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A New Medium for Triplet-triplet Annihilated Upconversion and Photocatalysis Application

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ABSTRACT: Since the triplet-triplet annihilated upconversion (TTA-UC) materials work efficiently only in degassing organic solvents, it is of significance to find a new medium without toxicity and volatility and with promoting TTA-UC. Here, we firstly reported the OH-containing medium effect on low power upconversion and found that in alcohol solvent with β-cyclodextrin (β-CD), the phosphorescence lifetime (τ_P) of sensitizer (PdTPP) and the fluorescence quantum yield (Φ_f) of acceptor (DPA) were enhanced with the OH-group of medium increasing. Large triplet-triplet quenching constant (k_q, $1.91 \times 10^9 \, M^{-1} \cdot s^{-1}$) and high upconversion efficiency (Φ_{UC}, ~36%) of PdTPP/DPA were obtained under the excitation of diode laser (532 nm, 60 mW·cm^{-2}). Under our green-to-blue upconversion irradiation, a demonstration experiment of the photocurrent was recorded at 0.09 μA/cm^2, resulting from photocatalytic water splitting by $Cd_{0.7}Zn_{0.3}S$ photoanode and Pt counter electrode in a photoelectrochemical cell. The importance in this study suggests that upconversion-powered photoelectrochemistry possesses the potential application for hydrogen generation from water under excitation of sun energy.

Introduction

Photon upconversion (UC) can convert low-energy photon to high-energy photon based on two-photon absorption (TPA)[1-3] or triplet-triplet annihilation (TTA)[4-7] mechanism. The triplet-triplet annihilation upconversion (TTA-UC) mechanism involves in a bimolecular system containing sensitizer and acceptor. Firstly, the sensitizer harvests the excitation energy toward its triplet excited state by the intersystem crossing (ISC), then the triplet energy of the sensitizer transfers to the acceptor (i.e., triplet-triplet energy transfer, TTT). Lastly, two excited triplet acceptors would annihilate

(i.e., triplet-triplet annihilation, TTA) and one of them irradiates the high-energy light (upconversion) from the excited state to the ground state.[5] Since the processes mentioned above, including ISC, TTT and TTA, are transition-allowed, the TTA-UC can achieve at ultra-low excitation power less than the terrestrial solar radiation (ca. 100 mW·cm^{-2}),[6,7] which shows widespread practical applications such as solar cell,[8-13] photocatalysis/ photodegradation,[14-16] photodynamic therapy of cancer[17-19] and display.[20]

Presently, the TTA-upconversion was investigated either in solution[21-25] or in solid state.[26-33] The reported upconversion efficiencies (Φ_{UC}) in solid matrixes never exceed 6% under the excitation intensity of 100 mW·cm^{-2}. Because the TTA-UC is diffusion controlled[34] and the diffusion is intrinsically inhibited in the solid state.[26] On the other hand, the chromophore diffusion in solution can be significantly promoted, which makes the solution-based upconversion possess very large efficiency (as high as 39%).[21-25] However, the employed TTA-UC solvents usually are organic solvents such as benzene,[7] DMF,[21,22] toluene,[23] dichloromethane,[24] and acetonitrile,[25] *etc.* These deleterious organic solvents obviously produce critical environment problems. Moreover, since the TTA upconversion materials work efficiently only in the degassing solution,[35,36] the volatile organic solvents apparently bring about some application limitation.

We herein reported a new OH-containing medium, comprised of alcohol solvent and β-cyclodextrin (β-CD), acting as an effective solvent for TTA-UC performance. Dynamic data indicated that in this medium, sensitizer (PdTPP) presented long phosphorescence lifetime (28.31 μs) and acceptor (DPA) lay in favorable fluorescence deactivation. Stern-Volmer equation confirmed that efficient triplet-triplet energy transfer (TTT) from sensitizer to acceptor was achieved in this medium. Selective excitation of metalloporphyrin (PdTPP) in the media of *n*-propanol/glycerol/β-CD containing DPA resulted in green-to-blue upconversion with the efficiency as high as ~36%. Since the OH-containing medium shows many advantages, such as absence of toxicity and volatility, being economic and

environmental, it is of great significance for TTA-upconversion applications. Photocatalysis under our green-to-blue upconversion (λ=436 nm) irradiation is firstly investigated in a photoelectrochemical (PEC) cell. Using $Cd_{0.7}Zn_{0.3}S$ as photoanode and Pt-rod as the counter electrode, the upconversion-powered photocurrent was obtained. Based on the energy level analysis, O_2 evolution on photoanode $Cd_{0.7}Zn_{0.3}S$ and H_2 evolution on the Pt-pole were achieved.

