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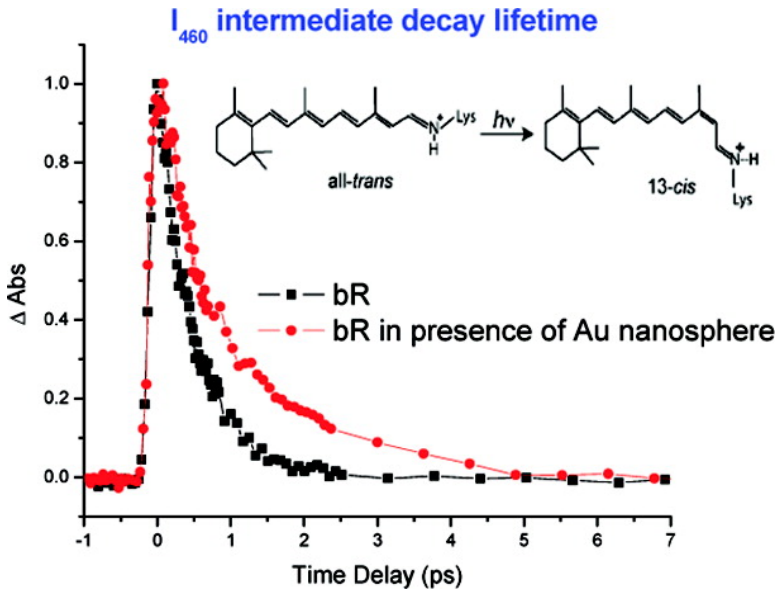

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Gold Nanoparticle Plasmonic Field Effect on the Primary Step of the Other Photosynthetic System in Nature, Bacteriorhodopsin

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The strong local electric fields resulting from the surface plasmon resonance (SPR) oscillations of optically excited plasmonic (gold and silver) nanoparticles lead to a strong enhancement of the optical signals from molecules in the vicinity of the nanoparticles.[1] Important examples include metal plasmon-enhanced fluorescence,[2] which has a demonstrated utility in sensing[3] and surface-enhanced Raman scattering (SERS)[4,5] with enhancement factors large enough to allow single molecule detection[6,7] and to enhance second harmonic generation[8,9] in molecular systems adsorbed on the nanoparticle's surface or in its vicinity. This field decays over a distance comparable to the nanoparticle size (tens of nanometers) and is much stronger for aggregated particles.

The effect of such a field on protein dynamics should be of great interest to the field of biology and could be of potential use in medicine. Bacteriorhodopsin (bR), the other photosynthetic system in nature besides chlorophyll, is a widely studied system that is able to utilize the free energy from the absorbed photon to retinal protein membrane and the best studied proton pump system in biology. Upon photon absorption its protonated base Schiff (PBS) triggers a photocycle involving several intermediates having lifetimes extending from subpicoseconds to milliseconds time range.[10] The initial steps leading to the retinal isomerization of the PSB from the all-trans to the 13-cis form (K_{610}) are

$$bR_{568} + h\nu \rightarrow (bR)_{FC}^{*} \rightarrow I_{460} \xrightarrow{500\ fs} J_{625} \xrightarrow{3\ ps} K_{610}$$

The prevailing model for describing the evolution of PSB out of the Frank-Condon (FC) region after absorption of a photon is based on early pump−probe experiments with subpicosecond resolution.[12,13] It is believed that a relaxation of about 100 fs takes place from the FC region to the I_{460} excited electronic states of the PSB chromophore.[14] Time-resolved Raman confirmed that no actual rotation takes place during this time along the C_{13}═C_{14} bond but instead that the double bond distance changes[15] followed by the rotation process. The twisting is believed to happen while going from the I_{460} to J_{625} intermediates[16] although in literature there are papers questioning this proposal as well.[17]

Even though the details of the dynamics of the first light-induced event in bR have not yet been completely understood, the lifetime of the intermediates I_{460} to J_{625} to K_{610} have been confirmed to be 0.5 and 3 ps, respectively. In the present study, the fs time-resolved pump−probe[18] experiment was designed to examine the effect of the plasmon field of citrate capped Au-nanoparticles during the transition of the intermediates I_{460} and J_{625}. The pump pulse, which has a width of 100 fs, energy of 50 nJ and wavelength of 560 nm focused on the sample with diameter of 300 μm, excites the retinal of bR in presence of the nanoparticle field. The probe was at 490 nm with a pulse width of 150 fs and energy of 2 nJ also excited the plasmon resonance of the gold nanoparticles. bR from strain S9 was obtained by standard purification, and solutions were prepared in 50 mM phosphate buffer and pH 7; all the solutions were light adapted before the measurement. The decay of the excited bR (I_{460}) was monitored by measuring the absorption at 490 nm at different delay times after the pump pulse. When the gold nanoparticles (Au-NPs) are present the surface plasmonic field is formed by both the pump and the probing laser pulse instantly and decays in a few femtoseconds. However the field gets instantly turned on by the probing pulse at different delay times after excitation. Thus the observed decay of the intermediate I_{460} is determined in the presence of the plasmon field induced by the monitoring light, when gold nanoparticles are present. As shown in Table 1, the lifetime of I_{460} increases when 40 nm Au-NPs are present.

