm can excite AlSPc but not QDs. The typical 690 nm fluorescence band of AlSPc was found in the composite solution, confirming the attachment of AlSPc on QDs. To determine the loading amount of AlSPc in composites, the AlSPc calibration curve of the fluorescence intensities with different concentration AlSPc water solutions was made under the excitation of 630 nm. By comparing the fluorescence intensity of AlSPc in QD–Pc composite solution with the AlSPc calibration curve, the linked amount of AlSPc on QDs was estimated as about 20 AlSPc molecules per QD. The carboxyl in the terminal of surface thiol of QDs probably reacted with the Al at the axial position of AlSPc, forming the $\text{COO}-\text{Al}$ bond.

Near-Infrared Detection of Singlet Oxygen. The $^1\text{O}_2$ is the excited state of oxygen with a phosphorescence emission band at 1270 nm, so that the $^1\text{O}_2$ can be directly measured at this wavelength. The measuring system was similar to Niedre's method.²³ The 1270 nm emission of the sample solution was measured by an ultrasensitive Germanium detector (Edinburgh Instruments, EI-P) combined with a 1000 nm long pass filter

(Omega, 3RD 1000 CP) and a 1270 nm band pass filter (Omega, C1275, BP50), under the excitation of laser pulses of 532 nm from an Nd:YAG laser (Quanta-Ray, 1.5 J) with a single pulse energy of 240 mJ and a pulse width of 7 ns and a repetition rate of 10 Hz. The near-infrared emission of the sample was focused to the detector by a lens (Edmund, NT 48-157) with a detection direction perpendicular to the excitation laser beam. The detected signals were averaged with a digital oscilloscope (Tektronics, TDS3000) to show the dynamic decay of $^1\text{O}_2$. The lifetime of $^1\text{O}_2$ was obtained by the decay curve fitting, and the QY of $^1\text{O}_2$ was determined by comparing the intensity of the 1270 nm signal with that of Eosin Y, a reference sample with a known $^1\text{O}_2$ QY of 0.6.

Indirect Measurements of Singlet Oxygen. Differing from the above direct measurements of 1270 nm emission, $^1\text{O}_2$ can be detected indirectly by measuring the photodegradation of a chemical scavenger of $^1\text{O}_2$.^{24,25} The anthracene-9,10-diyl-bis-methylmalonate (ADMA), a chemical trap of $^1\text{O}_2$, was used here.²⁶ The QD D_2O solution (1.2×10^{-6} M) containing 6×10^{-5} M ADMA in a cuvette (2 mL) was irradiated by a 532 nm laser (240 mW) with a beam diameter of 5 mm. Under these conditions, no photobleaching of QDs was found. When being irradiated, the ADMA in QD solution was gradually degraded by the oxidation of $^1\text{O}_2$, which was photoproduced by QDs. The photodegradation rate of ADMA in QD solution was obtained from the decrease of the typical 379 nm absorption band of ADMA with the irradiation time. Taking the Eosin Y as the standard reference, the QY of QDs or QD–AlSPc can be determined.

3. Results and Discussion

The $^1\text{O}_2$ production of thiol-capped CdTe QDs in water solution was first measured in our system. Although Samia et al. reported that the CdSe QDs photoproduced $^1\text{O}_2$ in organic solution with a QY of 5%,¹⁴ so far several other groups all reported negative results on $^1\text{O}_2$ detection of QDs in water solution.^{17,27} We also cannot find clear signals of $^1\text{O}_2$ from the CdTe QDs in common water (H_2O) solution. However, in our previous work, we have found that sodium azide (NaN_3), a physical quencher of $^1\text{O}_2$, can effectively inhibit the QD photobleaching as well as photooxidation in both water solution and living cells,²⁸ implying that the $^1\text{O}_2$ should be produced during the oxidation process of these CdTe QDs though the $^1\text{O}_2$ yield may be low. Since the molar absorption coefficient of deuterated water (D_2O) at 1270 nm is smaller than that of H_2O ,²⁹ the usage of D_2O as the solvent replacing the H_2O may benefit the $^1\text{O}_2$ detection in water solution. When thiol-capped CdTe QDs dissolved in D_2O water with a concentration of 3×10^{-6} M, the 1270 nm time-resolved decay curve can be measured under the excitation of 532 nm laser pulses, as shown in Figure 1A. The lifetime of $^1\text{O}_2$ here was found to be 42 μs after the curve fitting, which is in the region of reported decay constants (33–100 μs) in the literature³⁰ but a little bit smaller than the commonly used value of 65 μs .²⁹ To confirm the detected curve was really the decay curve of $^1\text{O}_2$, the different concentration NaN_3 was added in the QD D_2O solutions, respectively, and then, the 1270 nm decay kinetics for each sample solution was measured correspondingly. As shown in Figure 1, with the increased concentration of NaN_3 added in the system, the $^1\text{O}_2$ lifetime (T) gradually shortened and the 1270 nm signal gradually decreased too (summarized in Table 1). The decreased 1270 nm signals imply that NaN_3 may react with QDs quenching the QD excited state as reported that NaN_3 can quench the triplet of photosensitizers,²³ while the shortened

