

Slow Back Electron Transfer in Surface-Modified TiO₂ Nanoparticles Sensitized by Alizarin

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Interfacial electron transfer dynamics of alizarin-sensitized surface-modified and unmodified TiO₂ nanoparticles has been studied using femtosecond transient absorption spectroscopy. The surface of TiO₂ nanoparticles has been modified by sodium dodecyl benzyl sulfonate (DBS). Electron injection has been confirmed by direct detection of the electron in the conduction band, cation radical of the adsorbed dye and by a bleach of the dye as monitored by transient absorption spectroscopy in the visible and near-IR region. The dynamics of back electron transfer (BET) of the injected electron from TiO₂ to the parent cation has been measured by monitoring the decay kinetics of the cation radical of the adsorbed dye, and it is found to be multiexponential. We have compared the BET dynamics of alizarin-sensitized unmodified and surface-modified nanoparticles, and it is found to be slow on the modified surface. Solvent polarity did not have much impact on the BET dynamics. As the molecule forms a strong charge-transfer (CT) complex with the TiO₂ nanoparticle, significant change in the electronic coupling is not expected. As the other parameters that govern the ET are not changed as a result of surface modification, the reduction in the BET on the surface-modified nanoparticles has been explained by the fact that on surface modification the Fermi level of the modified nanoparticles is pushed up in energy, increasing the overall free energy of reaction ($-\Delta G^0$) for the BET reaction. The high exoergic BET reaction in dye-sensitized TiO₂ nanoparticles surfaces falls in the Marcus inverted regime. As a result, with increasing free energy of reaction the BET rate is decreased on the modified surface.

1. Introduction

Sensitization processes resulting from photoexcitation of dye molecules (sensitizers) bound to semiconductor nanoparticles are of great importance for photochemical solar energy conversion.¹ Slow back electron transfer (BET) is a necessary condition for efficient conversion of light energy to electricity in dye-sensitized solar cells. Solar cells made out of ruthenium polypyridyl dyes are found to be suitable for their slow BET process as sensitized on TiO₂ nanoparticles.² However, these inorganic dye materials are comparatively expensive. On the other hand, several organic dye molecules, which have good ground state absorption in the visible region, have been sensitized, but none of them have shown good photoconversion efficiency as compared to the ruthenium polypyridyl dyes. Triphenyl methane (TPM) dyes, which exhibit intense ground state absorption in the visible region, could, in principle, be suitable sunlight-harvesting agents. However, the photocurrent efficiencies of the solar cells made by using these TPM dyes (e.g., bromopyrogallol red and pyrocatechol violet) are found to be <1%.³ Our transient absorption studies on TPM dye-sensitized TiO₂ nanoparticles have shown that a fast BET process is responsible for the low photoconversion efficiency.⁴

Alizarin (Alz) has been found to be an important dye molecule, which can anchor very strongly with TiO₂ nanoparticles^{5–10} with two chelating hydroxyl groups. TPM dye molecules also bind with TiO₂ nanoparticles in a similar way.⁴ Electron injection from the photoexcited Alz to TiO₂ nanoparticles has been found to occur in the sub-10 fs time domain.⁷ However, unfortunately because of the strong coupling limit in

the electron transfer (ET) process of Alz-sensitized TiO₂ nanoparticles, the BET reaction (charge recombination) has also been found to be very fast, thus diminishing the prospects of using it as a useful solar dye. It would be very interesting if this fast BET reaction could be retarded by changing the experimental conditions of these strongly coupled dye–nanoparticle systems.