Experimental Section

Chemicals and OH-containing solvents. Sensitizer Pd(II) tetraphenylporphyrin (PdTPP) was synthesized and characterized according to the literatures,[37,38] 9,10-Diphenylanthracene (DPA) and β-cyclodextrin (abbreviated as β-CD) were commercially available. β-CD was re-crystallized before measurements. OH-containing solvents, including n-butanol (abbreviated as BuOH), n-propanol (abbreviated as PrOH) and glycol (abbreviated as Gly) were spectral purity and used without further purification.

The solutions containing PdTPP, DPA and PdTPP/DPA are prepared in different alcohol solvents with the varying polar parameter ($E_T(30)$) (see Table 1), where the $E_T(30)$ values of BuOH and PrOH were referred to the literature,[39] and the $E_T(30)$ of mixed solvents were estimated based on the respective content (weight coefficient). We noticed that PdTPP, DPA and PdTPP/DPA were dissolved well in these alcohol solvents (shown in Figure S7).

$Cd_{0.7}Zn_{0.3}S$ was synthesized according to literature.[40] A amount of zinc acetate ($Zn(Ac)_2 \cdot 2H_2O$, 0.36 g) and cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, 0.92 g) was added into 40 mL deionized water under magnetic stirring. Then, 20 mL of sodium sulfide aqueous solution (Na_2S, 0.45 M) was added dropwise into the solution. The mixture solution was transferred to a 100 mL Teflon-lined autoclave and heated at 180^oC for 10 h. After centrifugation, the solid was isolated, washed with deionized water for 3 times and dried at 70 °C. The resultant yellow samples were stored in darkness before measurements.

Absorption and photoluminescence. The absorption spectra were recorded on Hitachi U-3500 spectrophotometer from quartz cuvettes of 1 cm path. Steady-state emission and time-resolved decay curves were measured on an Edinburgh FLS 920 fluorophotometer equipped with time-correlated single-photon counting (TCSPC) card. With the aid of nF900 software, the fluorescence lifetime (τ_f) was measured under detection of nF lamp at room temperature; while the phosphorescence lifetime (τ_p) was measured under nitrogen atmosphere at room temperature, with detection of microsecond xenon flash lamp (Edinburgh Analytical Instruments, μF900). For all radiation decays (fluorescence and phosphorescence), monoexponential or diexponential fits give acceptable statistics parameters of $\chi^2 < 1.1$ (χ^2 is the "reduced chi-square"). Fluorescence quantum yields (Φ_f) were measured with quinine sulfate (in 0.1 $mM \cdot dm^{-3}$ aqueous NaOH, Φ_r=0.53) as the standard according to literature;[41] similarly, phosphorescence quantum yields (Φ_p) were obtained. The radiative ($k_f = \Phi_f/\tau_f$) and

nonradiative ($k_{nr} = k_f(1-\Phi_f)/\Phi_f$) decay rate constants for DPA in OH-containing media are calculated.

TTA-upconversion. Diode solid state laser (532 nm) was used as the excitation source for TTA-upconversion. The laser power was measured with photodiode detector. For TTA-upconversion experiments, the mixed solutions containing sensitizer and acceptor were degassed for about 10 min with N_2. Then the solution was excited with the laser. The upconverted fluorescence was observed with PR655 Spectra Scan colorimeter.

TTA-upconversion efficiency can b

$$\Phi_{UC} = 2\Phi_r \left(\frac{A_r}{A_s}\right)\left(\frac{F_s}{F_r}\right)\left(\frac{\eta_s}{\eta_r}\right)^2 \quad (1)$$

Eq. (1),[26] where subscript "s" and "r" represent sample (either sensitizer or acceptor) and reference (Rhodamine 6G in EtOH was used as standard, Φ_F = 88%), respectively. Φ_r is the fluorescence quantum yield of reference, A is the absorbance, F is the integrated fluorescence intensity and η is the refractive index of solvents. The equation is multiplied by a factor of 2, accounting for the fact that two absorbed photons are required to produce one upconverted photon.

Upconversion powered photoelectrochemistry. The photoelectrochemical behaviors were measured using a CHI660D potentiostat/galvanostat electrochemical analyzer in a three-electrode system consisting of a working electrode, a platinum wire as a counter electrode and Ag/AgCl (0.1 M) as a reference electrode.[42] The working electrode was prepared by coating the ethanol suspension of $Cd_{0.7}Zn_{0.3}S$ powders onto a clean indium tinoxide (ITO) glass and was dried under vacuum at 70 °C. The electrodes were immersed in a supporting electrolyte solution (1.0 M H_2SO_4). Prior to the measurement, the solution was deaerated by bubbling Ar for 1 hour. During the measurement, the working electrode was irradiated by our upconverting irradiation that from a quartz cuvette containing PdTPP/DPA in PrOH/Gly/β-CD (1/2/2.4, v/v/mM). The active area of $Cd_{0.7}Zn_{0.3}S$ was 1 cm^2 with 1 μm thickness deposited on ITO glass that was placed close to the quartz cuvette. Diode pumped solid state laser (532 nm, 60 $mW \cdot cm^{-2}$) was used as the excitation source for the upconversion.