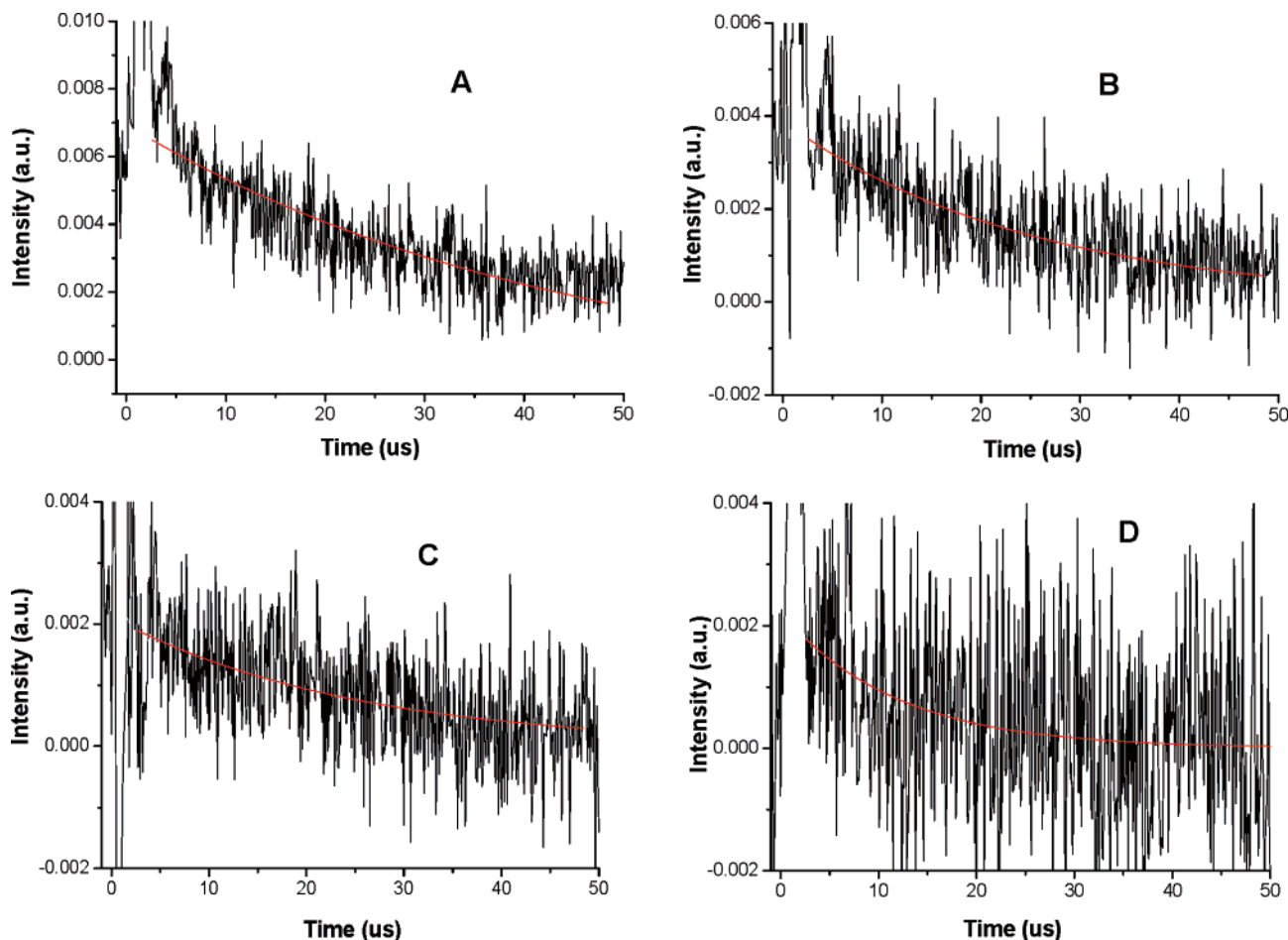


Figure 1. $^1\text{O}_2$ signals in CdTe QD D_2O solutions (3×10^{-6} M) containing different concentrations of NaN_3 , measured at 1270 nm excited by 532 nm laser pulses. $[\text{NaN}_3]$: A, 0 mM; B, 5 mM; C, 13 mM; D, 50 mM.