The performance of most of the semiconductor-containing devices is critically dependent on the electronic properties of the semiconductor surface band bending (V_s) and the surface recombination velocity (SRV).¹¹ These properties, in turn, depend on the density and energy distribution of surface states. As the surface state properties are controlled by the chemistry of the surface, much effort has been devoted to modifying the surface states by chemical treatments.¹² The use of suitable organic or organometallic molecules for surface treatments holds great promise for fine-tuning the desired surface electronic properties. Thus, a group that optimizes molecular binding to the surface can be augmented with auxiliary groups, which can provide control over light sensitization properties,¹⁰ hydrophilic/hydrophobic character, and so forth. Generally, surface modifiers can affect the semiconductor characteristic in many ways such as by (a) inhibiting charge recombination, (b) expanding the wavelength response range, and (c) changing the selectivity or yield of a particular product. Rajh et al.¹³ have reported a new route to improve the optical response of nanocrystalline TiO₂ in the visible region. Chelation of surface Ti atoms with electron-donating bidentate ligands in these systems changes the electronic properties of the nanocrystalline particles. Xagas et al.¹⁴ reported surface modification and photosensitization of TiO₂ nanocrystalline films with ascorbic acid. Rabani et al.¹⁵

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reported interfacial electron transfer dynamics in surface-modified nanocrystallite layers using laser photolysis techniques with nanosecond and microsecond resolution. Qu et al.¹⁶ reported the enhancement of the photoinduced electron transfer from cationic dyes to colloidal TiO₂ nanoparticles after modifying the surface with sodium dodecyl benzene sulfonate (DBS) molecules. The absorption dynamics of the cationic surfactant cetyltrimethylammonium bromide (C₁₆TAB) and anionic surfactant sodium dodecyl sulfate (SDS) at the TiO₂–water interface was investigated by Ninness et al.¹⁷ by using Fourier transform infrared-attenuated total reflection spectroscopy. However, no report is available in the literature on the effect of surface modification on interfacial ET dynamics in the ultrafast time domain. Interfacial ET dynamics (both electron injection and BET) in dye-sensitized nanoparticles takes place in the femtosecond to millisecond time domain. It will be interesting to see the effect of surface modification on the ET dynamics in dye-sensitized TiO₂ nanoparticles in the ultrafast time scale.

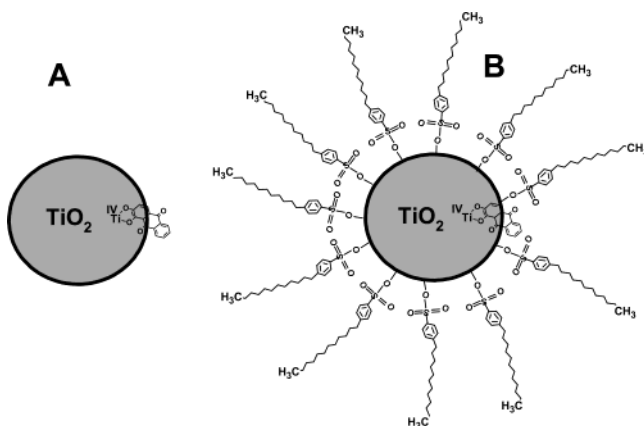
In the present investigation, we report the effect of surface modification on the BET reaction of Alz-sensitized TiO₂ nanoparticles using the femtosecond transient absorption technique in the visible and near-IR region. Many researchers^{5–7,9} have carried out interfacial ET dynamics on Alz-sensitized TiO₂ nanoparticles using fast and ultrafast techniques. We have also carried out transient absorption experiments with Alz-sensitized unmodified and modified TiO₂ nanoparticles to follow the effect of surface modification on interfacial electron transfer dynamics on the semiconductor surface. Surface modification of TiO₂ nanoparticles has been carried out using sodium dodecyl benzene sulfonate (DBS) as the modifier molecules as reported earlier.¹⁸ Electron injection has been confirmed by direct detection of the electron in the conduction band, cation radical of the adsorbed dye and a bleach of the dye. The BET dynamics of the injected electron from TiO₂ to the parent cation has been measured by monitoring the decay kinetics of the cation radical of the adsorbed dye as well as that of the electron in the conduction band, and it is found to be multiexponential. It has been observed that the BET reaction is much slower on the modified surface compared to the unmodified one. It has been explained that on surface modification the Fermi level of the modified nanoparticles is pushed up in energy, increasing the overall free energy of reaction ($-\Delta G^0$) for the BET reaction on the modified surface compared to the unmodified one; as a result, the BET rate decreases on the modified surface.