Results and Discussion

Absorption and photoluminescence properties As presented in Figure 1a, the absorption spectra of PdTPP in different alcohol solvents show strong absorptions in Soret-band (413 nm) and weak absorptions in Q-band (523 nm); and the photoluminescence spectra show dual fluorescence bands < 650 nm and dual phosphorescence bands > 650 nm, identified by the time-resolved decay measurements. Detail data of absorption and photoluminescence are presented in Table 1. With the increasing OH-group of solvent, the phosphorescence quantum yield (Φ_p) and phosphorescence lifetime (τ_{P2}) of PdTPP are increased from 0.86% and 14.39 μs in BuOH, 1.23% and 16.69 μs in PrOH, 2.74% and 18.13 μs in PrOH/Gly (2/1, v/v), 3.26% and 21.77 μs in PrOH/Gly (1/1, v/v), 4.86% and 26.03 μs in PrOH/Gly (1/2, v/v), to 5.34% and 28.31 μs in PrOH/Gly/β-CD (1/1/2.4, v/v/mM) (Figure 1b, Table 1).
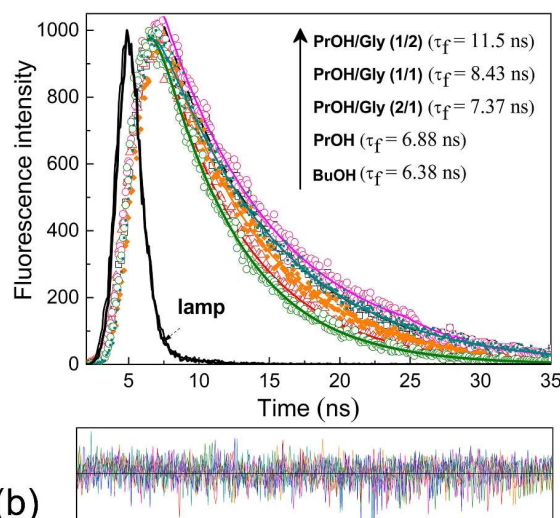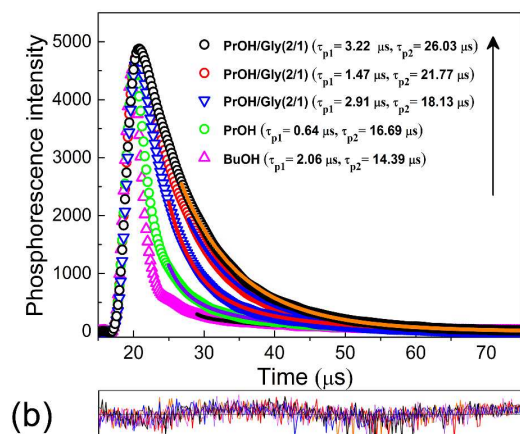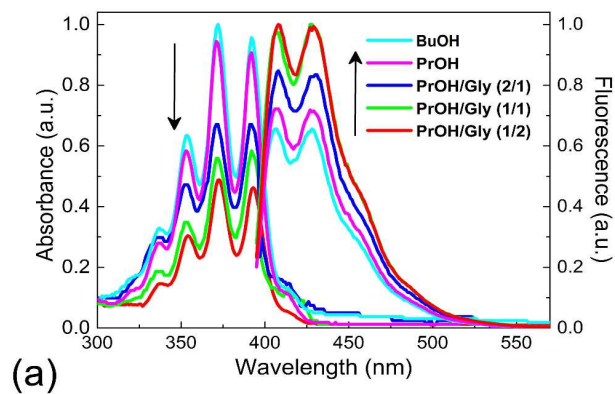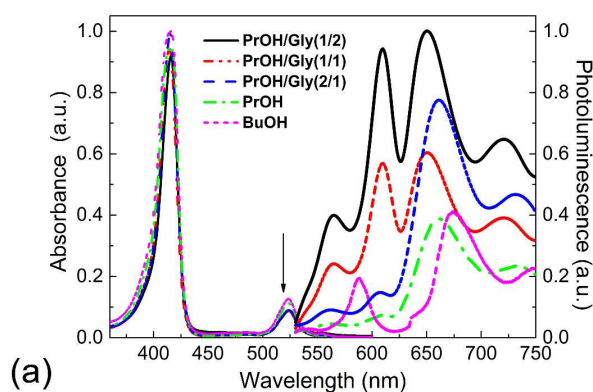
(a)

(a)

(b)

(b)

Figure 1 Absorption, photoluminescence spectra **(a)** and phosphorescence decay curves **(b)** for PdTPP in different solvents at 1×10^{-5} M (Emission spectra were obtained at N_2 atmosphere and room temperature under Q-band excitation).

