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Enhanced energy transfer in single glycerol/water microdroplets standing on a superhydrophobic surface

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Abstract

We demonstrate resonant enhancement of energy transfer from donor to acceptor molecules in single glycerol/water microdroplets standing on a superhydrophobic surface. At donor emission wavelengths resonant with a whispering gallery mode, we recorded energy transfer rates up to 10 times higher than the non-radiative (Förster) energy transfer rate, by using the gradual acceptor photobleaching technique. Optical images taken with donor and acceptor emission filters revealed the radiative (long-range) nature of the energy transfer mediated by the whispering gallery modes.

1. Introduction

Besides its fundamental importance for photosynthesis [1] and quantum optics [2], interaction between two dipolar emitters finds various applications in biophysics [3] and organic light emitting devices [4]. In the weak coupling limit of the interactions, energy can be transferred non-radiatively from donor to acceptor molecules provided that the two molecules (i) have similar dipole orientations, (ii) are located at a small separation ($<\lambda/10$), and (iii) have a sufficient spectral overlap. This non-radiative (Förster) energy transfer has proven to be an indispensable tool in performing molecular distance measurements [3], and developing high efficiency organic light emitting diodes and lasers [4].

Optical microcavities can enhance the energy transfer between donor and acceptor molecules located at small ($<\lambda/10$) as well as large ($>\lambda/10$) separations. For the case of small separations, the efficiency of the non-radiative (Förster) energy transfer can be increased due to the modified photonic mode density function in an optical microcavity. Experiments using vertically structured polymer microcavities, which possess relatively low quality factors, showed enhanced non-radiative (Förster) energy transfer from donor to acceptor molecules located at predefined small separations [4,5].

High quality resonances of an optical microcavity can also mediate efficient radiative energy transfer between donor and acceptor molecules separated by large distances ($>\lambda/10$). Using microdroplets [6] and silica microspheres [7] it was shown that photons emitted to the microcavity modes by the donor molecules can be efficiently absorbed by acceptor molecules that are largely separated from the donor molecules. Results indicated energy transfer efficiencies up to six orders of magnitude higher than the expected non-radiative (Förster) energy transfer efficiencies.

In this Letter we demonstrate the enhancement in the energy transfer between donor and acceptor molecules located in single glycerol/water microdroplets standing on a superhydrophobic surface. We have previously shown that the use of a superhydrophobic substrate can greatly facilitate the optical spectroscopy experiments performed on single microdroplets, since no additional position stabilization technique such as electrodynamical trapping or optical tweezing is necessary [8]. The robustness of the experimental configuration allows for the study of single

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microdroplets over prolonged time periods while keeping the influence of the external disturbances very low. In addition of using a substrate, our results differ from the previous studies [6,7] in various respects. First, in previous studies enhancement in the radiative energy transfer was achieved by either analyzing the ratio of donor emission intensity to acceptor emission intensity at different acceptor concentrations [6], or by using the technique of donor photobleaching [7]. In contrast, here we use the technique of gradual acceptor photobleaching to detect the efficiency of the energy transfer [9]. Second, we report a detailed study of the energy transfer through a specific whispering gallery mode (WGM) of a microdroplet, while previous studies relied on the integrated effect of many WGMs [6,7]. This improvement is due to the use of a high numerical aperture (NA = 1.4) microscope objective, and selecting relatively small microdroplet diameters (<6 μm).

2. Experimental

2.1. Surface preparation and experimental setup

Superhydrophobic surfaces were prepared by spin coating hydrophobically coated silica nanoparticles (Aeroxide LE2, Degussa AG) on microscope cover glasses. Coated glasses had nanometer scale surface roughness, and were transparent to visible light. The average contact angle for water droplets having several millimeters of diameter on these surfaces was larger than 150°. A solution of 10% Glycerol and 90% water containing 122 μM Atto 488 (donor) and 108 μM Rhodamine B (acceptor) molecules was sprayed onto the superhydrophobic surface using an ultrasonic nebulizer, generating microdroplets of diameters up to ~20 μm. Upon landing on the surface, water content in the microdroplets quickly evaporated, and microdroplets reached to their equilibrium sizes. Resultant microdroplets are estimated to have more than 90% glycerol content having approximate donor and acceptor concentrations of ~1.2 mM and ~1.1 mM, respectively. Normalized absorption (Atto 488 absorption spectrum is provided by ATTO-TEC GmbH) and emission spectra of the donor and acceptor molecules, and the calculated overlap function are shown in Fig. 1.