2. Experimental Section

2.a. Materials. Titanium (IV) tetraisopropoxide {Ti[OCH(CH₃)₂]₄} (Aldrich, 97%) and isopropyl alcohol (Aldrich) were purified by distillation. Alizarin (Alz) and sodium dodecyl benzene sulfonate (DBS) were obtained from Aldrich. Toluene, *N,N*-dimethyl formamide, and chloroform were obtained from Spectrochem India Ltd. and were used as received. For aqueous solutions Nanopure water was used.

2.b. Nanoparticle Preparation. We have synthesized DBS-capped TiO₂ nanoparticles following the method reported earlier.¹⁸ To 500 mL of freshly prepared TiO₂ colloids in water, synthesized as reported earlier,⁴ 250 mL of toluene was added in a round-bottom flask. The resulting mixture was stirred slowly for 15–20 min. To the stirred solution, 100 mL of 0.2M DBS (C₁₂H₂₅C₆H₄SO₃Na, sodium dodecyl benzene sulfonate) was added, and the final mixture was stirred slowly for 3 h. DBS can be dissolved only in water, because it is ionic in nature. As the surface of the TiO₂ nanoparticles is positively charged, DBS molecules can easily bind through the sulfonic group (SO₃[−])

CHART 1: Schematic Picture of Alz Coupled with (A) Unmodified TiO₂ Nanoparticles and (B) Surface-Modified TiO₂ Nanoparticles^a



^a The nanoparticle surface has been modified with sodium dodecyl benzene sulfonate (DBS).

with the nanoparticles. The newly capped TiO₂ nanoparticles look like reverse micelle (Chart 1) and can be dissolved in many organic solvents. In this situation the TiO₂ nanoparticles migrated from water to the organic phase (toluene). Then, by use of a separatory funnel the organic phase was separated out. At this stage the organic phase looked slightly cloudy. The organic phase was dried with CaCl₂ and transformed to an optically clear solution in toluene. The organic phase was then refluxed for 2 h, and then the solvent was removed with the use of a rotary evaporator in N₂ atmosphere. Dry TiO₂ nanoparticles, capped by DBS, which were left in the flask, could be dissolved in many nonaqueous solvents to get colloidal solutions.

2.c. Femtosecond Spectrometer. The femtosecond tunable visible spectrometer has been developed based on a multipass amplified femtosecond Ti:sapphire laser system from CDP-Avesta, Russia (1 kHz repetition rate at 800 nm, 50 fs, 300 μJ/pulse). The 800 nm output pulse from the multipass amplifier is split into two parts to generate pump and probe pulses. One part, with 200 μJ/pulse, is frequency doubled and tripled in BBO crystals to generate pump pulses at 800, 400, or 267 nm. The typical energy of the pump pulses were kept between ~6 and 7 μJ. To generate visible probe pulses, about 3 μJ of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. The intensity of the 800 nm beam has been adjusted by the iris size and ND filters to obtain a stable white light continuum in the region from 470 to over 1000 nm. The probe pulses are split into the signal and reference beams and are detected by two matched photodiodes with variable gain. The noise level of the white light is ~0.5% with occasional spikes due to oscillator fluctuation. We have noticed that most laser noise is low-frequency noise and can be eliminated by comparing the adjacent probe laser pulses (pump-blocked vs unblocked using a mechanical chopper). The typical noise in the measured absorbance change is <0.3%.