Figure 2 Absorption and fluorescence spectra **(a)** and fluorescence decay curves **(b)** for DPA in different solvents at 1×10^{-5} M.

Table 1 The data of absorption and photoluminescence for PdTPP in different OH-containing solvents

OH-containing solvent	BuOH	PrOH	PrOH/Gly (2/1, v/v)	PrOH/Gly (1/1, v/v)	PrOH/Gly (1/2, v/v)	PrOH/Gly/β-CD (1/2/2.4, v/v/mM)
$E_T(30)$	49.7	50.7	52.6	53.5	54.6	—
ε_{532nm} (M^{-1} cm^{-1})	7.1×10^3	6.5×10^3	5.6×10^3	5.4×10^3	4.7×10^3	4.7×10^3
λ_{max}^{phors} (nm)	675, 740	660, 732	662, 734	652, 724	652, 719	652, 719
Φ_p (%)	0.86	1.23	2.74	3.26	4.86	5.34
τ_P $\quad$ τ_{P1} (x%)	2.06 (9.35%)	0.644 (8.66%)	2.91 (4.72%)	1.47 (11.83%)	3.22 (17.59%)	2.98 (17.38)
(µs) $\quad$ τ_{P2} (1-x%)	14.39 (90.65%)	16.69 (91.34%)	18.13 (95.83%)	21.77 (88.17%)	26.03 (82.41%)	28.31 (82.62)

Table 2 Absorption, fluorescence and dynamics data for DPA in different OH-containing solvents

OH-containing solvent	BuOH	PrOH	PrOH/Gly (2/1, v/v)	PrOH/Gly (1/1, v/v)	PrOH/Gly (1/2, v/v)	PrOH/Gly/β-CD (1/2/2.4, v/v/mM)
Φ_f (%)	89.32	89.44	91.39	93.57	94.05	94.48
τ_f (ns)	6.38	6.88	7.37	8.43	11.45	12.84
k_f ($10^8 s^{-1}$)	1.40	1.30	1.24	1.11	0.82	0.74
k_{nr} ($10^7 s^{-1}$)	1.67	1.53	1.17	0.76	0.52	0.43
k_f/k_{nr}	8.38	8.50	10.60	14.61	15.77	17.21

Table 3 Upconversion efficiency (Φ_{UC}), phosphorescence quenching constants (k_q) for DPA/PdTPP in OH-containing solvents

OH-containing solvent	BuOH	PrOH	PrOH/Gly (2/1, v/v)	PrOH/Gly (1/1, v/v)	PrOH/Gly (1/2, v/v)	PrOH/Gly/β-CD (1/2/2.4, v/v/mM)
λ^{UC}_{max} (nm)	436	436	436	436	436	436
Φ_{UC} (%)	18.4	20.7	22.9	25.4	29.1	35.86
K_{sv} ($10^4\,M^{-1}$)	1.64	2.11	2.60	3.31	3.97	4.56
k_q ($10^9\,M^{-1}{\cdot}s^{-1}$)	1.22	1.37	1.48	1.71	1.80	1.91

Meantime, the quantum yield (Φ_f) of DPA presents increasing in different alcohol solvent with more OH-group. As shown in Table 2, the Φ_f values of DPA are increased from 89.32 % in BuOH, 89.44% in PrOH, 91.39% in PrOH/Gly (2/1, v/v), 93.57% in PrOH/Gly (1/1, v/v), 94.05% in PrOH/Gly (1/2, v/v) to 94.48% in PrOH/Gly/β-CD (1/1/2.4, v/v/mM), with concomitance of fluorescence lifetime (τ_f) 2-fold increasing. Calculated k_f/k_{nr} values of DPA are in order of 8.38 in BuOH < 8.50 in PrOH < 10.60 in PrOH/Gly (2/1, v/v) < 14.61 in PrOH/Gly (1/1, v/v) < 15.77 in PrOH/Gly (1/2, v/v) < 17.21 in β-CD (1/1/2.4, v/v/mM).

All of these discussed above suggest that the alcohol solvent with more OH-groups is not only beneficial to the triplet population of sensitizer (PdTPP), but also favorable to the fluorescence deactivation of acceptor (DPA), which probably result from solvent intermolecular H-bond formation. In the presence of β-CD that can provide much more OH-groups, the triplet lifetime of PdTPP (28.31 µs) was enhanced ulteriorly. At the same time, DPA trends to enter the cavity of β-CD and its free rotation is restricted, which results in the Φ_f value additional increasing.

