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Communication

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Encapsulated Triplet–Triplet Annihilation-Based Upconversion in the Aqueous Phase for Sub-Band-Gap Semiconductor Photocatalysis

Jae-Hyuk Kim and Jae-Hong Kim*

School of Civil and Environmental Engineering, Georgia Institute of Technology, 200 Bobby Dodd Way, Atlanta, Georgia 30332, United States

Supporting Information

ABSTRACT: We herein report the first instance of aqueous-phase photosensitization of semiconductor photocatalysts (WO_3 loaded with Pt) through triplet–triplet annihilation (TTA)-based upconversion of sub-band-gap photons. The TTA-based upconversion (UC) was achieved in the aqueous phase by encapsulating the solvent phase containing a benchmark platinum(II) octaethylporphyrin/9,10-diphenylanthracene sensitizer/acceptor pair in a rigid polymer shell in the form of aqueous dispersible microcapsules. A mixture of hexadecane and polyisobutylene was used as the inner solvent phase. This eliminated the need for the deoxygenation step that is essential for existing TTA-based UC processes and enabled stable UC to occur even after a month of exposure to the ambient environment. The photoluminescence properties were examined, and UC-assisted photochemical production of hydroxyl radical from green (532 nm) light irradiation was demonstrated for the first time.

Upconversion (UC) has been the subject of extensive research over the past decade for its potential to enhance the efficiency of photonic devices in an innovative way by allowing them to harvest otherwise-wasted lower-energy portions of the solar spectrum. UC is the process of absorbing two or more lower-energy photons, combining their energy, and emitting one higher-energy photon. UC based on transparent inorganic host materials doped with rare-earth metals, namely, lanthanide ions, functions via either sequential absorption of photons by a long-lived intermediate excited state or sensitized energy transfer among excited states.[1] Although numerous studies have been reported, this process suffers from the requirement of high incident light intensity (~10 to 10^4 W/cm^2) and inherently low external quantum efficiency. On the other hand, the triplet–triplet annihilation (TTA)-based UC process occurs through a completely different mechanism, wherein the photon energy absorbed by a sensitizer is transferred to an acceptor through triplet–triplet energy transfer (TTET), and two excited acceptors undergo TTA, producing upconverted singlet fluorescence. TTA-based UC (TTA-UC) is known to have a significantly higher quantum yield (3–40%) even at low excitation intensities (1–10 mW/cm^2).[2] Unfortunately, the application of TTA-UC in the ambient aqueous phase has been severely limited because it typically employs organic and metalloorganic chromophores that are soluble only in organic solvents. Moreover, to prevent triplet-state quenching, the medium must be devoid of oxygen, which is difficult to achieve in practical aqueous-phase scenarios.[2a,b,3]

The realization of efficient TTA-UC in the ambient, oxygen-rich aqueous phase environment shall open new doors for many sunlight-powered applications, including alternative energy technologies such as hydrogen production and environmental remediation technologies, where UC materials can be coupled with widely used semiconductor photocatalysts. Semiconductor photocatalysts produce electron–hole pairs upon absorption of photons with energies higher than their intrinsic band-gap energy and subsequently generate a redox potential that can be further utilized for a wide range of applications. For example, photocatalysts such as titanium dioxide (TiO_2) have been employed with some notable commercial success in the production of reactive oxygen species from redox reactions with hydroxide ions and water molecules for the purpose of degrading organic/inorganic pollutants[4] and inactivating pathogenic microorganisms.[5] Unfortunately, the band-gap energy of traditional semiconductor photocatalysts such as TiO_2 is ~3.2 eV, which corresponds to the UVA region; hence, photons with energy lower than the band-gap energy, which account for more than 98% of the solar spectrum, cannot be utilized to sensitize photocatalysts. Accordingly, numerous past studies have focused on developing visible-light-sensitizable photocatalysts. These include doping with carbon,[6] nitrogen,[7] or rare-earth metals[8] (with TiO_2 as the most common substrate); formation of composites with other inorganic photocatalysts;[9] and combination with other photosensitizers.[10] Photocatalysts with a narrower band gap (2.6–2.8 eV), such as WO_3,[11] CdS,[12] and Bi_2WO_6,[13] have also been pursued as alternatives to TiO_2.