TABLE 1: Decay Constants of $^1\text{O}_2$ Products in CdTe QD D_2O Solutions Containing Different Concentrations of NaN_3 (Excitation: 532 nm Laser Pulses)

NaN_3 concentration (mM)	0	1	5	13	50
$^1\text{O}_2$ lifetime (μs)	42	37	27	22	12
initial PL intensity (au)	6.3	4.7	3.7	2.3	2.1

lifetimes of $^1\text{O}_2$ reflect the quenching effect of NaN_3 on $^1\text{O}_2$. Taking the ratio of T_0 (without NaN_3) to T (containing NaN_3) as the quenching mark of NaN_3 , the Stern–Volmer relationship was plotted with the concentration of NaN_3 , as shown in Figure 2. The linear relationship supports the $^1\text{O}_2$ generation of QDs under excitation of 532 nm laser pulses. However, the quenching rate of NaN_3 for $^1\text{O}_2$ in QD solution obtained from Figure 2 is very small ($<10^7 \text{ M}^{-1} \text{ s}^{-1}$) as compared with the published value of $4 \times 10^8 (\text{M}^{-1} \text{ s}^{-1})$.³¹ It has been known that, when photosensitizers photoproduct not only $^1\text{O}_2$ but also other reactive oxygen species (ROS), the quenching rate of NaN_3 for $^1\text{O}_2$ in such a system would be lower, as shown in the literature that in riboflavin (photosensitizer) solution the quenching rate of NaN_3 was found to be $1.5 \times 10^7 (\text{M}^{-1} \text{ s}^{-1})$.³² Therefore, the above results of near-infrared measurements and the NaN_3 effect suggest that QDs photoproduct $^1\text{O}_2$ and perhaps other ROS as well. Regarding the fact that the $^1\text{O}_2$ was probably not the sole product, the small value of quenching rate of NaN_3 for $^1\text{O}_2$ obtained from the Stern–Volmer relationship (Figure 2) was not suitable for calculating the $^1\text{O}_2$ QY. The $^1\text{O}_2$ QY of the QD solution was determined by directly measuring its 1270 nm intensity and comparing this intensity with that of the standard $^1\text{O}_2$ sample measured in parallel. Taking the Eosin Y

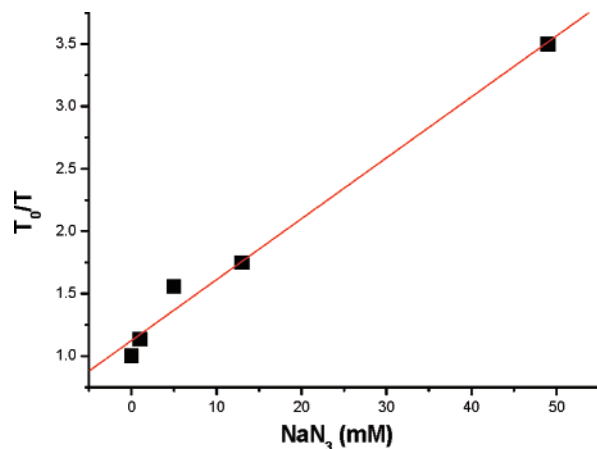


Figure 2. Stern–Volmer relationship of the inhibiting effect of NaN_3 on $^1\text{O}_2$ in CdTe QD D_2O solutions (3×10^{-6} M).

as the reference sample with the known $^1\text{O}_2$ QY of 0.60 for quantitative comparison,³³ the $^1\text{O}_2$ QY of thiol-capped CdTe QDs in D_2O was determined as $1 \pm 0.1\%$. This low QY could explain why some other groups did not find the $^1\text{O}_2$ products in water-soluble QDs. Due to the low QY of $^1\text{O}_2$, water-soluble QDs are not suitable to be used as photosensitizers.