3. Result and Discussion

3.a. Steady State Spectroscopy and Interaction with Nanoparticles. Figure 1 shows the steady state absorption spectra of free Alz in water (5% methanol + 95% water), toluene, DBS/water, and Alz-sensitized unmodified TiO₂ nanoparticles in water as well as surface-modified (SM) TiO₂ nanoparticles in toluene. It can be observed from Figure 1 that

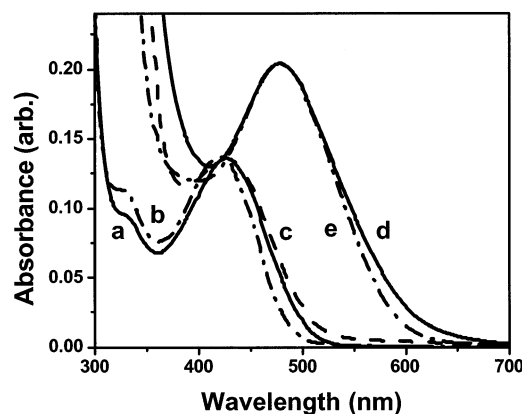


Figure 1. Optical absorption spectra of (a) Alz in water (—), (b) Alz in toluene (---•---), (c) Alz in sodium dodecyl benzene sulfonate (DBS)/water solution (---), (d) Alz-sensitized unmodified TiO₂ nanoparticles (10 gm/L) (—), and (e) surface-modified TiO₂ nanoparticles (10 gm/L) in toluene (---•---).

the Alz molecule shows an absorption peak at 422 nm in toluene and at 428 nm in water. To find out whether there is any ground state interaction between the sensitizer, that is, Alz, and the surfactant (DBS) molecule, ground state absorption measurements of Alz in the presence and absence of DBS have been carried out. It is seen from Figure 1 that the absorption maximum of Alz in DBS/water is around 429 nm which is very similar to that in water indicating a negligible ground state interaction between the sensitizer and the surfactant. Steady state fluorescence measurements of Alz in water and DBS/water have shown that there is no significant interaction between the surfactant and the excited state of Alz. This may be because of the fact that Alz is a neutral molecule, and hence, it cannot have any special interaction with the ionic DBS surfactant. Now, in the presence of both unmodified and surface-modified TiO₂ nanoparticles, the absorption spectrum of Alz became broad and shifted to longer wavelengths with an increase in the extinction coefficient. It can be observed from Figure 1 that the absorption peak of Alz/TiO₂ is around 480 nm with higher optical density pointing to a strong interaction between Alz and TiO₂ with the formation of a charge-transfer (CT) complex as reported earlier in the Alz–TiO₂ system.^{5–10} It is interesting to see that the Alz molecules bind very similarly on both the unmodified and the modified surface indicating that the surfactant has no role to play in the interaction between the Alz and the TiO₂ nanoparticles. However, Qu et al.¹⁶ have observed that interaction between cationic dyes such as rhodamine B (RB) and *n*-hexadecylrhodamine (C₁₆-RB) with TiO₂ nanoparticles drastically changes in the presence of DBS molecules. As both RB and C₁₆-RB are cationic in nature, they do not interact with the positively charged TiO₂ surface. But in the presence of DBS, which is a good candidate to coabsorb positively charged RB dyes to the same positively charged TiO₂ surface, interaction between RB dyes and TiO₂ is possible.

3.b. Excited State Dynamics of Free Alizarin. We have carried out transient absorption measurements to study the excited state dynamics of the Alz molecule in methanol and in DBS/methanol media exciting with 400 nm laser light. Excited state dynamics of Alz in methanol have already been reported by Huber et al.⁶ as measured using transient absorption spectroscopy in the subpicosecond time domain. They have observed a transient absorption peak at 510 nm and a negative absorption with a peak around 640 nm due to stimulated emission. The excited lifetime was determined to be 63 ps by monitoring transient absorption decay as well as the decay of