A strategy to enhance semiconductor photocatalysis via incident light manipulation by TTA-UC is in marked conceptual contrast to the previous efforts, which were almost exclusively devoted to modifying the photocatalysts themselves. Notably, even for the aforementioned photocatalysts with enhanced visible-light susceptibility, the absorption range does not extend beyond the blue-light region (~450 nm) of the solar spectrum. Some studies have reported photocatalysis assisted by UC, but only with a much less efficient lanthanide-based inorganic system.[1a,b] TTA-UC was coupled with semiconduc-

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tors for the first time in a recent study by Khnayzer et al.[2d] Water splitting in a photoelectrochemical cell with a WO_3-coated electrode was driven by sub-band-gap light irradiation through UC.[2d] However, for the aforementioned reasons, this system consisted of a sensitizer/acceptor pair dissolved in a deoxygenated solvent that was sealed and separated from the aqueous phase, which is nonideal for the most efficient performance.[2d] Although a few attempts have been made in the past to achieve TTA-UC in the aqueous phase by encapsulating or embedding chromophores in polymers,[14] silica particles,[15] or micellar carriers,[16] they had critical limitations such as the need for deoxygenation or relatively low quantum efficiencies.

Herein we report the first demonstration of semiconductor-based photocatalysis induced by a TTA-UC system dispersed in an oxygen-rich aqueous phase. To achieve TTA-UC in the aqueous environment, a solvent containing sensitizer/acceptor pair was encapsulated using a rigid polymer shell of micrometer scale. Platinum-loaded tungsten oxide (Pt/WO_3), which generates ·OH when photoactivated, was selected as a representative visible-light-absorbing photocatalyst.[11,17] Since Pt/WO_3 absorbs in the blue region but not in the green,[17] we employed a benchmark platinum(II) octaethylporphyrin (PtOEP)/9,10-diphenylanthracene (DPA) green-to-blue UC sensitizer/acceptor pair.[18] Figure S1 in the Supporting Information (SI) shows the chemical structures of PtOEP and DPA along with their normalized absorption and emission spectra in degassed tetrahydrofuran (THF). Figure S2 presents a conceptual illustration of this study.

The core solvent phase was hexadecane (HD), which has previously been used for the fabrication of similar two-phase microcapsules.[19] HD is also less toxic and less volatile than solvents that have commonly been used as media for TTA-UC, such as toluene,[2a,d,3b] THF,[20] and acetonitrile.[2c,3b] To HD was added polyisobutylene (PIB; MW ≈ 1350 Da) at 5 wt % to overcome two critical limitations of this solvent-necessary UC process. First, PIB increases the solubility of PtOEP and DPA. Second and more importantly, we observed that UC was achieved by simply adding PtOEP and DPA to the HD/PIB mixture without the need for the deoxygenation step that is essential in any existing solvent-based TTA-UC processes. The UC system based on simple addition of PtOEP/DPA to HD/PIB in the ambient atmosphere was remarkably stable and observed to last for more than 2 weeks of exposure to the atmosphere (Figure S3). The UC quantum yield of the 0.02 mM PtOEP/0.38 mM DPA system in HD/PIB gradually increased with the laser power density, reaching 28% at ~1.9 W/cm^2 (Figure S4). This value is relatively high and comparable to those reported in deoxygenated volatile organic solvents,[2b,c,21] indicating that the HD/PIB mixture can serve as an appropriate medium for efficient TTA-UC under atmospheric conditions. We also observed equally efficient UC using another well-known chromophore pair (i.e., PdOEP/DPA)[2d,e,22] by simply dissolving this pair in HD/PIB in the same manner (data not shown). While the exact role of HD and PIB in avoiding oxygen quenching was not the focus of this study and is currently unknown, we postulate that it is related to the oxygen impermeability of PIB.[23]

The shell of the microcapsule was made from ethoxylated trimethylolpropane triacylate ester (ETPTA). The polymer phase was extruded through a glass capillary and integrated with a flow of the PtOEP/DPA-containing HD/PIB phase from an adjacent capillary (Figure S5). The polymer phase then encapsulated the solvent to form discrete emulsion globules as they were dispersed in the aqueous phase containing poly(vinyl alcohol) as a surfactant. Finally, the polymer phase was instantly cured to form a rigid polymer shell by UV irradiation of a phosphine oxide derivative photoinitiator. Small amounts of amine acrylate and benzophenone were added to the polymer phase to minimize oxygen inhibition during photopolymerization. The detailed procedure is given in the SI.

