

## Photoinduced Charge Separation Reactions of J-Aggregates Coated on Silver Nanoparticles

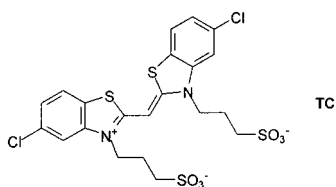
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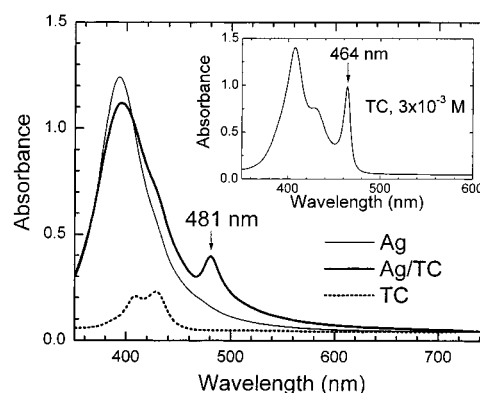
Received October 1, 2001; Revised Manuscript Received February 15, 2002

J-aggregates are characterized by a red-shifted and sharp absorption band relative to the monomer band, a result of exciton delocalization over the molecular building blocks of the aggregate.<sup>1-4</sup> In addition to their use as photographic sensitizers, the large oscillator strength and fast electronic response of J-aggregates are of interest in many fields, such as modeling energy transfer in photosynthetic reaction center antenna, nonlinear optics related to superfluorescence, and solar photochemical energy conversion.<sup>3-14</sup> Since organics frequently possess enhanced optical properties on metal surfaces,<sup>15</sup> the exciton dynamics of J-aggregates near bulk metal surfaces have been explored.<sup>16</sup> In general, coupling of the exciton to the plasmon of the metal leads to ultrafast quenching of the exciton and its fluorescence.<sup>16</sup> Very recently, however, the J-aggregation of cyanine dyes on the surface of noble metal nanoparticle colloids was reported.<sup>17,18</sup> This offers a unique opportunity to study the interaction of molecular J-aggregates with the larger near-field enhancements and modulated electrochemical properties of metallic colloidal nanoparticles when compared to bulk metal surfaces. We show here that photoexcitation of the plasmon in Ag nanoparticles coated with J-aggregates leads to exciton dynamics that are much different than for J-aggregate monolayers on bulk metal surfaces. Specifically, charge-separated states with a lifetime of  $\sim 300$  ps between the J-aggregate and Ag colloid are formed.

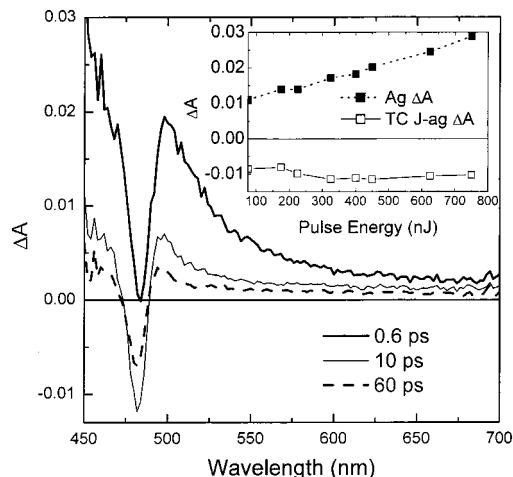
We used the procedure described by Kometani et al. to prepare the J-aggregate coated Ag nanoparticles.<sup>17</sup> The dye used was a cyanine derivative, 5,5'-dichloro-3,3'-disulfopropylthiacyanine sodium salt (TC, Hayashibara Biochemical Laboratories, Japan). The



silver nanoparticles were prepared through the reduction of metallic Ag ions by NaBH<sub>4</sub> in aqueous media to produce a relatively narrow size distribution of particles with an average diameter of 8 nm.<sup>17,19</sup> We used a TC concentration of  $5 \times 10^{-6}$  M and a silver nanoparticle concentration of  $4 \times 10^{-9}$  M. The ground-state absorption spectrum of the Ag/TC solution is illustrated in Figure 1, along with the spectra for the silver nanoparticles and TC alone in solution. The new absorption band at 481 nm is the J-aggregate. The morphology of the TC aggregate is such that the thiacyanine chromophore is adsorbed on the particle and the SO<sub>3</sub><sup>-</sup> groups extend away from the nanoparticle to provide solubility.<sup>18</sup> As reported by Kometani et al., no J-aggregates form at this TC concentration in the absence of metal nanoparticles.<sup>17</sup> Previous STM studies indicate that a homogeneous coverage is obtained on nanoparticle surfaces.<sup>18</sup> The



**Figure 1.** The ground-state absorption spectra of the Ag nanoparticle/TC J-aggregate solution is shown, along with the spectra for the original solutions of Ag nanoparticles and TC.



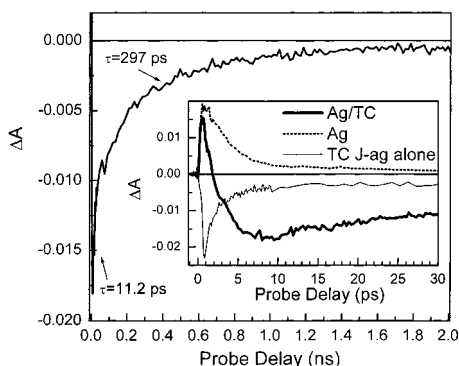
**Figure 2.** Transient absorption spectra for the Ag nanoparticle/TC J-aggregate are shown. The inset illustrates the different dependence of  $\Delta A$  vs pulse energy for the Ag plasmon and J-aggregate at 475 nm.

inset illustrates the absorbance of TC solution at  $3 \times 10^{-3}$  M, which is the concentration that shows significant J-aggregation in the absence of metal nanoparticles. There is a shift of the J-aggregate absorption band to 464 nm.