TTA-upconversion in OH-containing media

Using the diode laser (532 nm, 60 mW·cm^{-2}) as the excitation source, the green-to-blue upconversion located at 436 nm was observed (Figure 3a). Power-dependent upconversion intensity of DPA/PdTPP in PrOH exhibited a quadratic integral enhancement as a function of incident power density of 10.3~60.0 mW·cm^{-2} (Figure 3b and insert), implying that TTA-UC is a nonlinear optical process. Based on Eq. (1), the Φ_{UC} values of DPA/PdTPP in different solvents are calculated at 35.89% in PrOH/Gly/β-CD (1/2/2.4, v/v/mM) > 29.1% in PrOH/Gly (1/2, v/v) > 25.4% in PrOH/Gly (1/1, v/v) > 22.9% in PrOH/Gly (2/1, v/v) > 20.7% in PrOH > 18.4% in BuOH (Table 3), showing a dramatic increase as the OH-group increasing of medium.

To gain insight whether the solvent effect on the TTA-upconversion is caused by polarity or not, we investigated polarity-dependent TTA-upconversion of DPA/PdTPP under the identical measurement conditions. Interestingly, the results indicated that the protonic and aprotic solvent effects exhibit two different trends (Figure 4). That is, Φ_{UC} in protonic solvent is increased with an increasing of solvent polarity parameter E_T (30). For example, The Φ_{UC} value is increased from 18.4% in BuOH (E_T(30), 49.7), 20.7% in PrOH (E_T(30), 50.7), 22.9 in PrOH/Gly (2/1, v/v) (E_T(30), 52.6); 25.4% in PrOH/Gly (1/1, v/v) (E_T(30), 53.5), to 29.1% in PrOH/Gly (1/2, v/v)

(E_T(30), 54.6). In contrast, the Φ_{UC} in aprotic solvent is decreased with increasing of solvent polarity, that is, at 8.1% in acetonitrile (E_T(30), 45.6), 12.9% in DMF (E_T(30), 43.2), 25.6% in ethylacetate (E_T(30), 38.9), 30.7% in toluene (E_T(30), 33.9) and 35.4% in cyclohexane(E_T(30), 30.9) (Figure 4, insert). (Detailed absorption and photoluminescence spectra of PdTPP and DPA as well as the upconversion spectra of DPA/PdTPP in aprotic solvents are presented in Figure S1-S5 and Table S1). So, the comparative investigation of protonic and aprotic solvent effect upon the TTA-upconversion implied that the influence of OH-solvent on the TTA-upconversion is not by polarity but by intermolecular H-bond.
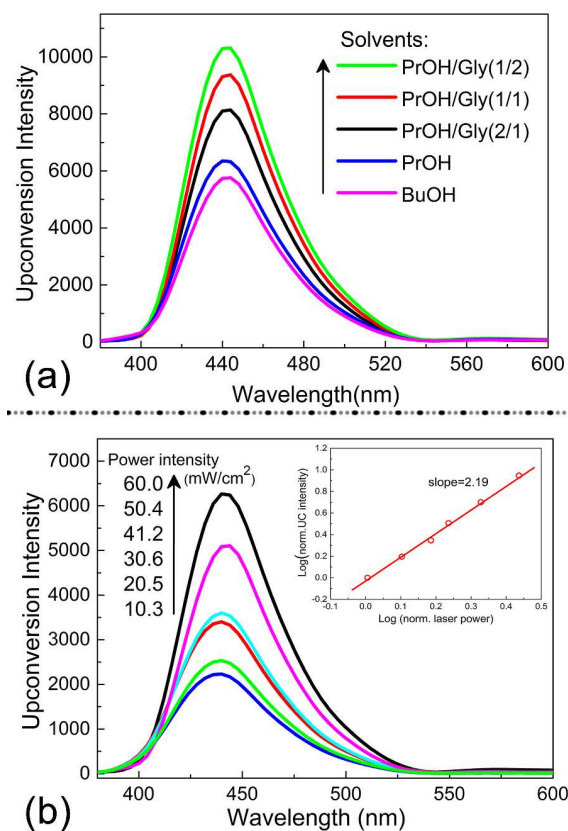