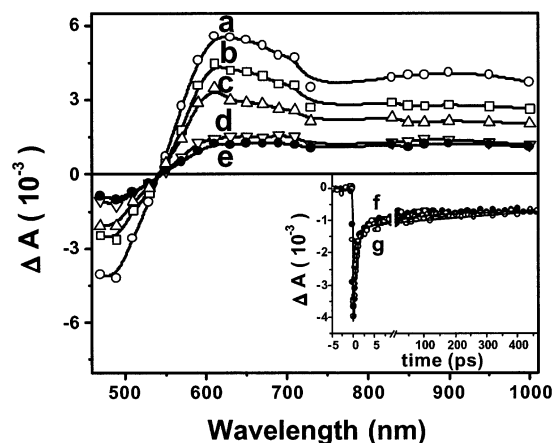


Figure 2. Transient absorption spectra of Alz-sensitized unmodified TiO₂ nanoparticles in water at (a) 100 fs, (b) 500 fs, (c) 1 ps, (d) 5 ps, and (e) 10 ps after excitation at 400 nm. The spectrum at each time delay consists of a bleach in the 470–540 nm wavelength region with a peak centered around 490 nm, a positive absorption with a peak at 610 nm, and a broad positive absorption feature in the whole spectral region (700–1000 nm). These features are assigned to the ground state bleach, the cation radical of the Alz dye, and the injected electron in nanoparticles, respectively. [Inset: Bleach recovery kinetics at 490 nm (f) and electron decay kinetics (reverse) at 900 nm (g) of Alz-sensitized unmodified TiO₂ nanoparticles].

stimulated emission. Similar transients for the case of Alz in DBS/methanol have been observed as for that of Alz in methanol. Analysis of the stimulated emission decay gave the excited state lifetime of about 109 ps for Alz in the presence of the surfactant. The increased excited singlet state lifetime of the Alz molecule in DBS/methanol medium can be explained as follows. In methanol, DBS molecules form a micellar type of environment. We have observed earlier¹⁹ that the excited state lifetime of the probe molecule increases in noninteracting micellar media as compared to that in neat solvents. In micellar media, because of the restricted environment, the nonradiative decay pathway decreases. As a result, the lifetime of the excited state increases. Similarly, we have observed in the present investigation that the lifetime of the Alz molecule increased in DBS/methanol media as compared to that in neat methanol.

3.c. Transient Absorption Measurements of Alizarin/TiO₂.

We have carried out transient absorption experiments for Alz-sensitized unmodified TiO₂ nanoparticles in water and surface-modified (SM) TiO₂ nanoparticles in toluene exciting at 400 nm to follow the interfacial electron transfer dynamics on the semiconductor surface. Figure 2 shows the time-resolved transient absorption spectra for Alz-sensitized unmodified TiO₂ nanoparticles. The spectrum at each time delay consists of a bleach in the 470–540 nm wavelength region with maximum at circa 490 nm, an absorption peak at circa 610 nm, and another broad positive absorption band in the 700–1000 nm region. The absorption peak at 610 nm has been assigned to the Alz cation radical.^{6,7} The broad absorption band in the 700–1000 nm region has been attributed to the conduction band electrons in the nanoparticles.^{4,20} Recombination dynamics (BET) of the injected electron and the parent cation can be determined by either monitoring the decay of the electron in the conduction band at 900 nm or following the bleach recovery kinetics at 490 nm. Figure 2 (inset) shows the kinetic decay trace of the conduction band electron at 900 nm and the bleach recovery kinetics at 490 nm for Alz-sensitized unmodified TiO₂ nanoparticles. As the information that is obtained from both the traces is same, it is very interesting to see that the bleach recovery kinetics and transient decay kinetics of the electron follow