A continuous wave Argon ion laser ($\lambda = 488$ nm) was used in recording the fluorescence spectra and fluorescence images of single microdroplets. Excitation powers of 2.5 μW and 0.1 μW were used in the spectroscopy and imaging experiments, respectively. After reflection at a dichroic mirror, the excitation beam was focused to a resolution limited spot near the rim of the microdroplet by a high numerical aperture oil-immersion microscope objective (60×, NA = 1.4) in the inverted geometry. The fluorescence was collected by the same objective, transmitted through the dichroic mirror, and a 1.5× magnification element. For spectroscopy experiments, the fluorescence was dispersed by a 50 cm monochromator using a 300 grooves/mm grating (spectral resolution 0.24 nm), and imaged by a CCD camera. 500 ms exposure time was used in all the fluorescence spectra presented in this Letter. A shutter was used to block the beam during the unexposed time intervals of the CCD camera. For imaging experiments, the fluorescence was sent through a bandpass filter (donor filter: 525/50 or acceptor filter: 607/67), and recorded by a monochrome CCD camera. Gradual acceptor photobleaching was achieved with long-time (0.5–2 min) exposures of the microdroplets to a continuous wave solid state laser ($\lambda = 532$ nm, excitation power = 18 mW) beam. Using a flippable lens placed before the microscope objective, solid state laser beam was collimated to a diameter of ~80 μm during the periods of acceptor photobleaching.

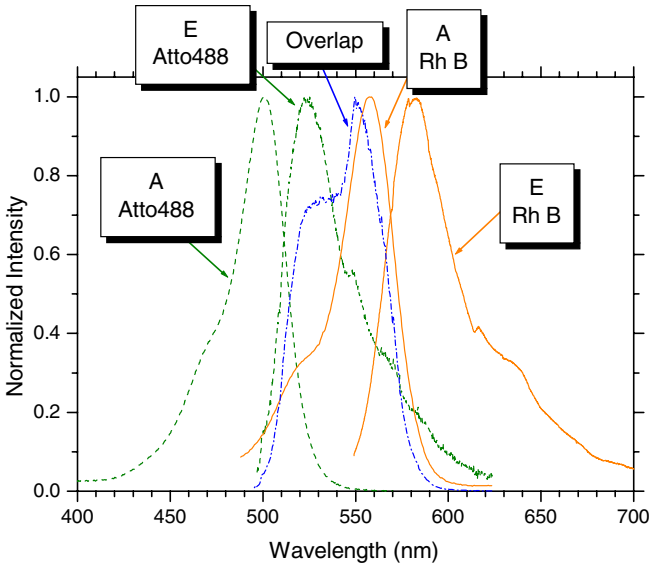

Fig. 1. Normalized absorption (A) and emission (E) spectra of the donor and acceptor dye molecules, and the calculated overlap function.

2.2. Fluorescence spectroscopy studies

Fig. 2 shows five donor emission spectra recorded from a 5 μm diameter microdroplet, while acceptor molecules were gradually photobleached. Photobleaching times are 5, 4, 4, and 2 min between the spectra with numbers I–II, II–III, III–IV, and IV–V, respectively. Between the spectra I to IV, gradual photobleaching of the acceptor molecules causes donor emission to increase in intensity. This enhancement is a direct indication of the energy transfer from donor to acceptor molecules. The difference between the levels of enhancement observed in the background donor emission and donor emission resonant with WGMs provides the signature of the enhanced energy transfer from donor to acceptor molecules through the WGMs. Even though the 532 nm laser line is mainly absorbed by the acceptor molecules, donor molecules also have a small absorption at this wavelength (Fig. 1). This causes the intensity drop (donor photobleaching) observed between the emission spectra IV and V in Fig. 2. The observed