Figure S6 and Figure 1 present optical and fluorescence microscopy images of the prepared UC microcapsules. The resulting microcapsules were spherical and monodispersed without any noticeable agglomeration in water. The red color in the capsule shell (Figure 1a) resulted from phosphorescence of PtOEP that diffused from the core to the polymer phase during emulsification and became entrapped during photocuring. DPA should also have been present in the shell, but UC was prohibited because the rigid polymer matrix did not allow diffusive interactions between PtOEP and DPA. In contrast, UC from green to blue was clearly observed in the HD/PIB core phase (Figure 1b). Consequently, both Stokes- and anti-Stokes emission under green-light excitation was demonstrated in a single microcapsule (Figure 1c). Control experiments performed with only PtOEP or only DPA showed only Stokes emission (Figure S7). Notably, the upconverted blue-light emission from UC microcapsules dispersed in water was intense enough to be observed readily with the naked eye in daylight after the incident scattered light was removed using a 450 nm bandpass filter. In addition, the intense UC emission was readily observed even after the microcapsules were stored in oxygen-rich water for more than a month. We were further able to control the size of the microcapsules from 150 to 400 μm simply by adjusting the tip diameters of the glass capillaries (Figure 2). In addition, microcapsules with varying shell thickness (and therefore a varying core/shell volume ratio) were also synthesized by controlling the ratio of the flow rates of the HD/PIB and polymer phases (Figure S8).

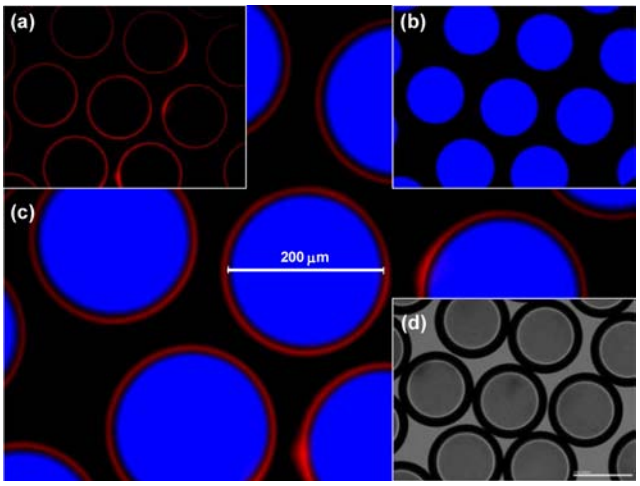

Figure 1. Fluorescence microscopy images of microcapsules containing PtOEP/DPA in the HD/PIB core phase under xenon arc lamp irradiation through a ~540 nm bandpass filter. The images in (a) and (b) were obtained by using (a) red (620 nm) and (b) blue (445 nm) bandpass filters, respectively, and the image in (c) was obtained by merging (a) and (b). A reference image (d) was obtained using an optical microscope. All of the images were captured at the same spot.

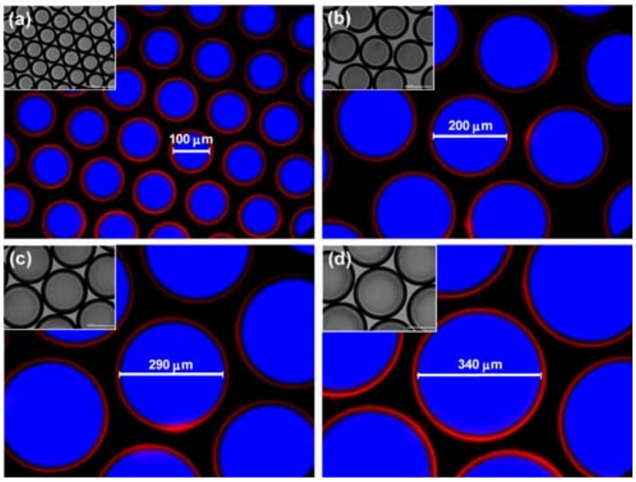

Figure 2. Fluorescence microscopy and (insets) optical microscopy images of microcapsules with diameters of (a) 150, (b) 250, (c) 350, and (d) 400 μm.