In this Letter, we focused on the $^1\text{O}_2$ production of QDs, leaving the study of possible ROS intermediates to the next work. In addition to the above direct near-infrared measurements, the indirect measurement of $^1\text{O}_2$ in QD solution can provide further evidence. The ADMA photodegradation experi-

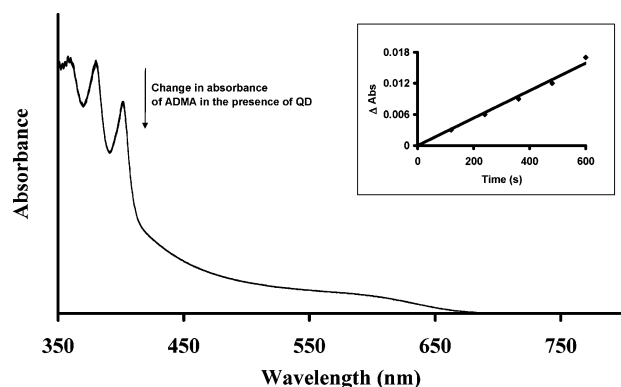


Figure 3. Photodegradation of ADMA in QD solution (1.2×10^{-6} M) under 532 nm laser irradiation. The typical absorption bands (379, 405 nm) of ADMA gradually decreased with the irradiation time.

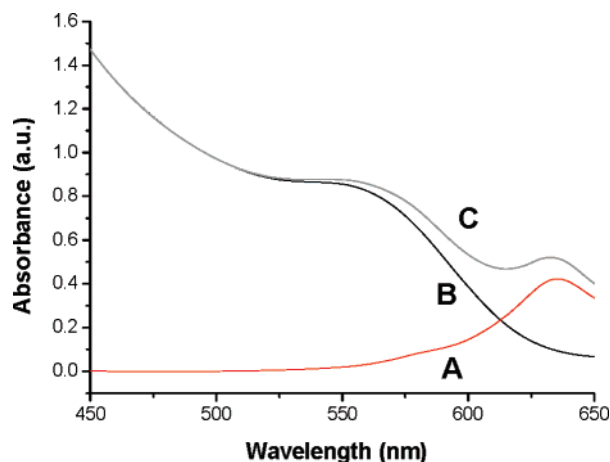


Figure 4. Absorption spectra of (A) AISPc water solution (1×10^{-4} M), (B) QD water solution (3×10^{-6} M) and (C) obtained QD-Pc composites from a mixture of (A) and (B) in water solution.

ments were carried out in QD solution as the indirect measurement, since the photodegradation rate of the chemical trap of $^1\text{O}_2$ (ADMA) was reported to be directly proportional to the $^1\text{O}_2$ production.²⁵ As shown in Figure 3, the ADMA can be photodegraded in QD solution. ADMA alone was not affected by the 532 nm laser irradiation. Because the ADMA photodegradation is linearly proportional to the irradiation time (inset of Figure 3), the degradation rate can be used to evaluate the $^1\text{O}_2$ yield. Taking the Eosin Y as the reference sample with the known QY of $^1\text{O}_2$, the photodegradation of ADMA by Eosin Y photosensitization was also performed. By quantitative comparison, the $^1\text{O}_2$ QY of QDs in D_2O was calculated as $1.2 \pm 0.1\%$, which is in good agreement with the value of direct measurements of $^1\text{O}_2$ 1270 nm emission.

When AISPc molecules connected to the CdTe QDs forming QD-Pc composites, the absorption of QD-Pc composites in the visible region was dramatically enhanced as compared with that of the AISPc (Figure 4). The 650 nm PL band of QDs is well overlapped with the Q-band absorption of AISPc, which would facilitate the FRET in QD-Pc composites from the QD to AISPc moiety. The emission spectrum of QD-Pc composites was compared with that of AISPc alone under the excitation of 532 nm, as shown in Figure 5. The absorption coefficient of AISPc at 532 nm is very poor, which caused a very low fluorescence emission for the case of AISPc. However, the 690 nm emission band of the AISPc moiety in composites under the same excitation is remarkably enhanced, while the 650 nm PL band of the QD moiety is decreased obviously, indicating

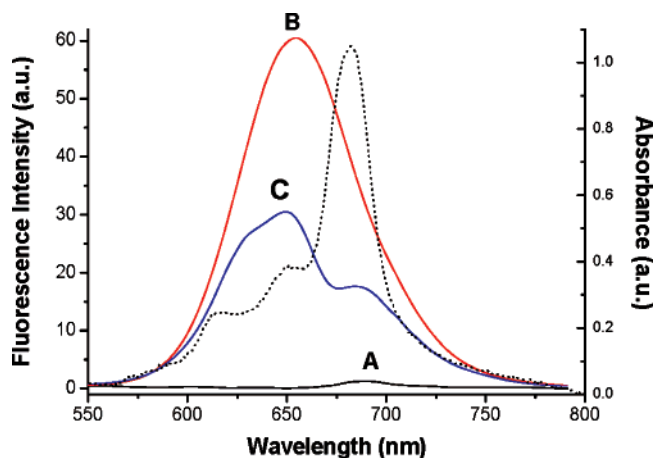


Figure 5. Emission spectra of (A) AISPc water solution (1×10^{-4} M), (B) CdTe QD water solution (3×10^{-6} M) and (C) QD-Pc composites obtained from a mixture of (A) and (B). Excitation: 532 nm. The dotted line is the absorption spectrum of AISPc water solution.