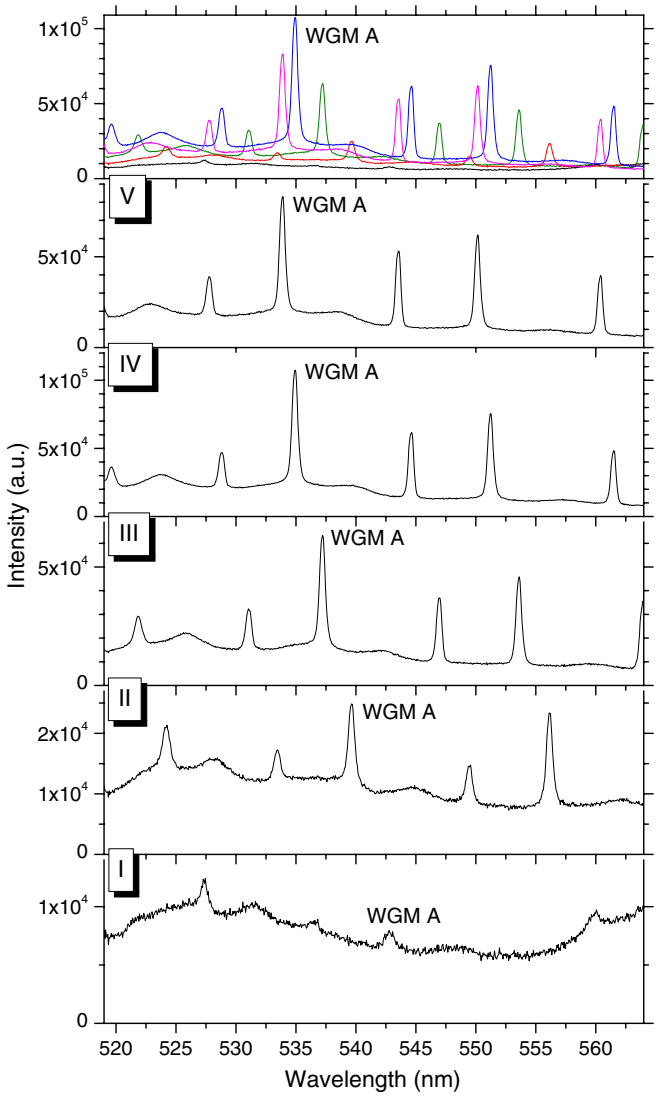

Fig. 2. Donor emission spectrum obtained from a microdroplet of diameter 5 μm after gradual acceptor photobleaching. Photobleaching times are 5, 4, 4 and 2 min between spectra I–II, II–III, III–IV, and IV–V, respectively. In spectra I–IV, the increased contrast between the emission through the WGM A and the background emission indicates the enhanced energy transfer. The intensity drop in spectrum V is due to donor photobleaching. Evaporation due to laser heating results in blue shifting of the WGMs with gradual acceptor photobleaching. Spectra I–V are shown on the same graph at the top.

intensity drop after 13 min of irradiation is consistent with the photobleaching time of Atto dyes under low excitation intensities [10]. With gradual acceptor photobleaching, spectral drift of the WGMs to smaller wavelengths is also observed. This indicates evaporation of the microdroplet caused mainly by heating of the 532 nm laser.

Quantitative analysis of the enhanced energy transfer through the WGMs is demonstrated in Fig. 3. In this figure we plot the area of the Gaussian fits to the WGM denoted by A in Fig. 2, and the offset level obtained from the Gaussian fits as a function of the acceptor photobleaching time. The values plotted in Fig. 3 are normalized to 1 at the beginning of the experiment. After 13 min of acceptor