Table 1. Dependence of the Decay Lifetime of the Intermediate I_{460} on the Gold Nanoparticle Concentration and Size

sample	Au-NPs conc. 10^{-11} M	NPs size nm	decay lifetime fs
BR			470 ± 25
solution A	1.3	40	515 ± 25
solution B	2.5	40	720 ± 35
solution C	3.8	40	800 ± 40
solution D	3.7	13	530 ± 25

Furthermore, as the concentration of NPs increases so does their effect on the I_{460} lifetime. The effect is size dependent as well. Solution D that has a similar concentration of Au-NPs as solution C, but of smaller size NPs (and thus smaller plasmonic field), clearly shows a smaller effect on the decay lifetime as shown in Figure 2. Could it be due to the overlap of the decay of the bleached NPs and the 490 nm absorption of bR? The OD ratio between bR and the NPs at 560 nm ranges from about 30 to 6 for the measured solutions; while the contribution to the total signal decay from the pure NPs was estimated to be less than 2% for the highest concentration. Could the effect be a result of the photothermal effect of the gold nanoparticles? The phonon−phonon relaxation time in gold nanospheres is one hundred picoseconds.[19] This and the fact that the repetition rate of the laser system is 500 Hz eliminates the possibility that the observed change in the dynamic is a result of thermal effects resulting from the phonon−phonon relaxation of the gold nanoparticles. This suggests that the field generated upon the plasmon excitation is the only cause of the observed changes in the excited state I_{460} intermediate lifetime.

To understand the origin of the observed effect of the plasmon field on the I_{460} decay time, the dynamic evolution of the excited-state of the protonated Schiff base of bR within the protein cavity has to be considered. An aspect where theoretical calculation and experiment agree upon is the large charge redistribution in PSB following the retinal absorption of light in bR.[20,21] In fact a theoretical prediction for a Schiff base immediately after excitation consists of a system having a neutral amino group and a positively charged polyene chain,[22] a result that is supported by other indirect

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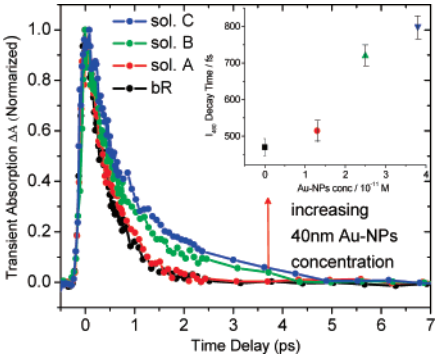

Figure 1. Effect of increasing the concentration of 40 nm Au-NPs on the dynamics of the primary step (the decay kinetics of I_{460}) of the photosynthetic system of bacteriorhodopsin.

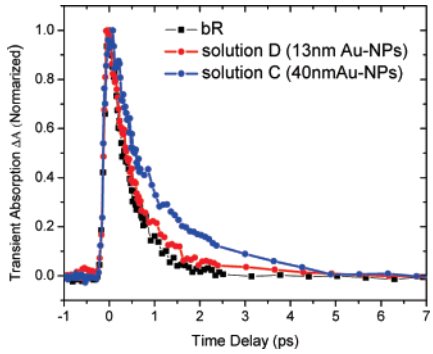

Figure 2. The effect of Au-NPs size (plasmonic field) on the dynamic of the primary step (the decay kinetics of I_{460}) of bacteriorhodopsin.

measurements.[23,24] This charge-unbalanced system should induce large polarization on the protein cavity around the retinal electronic system. In the presence of an oscillating plasmonic electric field, present because of the pump and probe light, the retinal electronic system is going to have a different potential energy surface than in the unperturbed system. This undoubtedly should affect the rate of its dynamic within the protein pocket, as shown by the experimental data in Figure 1.

As more and more NPs accumulate on a bR surface, favoring plasmon coupling with the strong enhancement of the electric field associated with it, the effect is amplified. The environment created by the protein is known to ensure selectivity of the photoproducts[25] and to ultimately acquire from the PSB the energy necessary for bR proton pump functions. Electronic theory[26,27] on protein response upon retinal excitation suggests that the early spectroscopic events are effected by the protein environment leaving no doubt for an active role of the protein itself. Experimental data on protein conformational changes though atomic force sensing (AFS) measurements seem to connect the large polarization change occurring at the chromophore site to protein structural changes.[28] It is more accurate then to think of the system as PSB−protein rather than as individual components. The plasmonic field thus affects both the protein and the retinal system as a whole.

The plasmonic field can propagate over distances comparable to the nanoparticle size. Thus the nanoparticles do not have to bind to the retinal to affect the rate of its excited-state decay. Furthermore, the observed field effect could result from aggregated nanoparticles, which is known to be much stronger. This might also explain the concentration effect. The size effect can be explained by the dependence of the plasmonic field on the nanoparticle size. Furthermore, different sizes could occupy different sites on the protein, causing a different effect as shown in Figure 2.

The lifetime of J_{625} is found not to be affected by the presence of NPs, and it remains at 3 ps. It should be mentioned, however, that the decay of J_{625} to form K_{610} does not involve a charge rearrangement. J_{625} is believed to be a vibrationally hot 13-cis retinal isomeric form[29] of K_{610}. According to the explanation given for the changes observed in I_{460} it would not be expected for this transformation to be perturbed by the plasmonic field as observed.

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