Figure 3 (**a**) Upconversion spectra of DPA/PdTPP (2.4 mM/8 µM) in different OH-containing solvents excited by diode laser (532 nm, 60 mW·cm^{-2}); (**b**) power-dependent upconversion intensity of DPA/PdTPP (2.4 mM/8 µM) in PrOH (insert: logarithmic plots of upconversion integral versus power density).
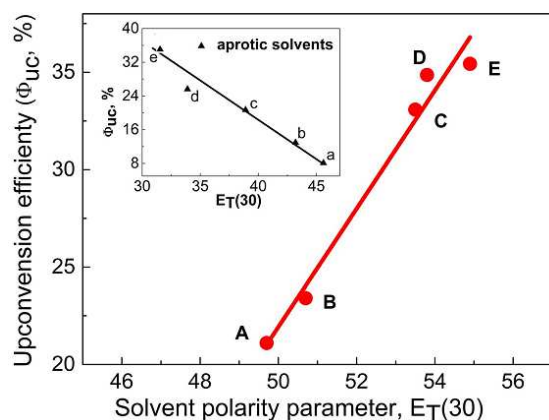
Figure 4 Solvent polarity-dependent upconversion efficiencies (Φ_{UC}) of DPA/PdTPP (2.4 mM/8 μM) in protonic solvents and aprotic solvents (Inset: a: acetonitrile; b: DMF; c: ethylacetate; d: toluene; e: cyclohexane.). Excitation conditions: 532 nm laser and 60 mW·cm^{-2}. (A: BuOH; B: PrOH; C: PrOH/Gly (2/1, v/v); D: PrOH/Gly (1/1, v/v); E: PrOH/Gly (1/2, v/v)).
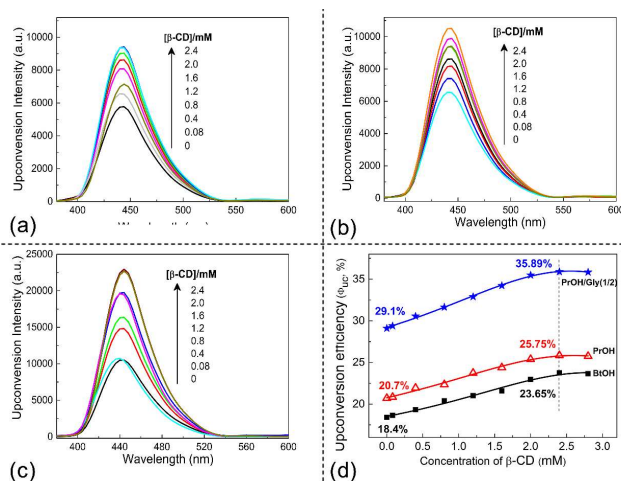

Figure 5 Upconversion spectra of DPA/PdTPP (2.4 mM/8 μM) in BuOH **(a)**, PrOH **(b)** and PrOH/Gly (1/2, v/v) **(c)** in the presence of different concentrations of β-CD and the corresponding upconversion efficiencies **(d)** under excitation of 532 nm and 60 mW·cm^{-2}.

In order to further examine the OH group effect on the upconversion efficiency (Φ_{UC}), we measured the TTA-upconversion behaviors of DPA/PdTPP in the presence of β-cyclodextrin (β-CD) that can provide much more OH-groups. As anticipated, with addition of β-CD to alcohol solvent, the upconversion intensities of DPA/PdTPP were indeed enhanced (Figure 5a-c). We noticed that the optimized additional concentration of β-CD is equal to the concentration of DPA (Figure 5d), suggesting that one molecule of DPA enters the cavity of β-CD to form the super-molecular DPA: β-CD (1: 1, mM/mM), where the free rotation of DPA is restricted within β-CD' hollow ring. As a result, the Φ_{UC} value shows increasing from 29.1 % in PrOH/Gly (1/2, v/v) to 35.89% % in PrOH/Gly/β-CD

(1/2/2.4, v/v/mM), reaching about 1.24-fold increase in comparison with the solvent (PrOH/Gly) without β-CD. Similar conditions are also observed in other alcohol solvents (see Figure 5d): that is, 18.4 % in BuOH *vs*. 23.65% in BuOH/β-CD (1/2.4, v/mM) and 20.7 % in PrOH *vs*. 25.75% % in PrOH/β-CD (1/2.4, v/mM).

Theoretically, TTA-UC efficiency (Φ_{UC}) is affected by a series of processes including the triplet-triplet energy transfer (TTT) from sensitizer to acceptor, the fluorescence quantum yield (Φ_f) and the triplet-triplet annihilation (TTA) of acceptor, as presented by Eq. (2).