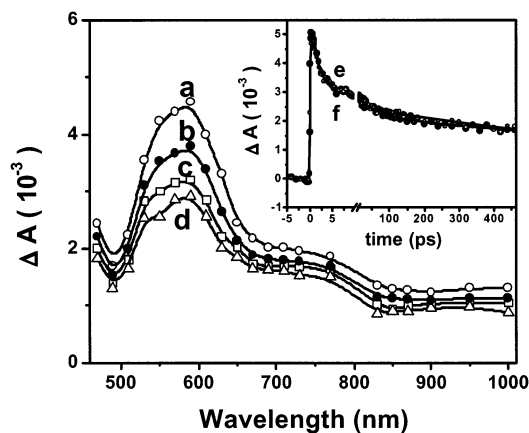


Figure 3. Transient absorption spectra of Alz-sensitized surface-modified TiO_2 nanoparticles in toluene at (a) 100 fs, (b) 2 ps, (c) 5 ps, and (d) 10 ps after excitation at 400 nm. The spectrum at each time delay consists of an absorption peak at 590 nm and a broad positive absorption feature in the whole spectral region (700–1000 nm). These features are assigned to the cation radical of the Alz dye and the injected electron in the nanoparticles, respectively. [Inset: Decay kinetics of the cation radical of Alz at 610 nm (e) and the electron in the conduction band (e_{CB}^-) at 900 nm (f) of Alz-sensitized surface-modified nanoparticles in toluene].

exactly similar dynamics. We have observed that BET dynamics in Alz/ TiO_2 is very fast and follows a multiexponential function with time constants of 0.6 ps (75%), 7 ps (10%), and >400 ps (15%).

In an effort to understand the effect of surface modification on electron transfer dynamics, femtosecond transient absorption experiments have been carried out on Alz-sensitized surface-modified TiO_2 nanoparticles in toluene, and the results are shown in Figure 3. The spectrum at each time delay consists of an absorption peak at 590 nm and a broad positive absorption in the 700–1000 nm region. The absorption peak at 590 nm can be assigned to the Alz cation radical.^{6,7} The broad spectral absorption band (700–1000 nm) has been attributed to the conduction band electrons in the nanoparticles.^{4,20} It can be observed from the figure that the spectral features in the case of Alz/SM- TiO_2 are different from those of Alz on unmodified TiO_2 nanoparticles. The bleach centered at 490 nm which has been observed in the case of unmodified TiO_2 nanoparticles is not seen in Alz/SM- TiO_2 . The cation peak on the modified surface shifted toward the blue wavelength region compared to that on the unmodified surface, and also the molar extinction coefficient (ϵ) of the Alz cation radical on modified TiO_2 nanoparticles is larger compared to that on the unmodified TiO_2 nanoparticles. The observation of these spectral features can be rationalized in the following way. In the case of SM TiO_2 nanoparticles, the DBS molecule forms a semimicelle type of arrangement on the nanoparticle surface (Chart 1). It has been reported in the literature that the molar absorptivity of metal–dye systems can be enhanced remarkably through surfactant sensitization.²¹ It is also reported in the literature²² that the spectrum of a dye cation radical becomes broad and the extinction coefficient (ϵ) increases dramatically in the presence of surfactant molecules. A similar analogy can explain the blue shift as well as the increased extinction coefficient of the cation radical on the SM surface. As the extinction coefficient of the cation is enhanced on the SM TiO_2 , it can absorb on top of the bleach thereby nullifying the bleach. However, bleach features are still observed for the case of surface-modified nanoparticles in toluene.

Figure 3 (inset) shows the kinetic decay trace of $\text{Alz}^{+\bullet}$ at 610 nm and the conduction band electron (e_{CB}^-) at 900 nm for Alz-sensitized modified TiO_2 nanoparticles. The BET dynamics of the injected electron and parent cation can be determined by monitoring both the cation radical at 610 nm and the electron in conduction band at 900 nm. It is interesting to see that the recombination dynamics of Alz-sensitized nanoparticles on the modified surface is much slower compared to that on the unmodified surface. The BET dynamics in Alz/ TiO_2 on the modified surface in toluene can be fitted with a multiexponential function with time constants of 1.9 ps (45.3%), 35 ps (12.9%), and >400 ps (41.8%).

