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Phosphorescent Enhancement

Metal-Enhanced 1270 nm Singlet Oxygen Phosphorescence**

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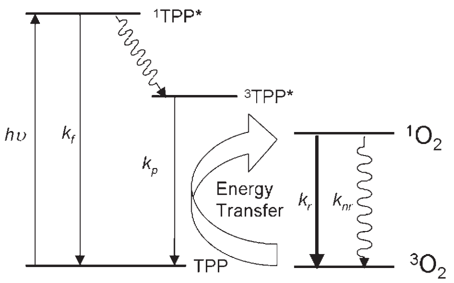
The first excited state of molecular oxygen, singlet oxygen ($O_2(a^1\Delta_g)$, or simply $^1O_2$), is a reactive intermediate of importance in processes ranging from polymer degradation[1] to cell death.[2] The most unambiguous way to detect $^1O_2$ is by its characteristic phosphorescence at 1270 nm.[3,4] However, this emission is very weak because the overall deactivation of $^1O_2$ is dominated by nonradiative pathways; typical phosphorescence yields (Φ_P) are on the order of 10^{-5} to 10^{-7}.[3] This can make optical detection of $^1O_2$ difficult, particularly in spatially resolved experiments from small volumes.[5,6] Thus, much would be gained if Φ_P could be increased. Herein, we demonstrate that the 1270 nm radiative decay of $^1O_2$ can be enhanced by coupling to localized surface plasmon resonances (LSPRs) in carefully designed gold nanostructures.

$^1O_2$ is commonly produced in a photosensitized process (Scheme 1) with Φ_P expressed as a product of the $^1O_2$ yield, Φ_Δ, and the fraction of $^1O_2$ molecules that decay radiatively, $\tau_\Delta k_r$ [Eq. (1)], where the $^1O_2$ lifetime, $\tau_\Delta = (k_{nr} + k_r)^{-1}$, is

$$\Phi_P = \Phi_\Delta \tau_\Delta k_r \quad (1)$$

expressed in terms of the radiative, k_r, and nonradiative, k_{nr}, rate constants for $^1O_2$ decay.

LSPRs associated with noble metal nanostructures[7] and plasmon-enhanced optical transitions are well studied.[8] Attempts have been made using silver nanoparticles to enhance yields of photosensitized $^1O_2$ production, Φ_Δ, by increasing the yield of photosensitizer excited states.[9] However, the issue of using a metal to directly enhance k_r has not been addressed.



Scheme 1. Photosensitized production and subsequent decay of singlet oxygen. Also shown are TPP fluorescence (k_f) and phosphorescence (k_p).

$^1O_2$ differs significantly from common phosphorophores. First, its emission occurs in a narrow band at circa 1270 nm.[3] This phosphorescence is further into the IR than those for which a metal-enhanced effect has been reported.[10–13] Thus, a carefully designed metal structure is needed to selectively enhance this transition. Second, oxygen is highly mobile and cannot be fixed at a certain distance from the metal structure. Thus, even if $^1O_2$ is produced close to the metal, it will diffuse in and out of the electromagnetic (EM) field enhancement regions induced by the LSPRs.

Herein we employed the novel technique of hole–mask colloidal lithography[14] to prepare gold nanodiscs of controlled size and aspect ratios on glass substrates (Figure 1). Compared to aggregates of metal particles used in most studies of emission enhancement, nanodiscs have well-defined and narrow plasmon resonances that allow for selective perturbation of an optical transition. Control of the diameter-to-height aspect ratio L_a (Figure 1) makes it possible to tune these resonances throughout the VIS-IR spectral domains. For this system, the EM-field enhancements from excited dipolar LSPRs are largest in the plane of the disc and extend tens of nanometers from the edge of the disc.[15]