Transient absorption spectra and kinetics were taken with an amplified Ti:sapphire laser system described previously.<sup>20</sup> The pump wavelength was 417 nm so as to be resonant with the Ag nanoparticle plasmon and not the J-aggregate. Transient absorption spectra were taken with variable optical delays at probe wavelengths of 450 to 700 nm. Figure 2 illustrates the transient absorption spectra for the Ag nanoparticle/TC solution. A strong bleaching of the J-aggregate absorption band is observed within the 140 fs time resolution of the instrument. As observed on bulk metal surfaces, the fluorescence is entirely quenched and is normally attributed to

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**Figure 3.** The transient absorption kinetics of Ag nanoparticles/TC J-aggregates are shown, along with control studies of Ag nanoparticles and TC J-aggregates alone.

efficient coupling of dipoles of the plasmon and J-aggregate exciton.<sup>16</sup> However, in the case of the Ag nanoparticles, we also find that the bleach remains for nearly 300 ps ( $1/e$  lifetime), as illustrated by the transient kinetics probed at 475 nm (Figure 3).

The inset to Figure 3 illustrates the fast temporal response of the Ag/TC composite system, along with the Ag nanoparticle solution alone probed at 475 nm and the highly concentrated J-aggregate solution without Ag nanoparticles probed at 464 nm. The silver nanoparticle solution illustrates similar behavior to previously reported ultrafast pump-probe studies of bare nanoparticles.<sup>21</sup> The signal is dominated by a 3.1 ps transient absorption decay attributed to hot electron relaxation. A weaker signal is due to lattice expansion that decays over several tens of picoseconds. A similar time constant of 2.6 ps for the Ag/TC solution is observed. However, the magnitude of the J-aggregate bleach is complete at the earliest times, indicating that the 2.6 ps decay is due to hot-electron decay and not the J-aggregate bleach formation. The J-aggregate solution alone illustrates a transient bleach at 464 nm dominated by a 600 fs ( $1/e$ ) decay whose magnitude and temporal response is strongly intensity dependent. This is typical of J-aggregate photophysics, where the ultrashort excited-state lifetime and superfluorescence are due to exciton-exciton annihilation.

The Ag nanoparticle/J-aggregate systems discussed here are remarkably different in many ways from all inorganic or organic systems. First, the number of photons absorbed per nanoparticle per pulse is approximately 80 at the lowest pump energy used (75 nJ). This is calculated by using the number of photons per pulse as  $1.6 \times 10^{11}$ , an optical density of 0.6 at 417 nm for a 0.5 cm thick cell, a spot size of 400  $\mu\text{m}$  diameter, and  $1.5 \times 10^9$  nanoparticles in the illumination volume. The inset of Figure 2 shows the  $\Delta A$  signal due to the plasmon photoexcitation, taken at the earliest time of maximum  $\Delta A$ , to be linear in the pump power as expected,<sup>21</sup> i.e., the number of photons absorbed by the nanoparticle is linear in this region. However, the amplitude of the J-aggregate signal, monitored at 10 ps, reaches a maximum bleach at approximately 300 nJ/pulse, or  $300 \pm 50$  photons absorbed per nanoparticle.<sup>22</sup>

We have shown that the fluorescence from the TC J-aggregate hybrid is quenched on silver nanoparticles, that the J-aggregate absorption is bleached on a pulse width limited time-scale, that the lifetime of the photoinduced state is  $\sim 300$  ps, that many more than one photon per hybridized nanoparticle is absorbed, and that the J-aggregate  $\Delta A$  saturates at low pump intensity while the plasmon  $\Delta A$  increases linearly with intensity. Given this set of observations, it is very likely that the J-aggregate exciton is strongly coupled to the nanoparticle plasmon and possesses enhanced charge transfer characteristics that lead to an instantaneous electron transfer to the nanoparticle upon photoexcitation of the plasmon resonance.

If the long-lived state were due to isolated excitons within the J-aggregate, fluorescence would be observed. Furthermore, the leveling off of the J-aggregate bleach at approximately 300 photons absorbed/nanoparticle correlates well with electrochemical reduction measurement of colloidal silver, which shows that similarly synthesized Ag nanoparticles can accept and store hundreds or more electrons.<sup>23,24</sup> Furthermore, a saturation of the J-aggregate bleach was not observed in the TC solution without nanoparticles, a possibility in molecular aggregates.<sup>10</sup> However, in the presence of the large fields near the surface of the particles, it is possible that the J-aggregate bleach is saturated and may also limit the number of electrons that can be transferred. There is also ample driving force for charge separation given the plasmon resonance peak at 3.1 eV, with the Fermi potential for surface modified Ag nanoparticles estimated to be  $-0.4$  V.<sup>25</sup> The TC monomer oxidation potential is approximately 1.4 V vs SCE and electrochemical measurements of J-aggregates themselves reveal that they are easier to oxidize by  $\sim 0.2$  eV than the monomers.<sup>26</sup> We also tried the identical J-aggregate experiment with Au nanoparticles, and found no 300 ps bleach, only ultrafast quenching of the exciton. Since the Au nanoparticle plasmon lies lower in energy (520 nm) than the exciton, no charge separation is observed.

We have shown that a reversible, photoinduced charge transfer reaction occurs in Ag nanoparticle/J-aggregate hybrid colloids. The observation is different than that for J-aggregates on the surface of bulk metals, where exciton quenching is observed.

**Acknowledgment.** This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38. This work also benefited from the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research.

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JA012263E