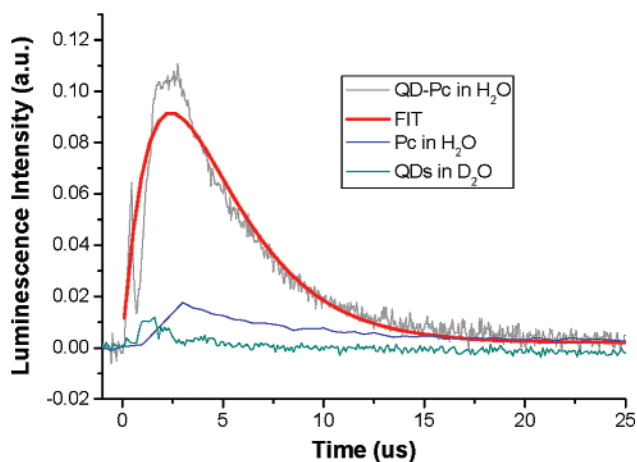


Figure 6. Time-resolved dynamic courses of $^1\text{O}_2$ produced by QD-Pc composites in H_2O solution, CdTe QDs in D_2O solution (3×10^{-6} M) and AISPc in H_2O solution (1×10^{-4} M), measured at 1270 nm excited by 532 nm laser pulses.

that the FRET occurred in QD-Pc composites. The FRET efficiency has been determined as 58% in our previous work.³⁴ Such a high FRET efficiency suggests a considerable $^1\text{O}_2$ production of QD-Pc composites under the excitation at the visible region.

The time-resolved curve of 1270 nm emission from the QD-Pc composite water (H_2O) solution is shown in Figure 6. Due to the fact that the 1270 nm signal produced in this case is much stronger than that of pure QDs, the dynamic course of $^1\text{O}_2$ concentration [$^1\text{O}_2$] can be clearly recorded, following eq 1 as theoretically described in the literature.²³

$$[^1\text{O}_2] = A \frac{\tau_D}{\tau_T - \tau_D} \left[\exp\left(\frac{-t}{\tau_T}\right) - \exp\left(\frac{-t}{\tau_D}\right) \right] \quad (1)$$

where τ_D is the lifetime of $^1\text{O}_2$, τ_T is the lifetime of AISPc at triplet state, t is the time in seconds and A is a coefficient involved in sensitizer concentration and $^1\text{O}_2$ QY. From the obtained time-resolved curve of QD-Pc composites in Figure 6, the AISPc triplet lifetime of $2.1 \pm 0.4 \mu\text{s}$ and $^1\text{O}_2$ lifetime of $2.7 \pm 0.4 \mu\text{s}$ were acquired by the curve fitting, which are consistent with the published data of 2.4 ± 0.5 and $3.0 \pm 0.3 \mu\text{s}$, respectively.²³ For comparisons, the weak near-infrared signals for the cases of QDs in D_2O water and AISPc in H_2O

water under the same excitation were also depicted in Figure 5. Comparing the 1270 signal of QD–Pc composites with that of reference sample Eosin Y at the same excitation, the $^1\text{O}_2$ QY of QD–Pc composite in water solution was calculated as $15 \pm 2\%$.

With the indirect measurement using ADMA, the $^1\text{O}_2$ QY of QD–Pc composite was found to be $9.5 \pm 1\%$ taking the Eosin Y as the reference sample also, confirming the considerable $^1\text{O}_2$ production of QD–Pc composites.

4. Conclusions

In summary, the $^1\text{O}_2$ QY of QDs in water solution is very low while that of QD–Pc composites is as high as 15%, reflecting that the QD–Pc composite could be a good $^1\text{O}_2$ generator. Although the 15% $^1\text{O}_2$ QY of composites is still lower than that of AlSPc itself (36%),³⁵ the advantages of QD–Pc composites, such as the new excitation window of 400–600 nm and enhanced absorption coefficient in this region, are evident, which makes the composites become more competitive and flexible for the $^1\text{O}_2$ generation and could promote the $^1\text{O}_2$ involved applications in various fields.

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