Plasmon-Enhanced Homogeneous and Heterogeneous

Triplet-Triplet Annihilation by Gold Nanoparticles

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Supporting Information

Chemicals

All reagents and solvents were used as received without further purification: Rose Bengal (RB), 1,3-diphenylisobenzofuran (DPBF), Gold(III) chloride trihydrate (HAuCl₄·3H₂O), cysteamine hydrochloride, sodium borohydride, N-hydroxysulfosuccinimide (sulfo-NHS) and spectroscopic grade N,N- dimethylformamide (DMF) were purchased from Sigma-Aldrich. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) was purchased from Thermo Fisher.

Molecular structures of RB and DPBF





(a) RB

(b) DPBF

Synthesis of cysteamine-capped gold nanoparticles

Cysteamine-capped gold nanoparticles (AuNPs) were synthesized following a previously reported procedure.^[S1] Briefly, 400 μ L of 213 mM cysteamine hydrochloride and 40 mL of 1.42 mM HAuCl₄ were mixed in a 125-ml Erlenmeyer flask. After stirring for 30 min at room temperature in the dark, 10 μ L of 10 mM NaBH₄ was added quickly into the mixture under vigorous stirring for 30 min. After stirring, the gold nanoparticles solution was stored in the refrigerator until later use. AuNPs were characterized with UV-vis absorption spectra, transmission electron microscopy (TEM).

Conjugation of cysteamine-capped AuNPs and Rose Bengal

The free amino groups on the AuNPs surface were used to conjugate with RB through the formation of an amide bond through EDC chemistry.^[S2] RB-conjugated AuNPs were prepared by the reported literature with suitable modification (Figure S1). ^[S3] In brief, 2 mg of EDC and 3 mg of sulfo-NHS were added into 5 mL of 0.2 mM RB solution, resulting in a 10-fold molar excess of EDC to RB. The molar ratio of EDC and sulfo-NHS was kept constant at 1:2 (EDC/sulfo-NHS). The reaction mixture was stirred for 30 min at room temperature. Thereafter, 1.5 mL of AuNP solution was introduced to the solution dropwise with a syringe pump. The reaction mixture was further stirred for 24 h at room temperature. In order to remove any free RB, the nanoparticles were washed by centrifugation (14,000 rpm, 7 times, 20 min each) until the supernatant wais colourless. The nanoparticles were then redispersed in water.



Figure S1. (a) TEM image of AuNP@RB. Scale bar is 50 nm. (b) Absorption spectra of RB, AuNPs and AuNP@RB.

Preparation of samples for spectroscopic measurements

Samples were prepared in the following manner. Equal amount of AuNP@RB solutions were placed in two vials. Excess NaCN solution was added into one of the vials, while same volume of water was added into the other, so as to maintain the same concentration of RB in the two vials. Separately, DPBF was dissolved into DMF. These DPBF, AuNP@RB and RB stock solutions were mixed proportionally to prepare the respective samples. Each mixture was deoxygenated through freeze-pump-thaw cycle for 3 times before taking the spectroscopic measurements.

Spectroscopic measurements

Absorption spectra were collected with a Cary 50 Bio UV-Vis spectrophotometer. Singlet oxygen generation emission spectra were collected on a QM-40 spectrofluorometer (PTI) equipped with a high performance InGaAs photodiode and a lock-in amplifier (MODEL 410, Scitec Instruments) by monitoring the phosphorescence emission at 1270 nm. Xenon arc lamp was used as the excitation light source. A long-pass filter (850 nm cut-off) was used to remove the higher-order artifact signals. Samples (AuNP@RB) dispersed in DI water were loaded into a quartz cuvette and placed in a light-tight chamber for testing. To dissolve the gold nanoparticles out of AuNP@RB hybrid, an excess amount of sodium cyanide (0.1 M) was added, which itself did not affect the singlet oxygen generation from RB.

TTA-UC spectra were collected on a home-built setup as illustrated in Figure S2. The system consists of a 532-nm DPSS laser (85-GCB-020, Melles Griot) and some optical elements (shutter, attenuator, microscopic objective and optical fibers), a monochromator (0.3-m focal length, triple grating turret, Acton Research) and a photon counting PMT (Hamamatsu R928P), data acquisition electronics & software (NCL and SpectraSense, Acton Research), and a PC.