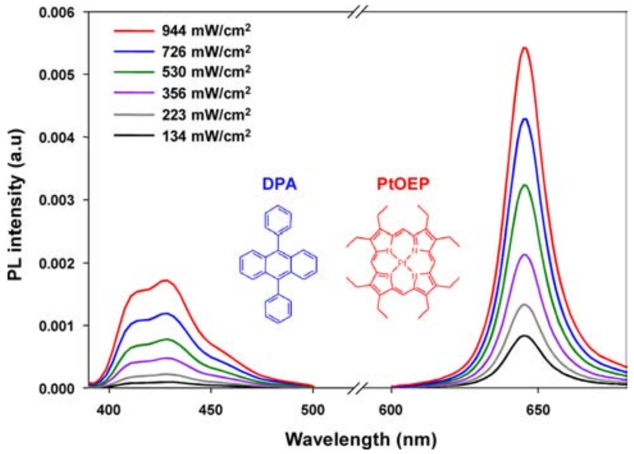

Figure 3. Emission profiles of 400 μm diameter PtOEP/DPA-core microcapsules dispersed in water as a function of incident laser power under excitation at 532 nm.

Figure 3 shows the spectrum of Stokes and anti-Stokes emission of UC microcapsules in the aqueous phase under selective laser excitation at 532 nm. Consistent with the fluorescence microscopy analysis, the triplet phosphorescence emission from ^{3}PtOEP* at 600−680 nm produced by excitation of ground-state PtOEP at 532 nm and subsequent intersystem crossing to the triplet state was observed. It should be noted that the phosphorescence emission originated mostly from the shell, where diffusive interactions between the chromophores were prohibited. In the capsule core, ^{3}PtOEP* further underwent TTET to ^{1}DPA^0, producing ^{3}DPA*. When two ^{3}DPA* molecules underwent TTA, ^{1}DPA* was produced and emitted upconverted singlet fluorescence at 400−500 nm, as shown in the figure. The intensities of both emissions were highly dependent on the incident laser power density.

Figure 4 presents double-logarithmic plots of the static intensities of the singlet fluorescence and triplet phosphorescence emanating from DPA and PtOEP, respectively, as a functions of incident light power density. The phosphorescence intensity showed a linear dependence throughout the laser power density range (slope of the log−log plot = 1). In contrast, the power dependence of the upconverted fluorescence intensity showed a crossover region where the dependence changed from quadratic (slope = 2) to pseudolinear (slope = 1.3). The quadratic dependence of the UC emission intensity on laser power density is well-documented in the literature.[2b,3] However, the onset of a linear dependence is more common in Stokes processes and has been reported for the anti-Stokes process only in a few recent studies.[2e,14b,22] In the linear-dependence regime, the UC quantum yield could be maximized, as most of the excited triplet-state acceptors are consumed via the TTA process rather than unimolecular decay.[22] In the present work, we did not observe a completely linear power dependence even at sufficiently high laser power density (>10^3 mW/cm^2). This might be due to inhibition of chromophore diffusion by PIB in HD. Regardless, the occurrence of a crossover from a quadratic to pseudolinear power dependence at a relative low incident power (~200 mW/cm^2) indicates promising potential to achieve the highest possible UC efficiency through the participation of a majority of the triplet-excited acceptors in this TTA process.