Samples were produced with A) no nanodiscs, B) nanodiscs with $L_a = 7.5$, and C) nanodiscs with $L_a = 14$. The spacing between the discs and spatial arrangement (short-range ordered arrays with no long-range order) were chosen to prevent coupling between the individual LSPRs[16] (see the Supporting Information for SEM images of the nanodiscs). Samples were coated with a thin layer (ca. 100 nm) of polystyrene (PS) doped with the $^1O_2$ photosensitizer, tetraphenyl porphyrine (TPP). Before coating, type B samples exhibited a resonance at 710 nm and type C samples a resonance at 1080 nm (see the Supporting Information). However, the larger refractive index of PS compared to air

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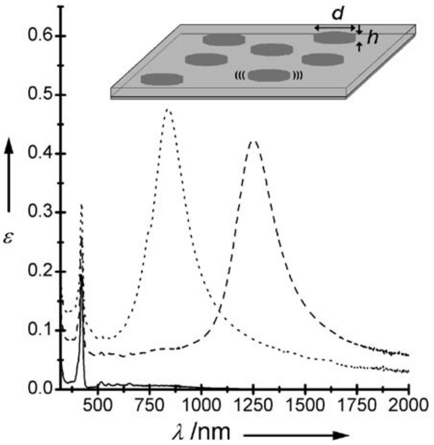

Figure 1. Extinction spectra of the samples examined. The TPP Soret band is seen at 420 nm and the gold nanodisc LSPR at 840 nm (dotted line, type B, discs with $L_a = 7.5$) and 1260 nm (dashed line, type C, discs with $L_a = 14$). The solid line shows the type A control with no discs. A schematic representation of the nanodisc array and LSPR field enhancement region of one nanodisc is shown above the spectra. $L_a = d/h$, $h = 20$ nm for all samples.

red-shifts the LSPRs to 840 nm and 1260 nm, respectively, after coating (Figure 1). TPP concentrations were about 50 mM, which yielded absorbances of circa 0.2–0.3 at 420 nm. No evidence of TPP aggregation or photobleaching was observed in the absorption or fluorescence spectra. In the $^1O_2$ experiments, TPP was excited at 420 nm. At this wavelength, gold also contributes slightly to the extinction spectrum (Figure 1), predominantly through absorption (interband transition) rather than scattering by the nanostructures.

Experiments were performed using a microscope configured for photosensitized $^1O_2$ experiments.[5,6] With the objective used (60 ×, NA 0.9), the irradiating laser beam was circa 1.4 μm in diameter at the sample[6] and thus covered 3.4–26 nanodiscs, depending on the sample type (see the Supporting Information). For a given position on the sample, emission was monitored at four different wavelengths: 650 nm (TPP fluorescence), 1200 nm, 1270 nm, and 1325 nm. Data from several positions were averaged. The samples appeared homogenous and the signals obtained did not vary notably across the samples.

A 1270 nm, time-resolved emission signal characteristic of $^1O_2$ production and decay in PS[17] was observed from all samples with TPP (Figure 2). The gold nanodiscs themselves did not produce a 1270 nm signal. The observed 1270 nm signal was assigned to $^1O_2$ phosphorescence on the basis of three points: 1) as expected,[17] a decrease in the rate of signal decay was observed when the medium was changed to perdeutero-PS; 2) the signal disappeared upon removal of oxygen from the film; and 3) $^1O_2$ does not emit at 1200 and 1325 nm,[3] and indeed only weak signals were observed at these wavelengths in all cases. These latter signals can be attributed to TPP emission. Values of τ_Δ obtained from our signals were independent of whether data were recorded from sample A, B, or C (i.e., τ_Δ was independent of the presence of the gold nanodiscs). However, the data are consistent with some quenching of $^1O_2$ by the sensitizer, which is expected at the TPP concentrations used (i.e., we typically obtained τ_Δ values of circa 16–18 μs instead of the circa 22–25 μs expected[17] for PS).