$$\Phi_{UC} = \Phi_{TTT} \times \Phi_{TTA} \times \Phi_f \qquad (2)$$

$$\frac{P_o}{P} = K_{SV}[Q]+1 = k_q\tau_o[Q]+1 \qquad (3)$$

Here, TTT efficiency (Φ_{TTT}) can be estimated according to Stern-Volmer equation (3), where P_o and P are the phosphorescence intensities of PdTPP without and with DPA. K_{SV} is Stern-Volmer constant; k_q is the phosphorescence quenching constant which can stand for the Φ_{TTT} value; τ_o is the phosphorescence lifetime of PdTPP and [Q] is the concentration of DPA. Thus, the relationship between P_o/P and [Q] was plotted in Figure 6, where the linear slope is equal to K_{SV} (Table 3), showing in order of 4.56 in PrOH/Gly/β-CD (1/2/2.4, v/v/mM) > 3.97 PrOH/Gly (1/2, v/v) > 3.31 in PrOH/Gly (1/1, v/v) > 2.60 in PrOH/Gly (2/1, v/v) > 2.11 in PrOH > 1.64 in BuOH. If the sensitizer phosphorescence lifetime ($\tau_p=\tau_{p1}\cdot$x%+$\tau_{p2}\cdot$(1-x%)) is taken into account (see Table 1), the quenching constants (k_q, 10^9 M^{-1}·s^{-1}) are in the order of 1.91 in PrOH/Gly/β-CD (1/2/2.4, v/v/mM) > 1.80 in PrOH/Gly (1/2, v/v) > 1.71 in PrOH/Gly (1/1, v/v) > 1.48 in PrOH/Gly (2/1, v/v) > 1.37 in PrOH > 1.22 in BuOH (Table 3), that is, the TTT efficiency (Φ_{TTT}) showing gradually increase as the OH-group of medium increasing. On the other hand, these k_q values show almost one order of magnitude lower than the diffusion limit in aprotic organic solvents such as benzene (k_d =1.1×10^{10} M^{-1}·s^{-1}) and DMF (k_d = 8.3×10^9 M^{-1}·s^{-1}),[21, 43] strongly suggesting that the triplet-triplet energy transfer (TTT) in alcohol solvents is different from that in aprotic organic solvents.
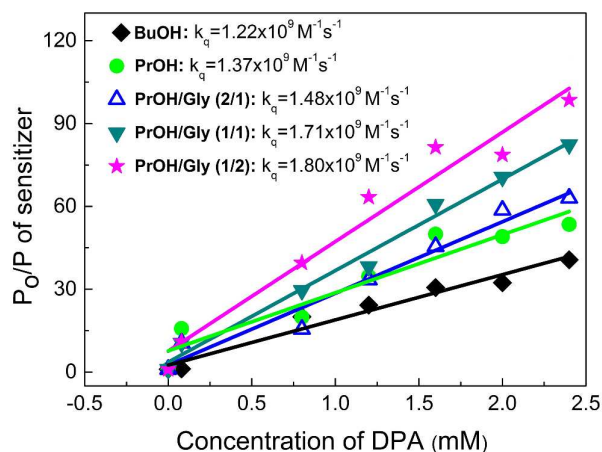

Figure 6 Stern-Volmer plots of the triplet-triplet quenching of PdTPP by DPA in different solvents under excitation of 532 nm and 60 mW·cm^{-2}.
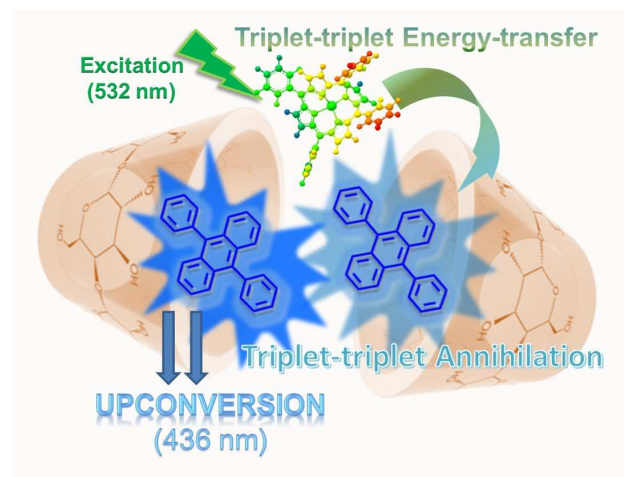
Figure 7 The proposed mechanism for triplet-triplet energy-transfer (TTT) and the triplet-triplet annihilation (TTA) and resulting upconversion (UC) in the presence of β-CD.

Based on the analysis above, the proposed TTA-UC mechanism in the OH-containing medium is that the intermolecular H-bond of medium has to contribution to the triplet-triplet energy transfer (TTT) and the fluorescence quantum yield (Φ_f). In the presence of β-CD, the hydrogen bond network of the cyclodextrin ring could slightly attract the metal ion of metallatedporphyrin to form weak metal-oxygen interactions,[44] which would like to beneficial to enhance TTT efficiency (kq, 1.91×10^9 $M^{-1}\cdot s^{-1}$). Meanwhile, the Φ_f of DPA shows further enhancement (94.48%) and the triplet-triplet annihilation (TTA) of DPA would be also increased since the free rotation of DPA is restricted and all other excited relaxation is decreased within β-CD. In this way (Figure 7), high the upconversion efficiency ($\Phi_{UC,}$ ~36 %) was lastly obtained.

Upconversion-powered photoelectrochemistry.

In recent years, many substantial efforts have been made towards the development of high efficiency energy conversion systems for turning solar light into chemicals, considering the sustainable and inexhaustible character of sunlight.[45-47] Here, a potentially useful strategy toward TTA-upconversion is firstly applied for upconversion-powered photocatalysis in a photoelectrochemical (PEC) cell that is the most advanced method to produce hydrogen by water splitting.[48] Under the excitation of diode laser (532 nm, 60 mW·cm^{-2}), the blue upconverted photons can radiate from the quartz cuvette containing the bimolecular PdTPP/DPA in the media of PrOH/Gly/β-CD (1/2/2.4, v/v/mM). By a computer controlled electrochemistry station, the photoelectronic current (I_i) can be recorded. In order to eliminate the photocurrent directly resulting from the upconverted composition, the contrastive experiment was conducted under identical conditions except for using a quartz cuvette containing only blank solvent. The results indicated that the $Cd_{0.7}Zn_{0.3}S$ photoanode produced photocurrent density (I_i) at ~0.09 μA·cm^{-2} (Figure 8a).