3.d. Effect of Surface Modification on Interfacial Electron Transfer Dynamics. The central theme of this paper is to investigate the effect of surface modification on interfacial electron transfer dynamics in Alz-sensitized TiO_2 nanoparticles. In earlier studies Rabani et al.¹⁵ have reported interfacial ET dynamics of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy \equiv bipyridine) and $\text{Ru}(o\text{-phen})_3^{2+}$ ($o\text{-phen}$ \equiv o -phenanthroline) sensitized surface-modified TiO_2 nanoparticles with nanosecond and microsecond resolution. They have mainly discussed their results in light of the semiconducting properties of the TiO_2 nanocrystallites and the hydrophobic and ionic interactions between the photosensitizers and the binders (surface modifiers). As both $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(o\text{-phen})_3^{2+}$ are positively charged species, these sensitizers cannot sensitize directly without binder molecules because TiO_2 nanoparticles have a positively charged surface. However, they have used Nafion, sodium dodecyl sulfate (SDS), and sodium dodecyl benzyl sulfate (SDBS) as binders (surface modifiers), which help to coadsorb the sensitizers on the nanoparticle surface. As a result, they have observed the effect of ionic strength and hydrophobicity on interfacial ET dynamics.

In the present investigation, Alz has been used for sensitization of semiconductor nanoparticles, which adsorb on the semiconductor surface very strongly with or without the presence of the modifier molecule (DBS). As it was already discussed in a previous section that Alz does not interact with DBS in both the ground and excited state, this is an ideal system to study the effect of surface modification on dye-sensitized semiconductors. We have observed in ground state optical absorption studies that Alz and TiO_2 nanoparticles interact strongly and similarly both on unmodified and modified surfaces. This indicates that electronic coupling between Alz and TiO_2 in the ground state is very similar in both cases. Electronic coupling is an important parameter for the forward electron transfer (electron injection) process in the dye/nanoparticle system. The above observations may lead us to speculate that there will be a negligible effect of surface modification on electron injection on Alz/ TiO_2 nanoparticle systems. To verify the above speculation we have carried out electron injection experiments in the Alz/ TiO_2 system on both the unmodified and modified surface by changing the solvent. Figure 4 shows the comparison of electron injection dynamics in the Alz/ TiO_2 system on both the unmodified and modified surface in different solvents after monitoring the appearance signal of the conduction band electron at 900 nm. It is very interesting to see that in all the cases electron injection is found to be pulse width limited. This is because of the fact that electronic coupling primarily drives electron injection between the initially populated electronic state in the molecular adsorbate and the delocalized electronic states of similar energy in the semiconductor.²³ We have discussed earlier that the modifier DBS molecule does not perturb the electronic coupling between the adsorbate and the

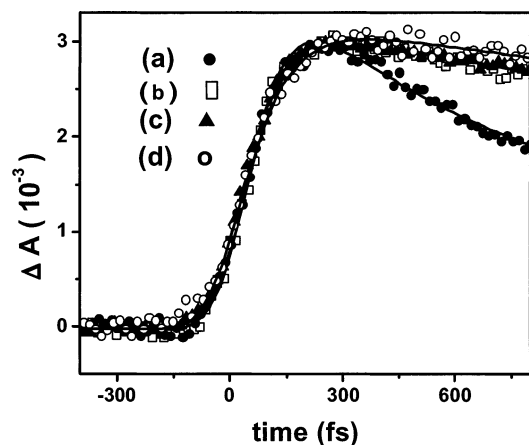


Figure 4. Comparison of electron injection dynamics in (a) Alz-sensitized unmodified TiO₂ nanoparticles in water (●), (b) Alz-sensitized surface-modified TiO₂ nanoparticles in DMF (□), (c) Alz-sensitized surface-modified TiO₂ nanoparticles in chloroform (▲), and (d) Alz-sensitized surface-modified TiO₂ nanoparticles in toluene (○). Probe wavelength is 900 nm.