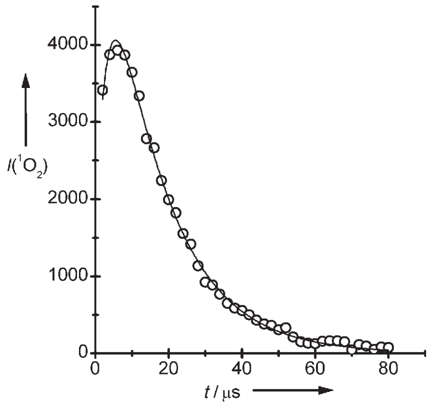

Figure 2. Time-resolved 1270 nm $^1O_2$ phosphorescence signal from a type C sample.

After correcting for differences in absorbance at the excitation wavelength, the intensities of signals observed at 1270 nm for type C samples were enhanced about 3.5 times relative to those from samples with no nanodiscs (type A samples, Figure 3). The key point is that the LSPR in the type C sample is spectrally coincident with $^1O_2$ phosphorescence (Figure 1). For type B samples, where the overlap of the plasmon resonance with the 1270 nm $^1O_2$ phosphorescence is much smaller, an enhancement factor of only 1.5 was observed (despite a higher density of nanodiscs; see the Supporting Information). No enhancement of the 650 nm TPP fluorescence was observed in either sample, indicating that the observed effect is not due to metal-enhanced absorption or to lateral scattering of excitation light leading to artifacts of increased path length. In any event, because the inherent $^1O_2$ yield for TPP is already high ($\Phi_\Delta \approx 0.7$),[4] an

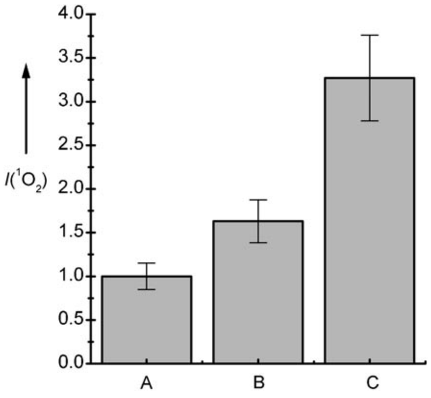

Figure 3. 1270 nm $^1O_2$ phosphorescence yields obtained from the metal-enhanced experiments (B and C) relative to the metal-free control (A). For C, the plasmon resonance is centered at 1260 nm (Figure 1). The type B sample used has a higher density of nanodiscs (see the Supporting Information). Data are averages of three independent experiments.

increase in the production efficiency of $^1O_2$ would not be able to account for the observed data. Rather, the data are consistent with a plasmon-dependent change in k_r [Eq. (1)]. This increase in k_r is not manifested in the values of τ_Δ obtained. Thus, $^1O_2$ decay in these samples is still dominated by nonradiative pathways.

The spatial extent of the enhanced EM field in the proximity of the nanodiscs is small, and, if we assume an EM field distance of no more than 20 nm,[15] corresponds to a volume that is less than 1 % of the total volume taken up by TPP/PS. Thus, the number of $^1O_2$ molecules that experience the effect of the enhanced field is only a small fraction of the $^1O_2$ population detected in this phosphorescence experiment. As such, the actual enhancement of the radiative rate must be significantly greater than the factor of 3.5 measured, and it is not unreasonable to propose an enhancement factor greater than 100–500-fold.

In conclusion, we have demonstrated that $^1O_2$ radiative deactivation can be enhanced by LSPRs associated with metal nanostructures. This phenomenon should be of benefit in the detection of $^1O_2$ in a plethora of systems, particularly in experiments performed at the level of a single cell.[18]

Experimental Section

Nanodiscs were prepared as previously described[14] and characterized by SEM (see the Supporting Information). TPP/PS was applied by spin-coating from a toluene solution. TPP excitation was achieved with a femtosecond laser, and emission at 650, 1200, 1270, and 1325 nm was detected with a custom-built microscope[6] using gated photon counting and appropriate band pass filters.

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