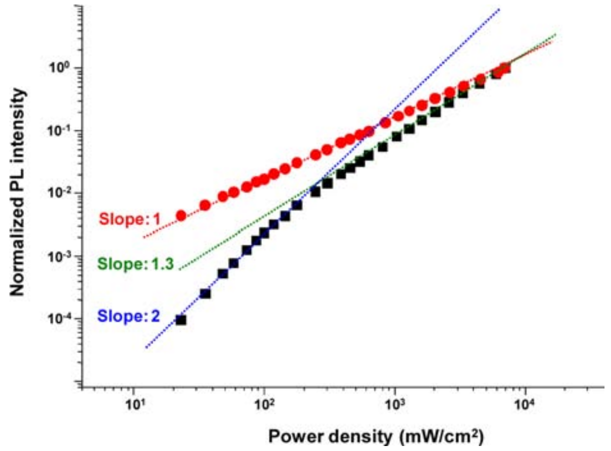

Figure 4. Normalized emission intensities of phosphorescence at 632 ± 5 nm (red ●) and upconverted fluorescence at 430 ± 5 nm (black ■) from UC microcapsule dispersed in water as functions of the power density of the incident laser (532 nm). The dashed lines are linear fits with slopes of 1.0 (red, linear), 1.3 (green, pseudolinear), and 2.0 (blue, quadratic).

Next, UC microcapsules were dispersed in an aqueous phase containing Pt/WO$_3$ photocatalysts with a band-gap energy of 2.8 eV and irradiated with green light at 532 nm (2.3 eV). As a probe molecule for ·OH, we used coumarin, which undergoes a highly selective reaction with ·OH to form 7-hydroxycoumarin, whose maximum fluorescence emission is centered at 460 nm (Figure S10); coumarin has been widely used to verify ·OH production in the aqueous phase.[11,24] Photocatalysis was performed in the moderate annihilation regime to maximize the UC efficiency of the microcapsules. Figure 5 confirms the production of ·OH, which increased with increasing incident light power. Control tests ensured that ·OH production was not observed when either the microcapsules or the Pt/WO$_3$ photocatalyst was individually present. This result is the first example of the production of ·OH (redox potential = 2.7 eV) through photosensitization of a photocatalyst whose band-gap energy (2.8 eV) is much larger than the photon energy (2.3 eV).

In summary, this study has presented a few critical advances that will broaden the application of TTA-based UC beyond past attempts that have mostly been confined to deoxygenated

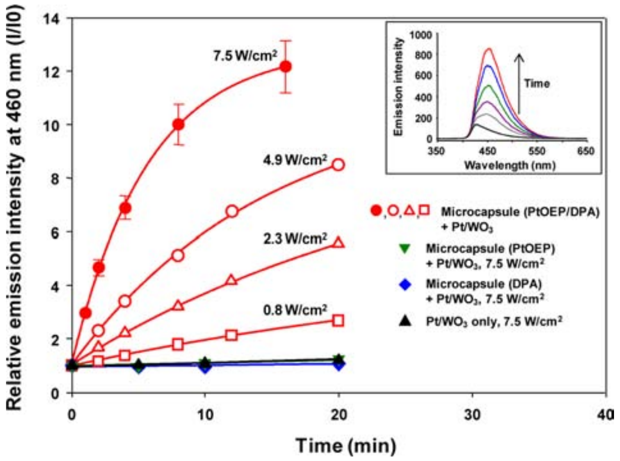

Figure 5. Formation of ·OH as evidenced by the production of the fluorescent coumarin−OH adduct, 7-hydroxycoumarin, in solutions containing coumarin (C_0 = 1.1 mg/L), microcapsules (∼18% v/v, diameter = 400 mm), and/or Pt/WO_3 (0.9 g/L) under green-light (532 nm) laser irradiation. Inset: time-dependent fluorescence spectra (7.5 W/cm^2).

solvent environments. First, we achieved stable TTA-UC in the aqueous phase by encapsulating the host medium inside rigid, spherical, monodispersed microcapsules. Second, the use of an HD/PIB mixture as the inner phase prevented oxygen quenching, which has been a critical hurdle for utilizing this process in ambient aqueous environments. Finally, ·OH production by photons with energy lower than the band gap of any existing semiconductor photocatalysts via aqueous phase TTA-UC was demonstrated for the first time. We expect that this microcapsule system can host a variety of sensitizer/acceptor pairs for various light manipulating scenarios and can be employed in a wide range of aqueous-based applications, including environmental remediation, hydrogen production, and bioimaging.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details regarding materials and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jaehong.kim@ce.gatech.edu

Notes

The authors declare no competing financial interest.

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