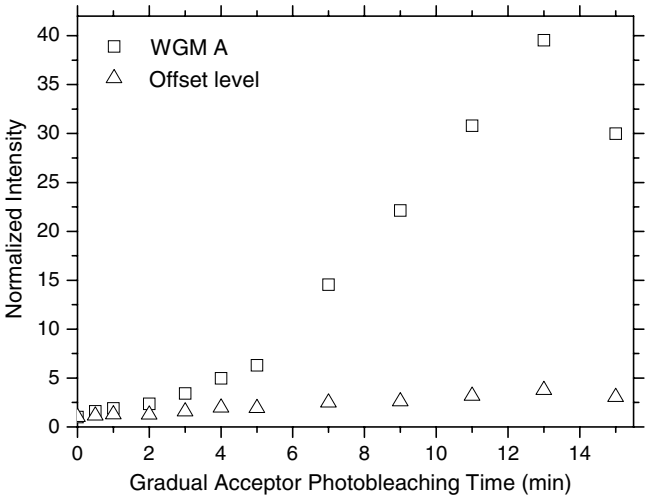

Fig. 3. Analysis of the peak area and the offset level obtained from the Gaussian fit to the WGM A as a function of the acceptor photobleaching time. Numbers are normalized to 1 at the beginning of the experiment. The peak area reaches a value of 40 when the offset level is 4. This shows a tenfold enhancement in the energy transfer rate at resonant wavelengths.

photobleaching, the background intensity, and the intensity of the WGM A increased by almost 4 and 40, respectively. This indicates a resonant enhancement in the energy transfer rate by almost a factor of 10 for this specific WGM.

The theory of enhanced energy transfer in an aerosol particle has been previously studied [11,12]. In [12] Leung and Young formulated the rate of energy transfer through a single microcavity resonance as:

$$\langle \Gamma_{\mathrm{tr}} \rangle = \frac{\pi^2 c^4}{qVn^4} \frac{\phi(\omega_0)}{\omega_0^2} D \frac{\sigma_{\mathrm{A}} \rho_{\mathrm{A}}}{\gamma + (c/n)\sigma_{\mathrm{A}} \rho_{\mathrm{A}}} \langle \Gamma_{\mathrm{f}} \rangle. \quad (1)$$

Here, V, q, $\phi(\omega_0)$, n, D, $\langle \Gamma_{\mathrm{f}} \rangle$, γ, σ_{A}, and ρ_{A} correspond to the volume of the microdroplet, quantum yield, donor emission spectrum normalized to the quantum yield, refractive index of the medium, mode degeneracy $(2 * l + 1)$, donor fluorescence rate in an extended medium of refractive index n, cold-cavity spectral width, absorption cross section, and concentration of acceptor molecules respectively. This prediction has also been experimentally verified [13]. For the WGM A shown in Fig. 2, the parameters can be estimated as: $V = 65.45 \times 10^{-18}\ \mathrm{m}^3$, $q = 0.87$, $\phi(\omega_0) = 2.156 \times 10^{-15}\ \mathrm{s}$, $n = 1.473$, $D = 2 \times 37 + 1$, $\gamma = 3.293 \times 10^{12}\ \mathrm{s}^{-1}$, $\sigma_A = 1 \times 10^{-20}\ \mathrm{m}^2$, $\rho_A = 6.62 \times 10^{23}\ \mathrm{m}^{-3}$. These yield a resonant energy transfer rate of $\langle \Gamma_{\mathrm{tr}} \rangle = 0.0055 \langle \Gamma_{\mathrm{f}} \rangle$ for the WGM A. Using the experimentally measured resonant enhancement factor of 10, in the extended medium an energy transfer rate of $0.00055 \langle \Gamma_{\mathrm{f}} \rangle$ is obtained over the 0.5 nm spectral window of the WGM A. Considering the ~50 nm spectral width of the overlap region, this translates into a total energy transfer rate of $\sim 0.055 \langle \Gamma_{\mathrm{f}} \rangle$ over the whole donor emission spectrum, in the extended medium. Nonresonant (Förster) energy transfer at this rate reveals an energy transfer efficiency of 5.2%, and an average donor to acceptor distance of $1.62 \times R_0 \approx 8.9$ nm

(Förster radius between Atto 488 and Rhodamine B molecules is calculated to be 5.5 nm). This calculated average distance is in agreement with the donor (~1.2 mM) and acceptor (~1.1 mM) concentrations used in the experiment.

2.3. Optical imaging studies

We performed optical imaging experiments in order to explore the nature of the dominant energy transfer mechanism. In case of a non-radiative (Förster) energy transfer, the donor molecules couple to acceptor molecules located nearby, within the Förster range ($>\lambda/10$). Therefore, the images taken with the acceptor filter (AF) and the donor filter (DF) are expected to be identical if a Förster mechanism is responsible for the energy transfer.