The laser beam was focused onto the polished end of a 400- μ m silica step-index optical fiber (NA = 0.22, RoMack) with a microscope objective (10×, NA = 0.25, Newport). The shutter and the variable neutral density filter (Newport) were used to adjust the laser intensity at the samples. Laser power was attenuated to 1.25 mW (or as noted in the figures) at the sample position, focused onto a spot of 2 mm in diameter. Samples were contained in a quartz cuvette placed in front of the fiber, and exposed to laser only during data acquisition to minimize photodegradation/photobleaching. All experiments were carried out at room temperature.



Figure S2. Schematic of instrumental setup for upconversion measurements.

Upconversion time decay measurements were carried on a home-built setup, which includes a 532-nm laser modulated by a rectangular waveform of 80 Hz, a function generator (Atten 20B) as a power supply for the laser, a photomultiplier tube (Hamamatsu R928P) placed after the monochromator (Acton Research, SpectroPro 500i), and a digital oscilloscope. The down slope of the modulation was used to trigger the oscilloscope, which monitored the output from the photomultiplier. Laser stray-light was reduced by using a 532-nm notch filter. All of the measurements were performed at room temperature.



Figure S3. (a, b) Normalized absorption and emission spectra of DPBF and RB in deoxygenated DMF, respectively, at room temperature.

Upconversion quantum yield determination

Upconversion quantum yield of AuNP@RB-DPBF and RB-DPBF with different concentrations was determined by the relative method using Eq.S1,^[S4]

$$\phi_{unk} = 2\phi_{std} \left(\frac{A_{std}}{A_{unk}}\right) \left(\frac{I_{unk}}{I_{std}}\right) \left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$
(S1)

where Φ , A, I and η represent the upconversion quantum yield, absorbance, integrated photoluminescence intensity from the spectra and refractive index, respectively. Subscript *std* denotes a reference fluorophore of known quantum yield and subscript *unk* the sample to be determined. Pure RB solution is used as the reference standard in this study. The quantum yield of RB is $\Phi_{std} = 0.11$ in ethanol at room temperature under 532 nm excitation.^[S5] The refractive indices of DMF and ethanol at 532 nm are $\eta(DMF) = 1.428$ and $\eta(EtOH) = 1.361$.^[S6,S7] The integrated intensity of the upconversion was measured in the region of 350-600 nm while that of RB was measured in the region of 500-750 nm. All measurements were carried out under the same experimental settings. The results are shown in Figure S4.



Figure S4. (a) Absorption spectra of RB in DMF at room temperature. (b) Linear fitting curve of absorbance at 563 nm.



Figure S5. (a, b) Emission spectra of AuNP@RB-DPBF and RB-DPBF (at ~585 nm) in deoxygenated DMF, respectively, at room temperature. Power density: 40 mW/cm².



Figure S6. (a, b) Upconversion and fluorescence spectra of AgNP@RB-DPBF (2 mM) and RB-DPBF (2 mM) in deoxygenated DMF, respectively, at room temperature. Power density: 40 mW/cm².



Figure S7. (a) Integrated fluorescence intensity of AuNP@RB-DPBF and RB-DPBF as a function of [DPBF]. (b) Excitation power dependence of upconversion and RB fluorescence intensities. Green and black colors are from the upconversion (485±5 nm) of RB-DPBF (2 mM) and AuNP@RB-DPBF (2 mM), respectively. Blue and red colors are from the fluorescence (585±5 nm) of RB-DPBF (2 mM) and AuNP@RB-DPBF (2 mM), respectively.



Figure S8. Time decay of upconversion emission at 485 nm from (a) RB (10.8 μ M)-DPBF (2 mM), and (b) AuNP@RB (10.8 μ M)-DPBF (2 mM), respectively.



Figure S9. Lifetime measurements of emission at ~585 nm of free RB and AuNP@RB. IRF refers to impulse response function.

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