The optical behavior of the $Zn_{0.3}Cd_{0.7}S$ film was investigated by UV-Vis diffuse reflection spectrum (Figure. S4). The absorption band

edge of $Zn_{0.3}Cd_{0.7}S$ film around 527 nm corresponds with its band gap energy (2.35 eV) with the valence band (VB) at 2.010 eV and the conduction band (CB) at -0.360 eV.[49] A possible mechanism of the photocatalysis is proposed in Figure 8b, which shows the redox potentials of $Zn_{0.3}Cd_{0.7}S$ in relation to the normal hydrogen electrode potential (NHE). The appropriate energy levels of the conduction and valence band edges assure that $Zn_{0.3}Cd_{0.7}S$ acts as photoanode. Under the green-to-blue upconversion irradiation, the photogenerated electrons (e) are excited from the valence band (VB) to the conduction band (CB) of $Zn_{0.3}Cd_{0.7}S$. The electrons then transfer to Pt-counter electrode, where they can react with H$^+$ to form H$_2$. The holes remained on the surface of $Zn_{0.3}Cd_{0.7}S$ react with water to produce O$_2$.
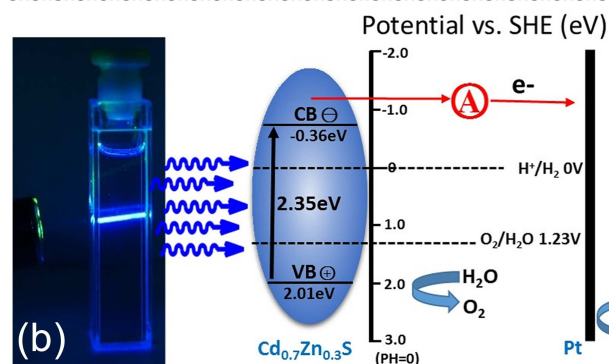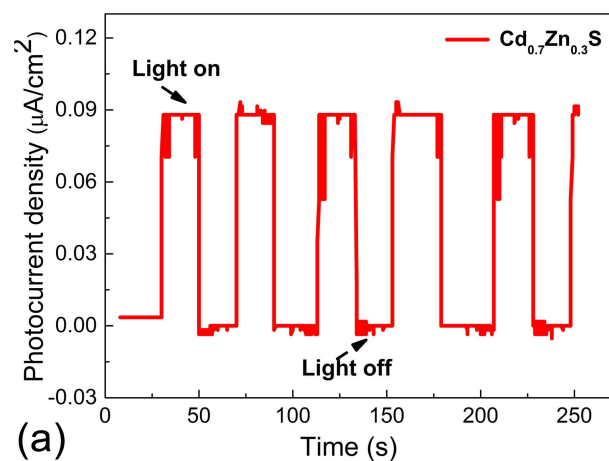

Figure 8 (**a**) The recorded photocurrent curve in the PEC and (**b**) the proposed mechanism for photocatalytic H$_2$-production under our green-to-blue upconversion irradiation.

Conclusions

We have demonstrated for the first time that the alcohol solvent with β-cyclodextrin (β-CD) is a feasible medium for triplet-triplet annihilation upconversion (TTA-UC). In this medium, sensitizer (PdTPP) is found to have longer phosphorescence lifetime (28.31 μs) and to promote the triplet-triplet energy transfer (TTT), confirmed by Stern-Volmer equation. In the presence of *β-cyclodextrin (β-CD)*, the free rotation of DPA is restricted with the result that both the fluorescence deactivation and the triplet-triplet annihilation of acceptor (DPA) are enhanced. Thus, a significant

increasing upconversion efficiency (Φ_{uc}) up to ~36% was obtained under excitation of low power density at 60 mW·cm^{-2} (λ_{ex}=532 nm).

A demonstration experiment of photocatalytic water splitting by semiconducting catalysts has carried out in a photoelectrochemical (PEC) cell, wherein the oxidation takes place at a $Zn_{0.3}Cd_{0.7}S$ semiconductor photoanode and hydrogen was produced at a platinum rod counter electrode. Thus, the photocurrent resulting from the hydrogen generation is recorded at ca. 0.09 µA/cm^2. The importance in this study suggests that upconversion-powered photoelectrochemistry possesses the potential application for hydrogen generation from water under excitation of sun energy.

Acknowledgments

Notes

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