In contrast, WGM enhanced energy transfer rate is strongly dependent on the relative donor/acceptor position, that is described by the angle θ between their radius vectors. It was shown that the WGMs will couple donor molecules to acceptor molecules located in their immediate vicinity, $\theta = 0°$, as well as to those located in their diametrical opposite, $\theta = 180°$ [11]. Hence, in case of a WGM enhanced energy transfer, we expect major differences in the AF and DF images of the microdroplet, specifically a more spatially symmetric AF image.

Fig. 4a and b show the DF image of a microdroplet of diameter 6 μm. DF image shows a main spot at the laser location, together with a second spot with a smaller intensity at its diametrical opposite, appearing as a result of focusing of light in the microdroplet. Fig. 4c and d show the 'acceptor image' of the microdroplet obtained by subtracting 0.33 of the intensity in Fig. 4a and b from the AF image, taken under the same excitation conditions. The value of 0.33 represents the cross-talk, and it is determined as ratio of the intensities recorded with DF and AF using a solution containing only donor molecules. Compared to the DF image, acceptor image possesses major differences. In the acceptor image the asymmetry between the two peaks is largely reduced. In addition, the intensity in the contours in the acceptor image is higher than it is in the DF image, hence the acceptor image looks more circular. These are clear indications of the radiative nature of the energy transfer mediated by the WGMs of the microdroplet, and are consistent with the observations made by Arnold et al. [14]. For almost ideally spherical microdroplets which were electromagnetically levitated, Arnold et al. observed the acceptor image to be more symmetrical due to the higher quality factors of the WGMs. In our case, the total radiative energy transfer taken place in the microdroplet is comparable to the total non-radiative (Förster) energy transfer. This causes the remaining asymmetry we observe in the acceptor image.

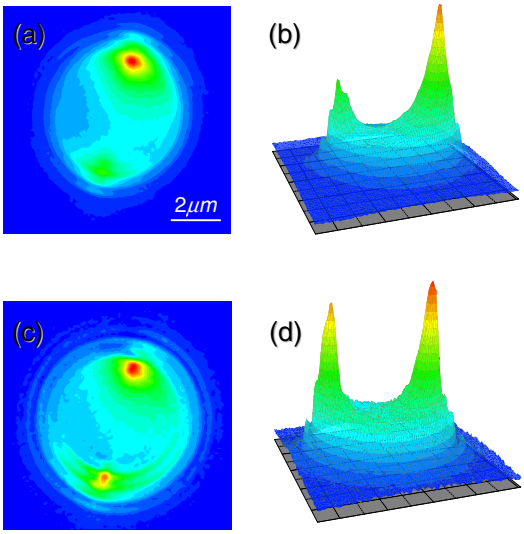

Fig. 4. Fluorescence microscope images of a 6 μm microdroplet. (a,b) Image taken with the donor filter (DF) shows a peak at the laser location together with a small peak at the diametrical opposite. (c,d) Acceptor image of the microdroplet obtained by subtracting 0.33 of the intensity in (a,b) from the acceptor filter (AF) image. The increased symmetry between the peaks at the laser location and at the diametrical opposite, and the intensity in the contours indicate the radiative nature of energy transfer. Contour and three dimensional surface plots of the same data are shown in (a) and (b) ((c) and (d)) respectively.

3. Summary

In this Letter we demonstrated enhanced energy transfer between Atto 488 and Rhodamine B molecules mediated by the relatively high quality WGMs of single glycerol/water microdroplets of diameters <6 μm, standing on a superhydrophobic surface. At WGM resonances, energy transfer rates up to 10 times higher than the non-radiative (Förster) energy transfer rates have been recorded. The nature of the energy transfer mediated by the WGMs was revealed to be radiative by the optical imaging experiments. We believe that the presented results show the potential of a microdroplet standing on a superhydrophobic surface as an attractive alternative to an electrodynamically levitated microdroplet, mainly due to the experimental ease. Our results might lead to applications in which optical interactions in minute amounts of specimens are analyzed with a high sensitivity in a microdroplet standing on a superhydrophobic surface.

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