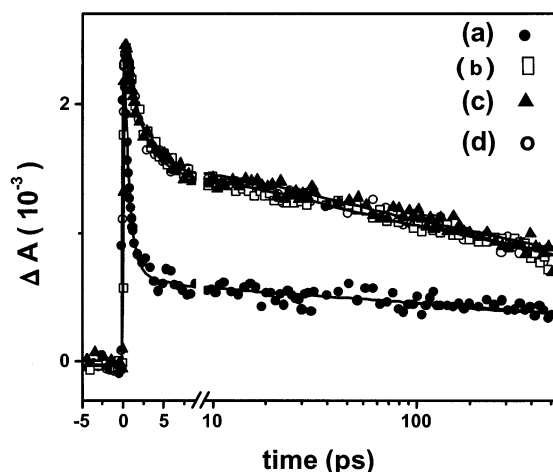


Figure 5. Recombination (BET) dynamics in (a) Alz-sensitized unmodified TiO₂ nanoparticles in water (●), (b) Alz-sensitized surface-modified TiO₂ nanoparticles in DMF (□), (c) Alz-sensitized surface-modified TiO₂ nanoparticles in chloroform (▲), and (d) Alz-sensitized surface-modified TiO₂ nanoparticles in toluene (○). Probe wavelength is 900 nm.

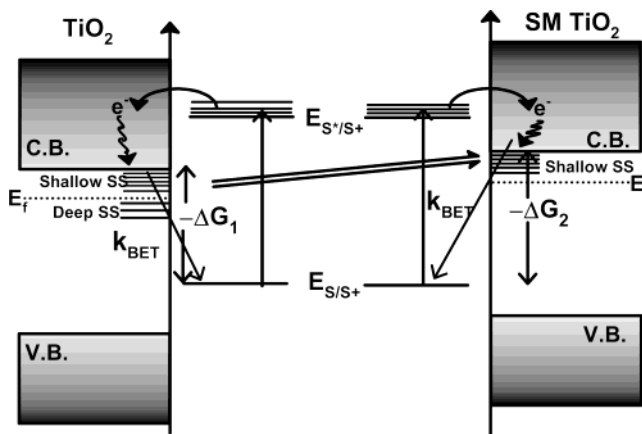
nanoparticle. As a result, surface modification does not have much effect on electron injection.

Now it will be very interesting to see the effect of surface modification on charge recombination (BET) dynamics. The BET dynamics between the injected electron in the nanoparticles and the Alz cation radical (Alz^{•+}) is followed by monitoring the transient absorption decay of Alz^{•+} at 610 nm as well as the conduction band electrons at 900 nm. Figure 5 shows the transient absorption decay of the conduction band electron (e_{CB}^-) at 900 nm in the Alz/TiO₂ system on both the unmodified and modified surface in different solvents. The decay of the observed signals can be fitted by multiexponential functions with time constants of 0.6 ps (75%), 7 ps (10%), and >400 ps (15%) for the Alz/unmodified-TiO₂ system and 1.9 ps (45.3%), 35 ps (12.9%), and >400 ps (41.8%) for the Alz/SM-TiO₂ system in toluene, respectively (Table 1). BET rates are also determined for the cases of Alz/SM-TiO₂ nanoparticles in *N,N*-dimethyl formamide (DMF) and chloroform and are given in Table 1. It is striking to see that the BET reaction between the

TABLE 1: Parameters for the Multiexponential Fits to the Back ET Kinetics of Alizarin-Sensitized TiO₂ Nanoparticles (Both Unmodified and Surface-Modified (SM)) in Different Media after Monitoring the Electron in the Conduction Band at 900 nm

sample	back electron transfer		
	τ_1 , ps (A ₁)	τ_2 , ps (A ₂)	τ_3 , ps (A ₃)
Alz/unmodified-TiO ₂ /H ₂ O	0.60 (75%)	7.0 (10%)	>400 (15%)
Alz/SM-TiO ₂ /DMF	2.1 (40%)	29 (13.8%)	>400 (46.2%)
Alz/SM-TiO ₂ /CHCl ₃	1.9 (41.5%)	32 (13.2%)	>400 (45.3%)
Alz/SM-TiO ₂ /toluene	1.9 (45.3%)	35 (12.9%)	>400 (41.8%)

SCHEME 1: Mechanistic Scheme of Electron Transfer (ET) and Effect of Surface Modification on ET in Alz-Sensitized Unmodified (Left) and Modified (Right) TiO₂ Nanoparticles^a



^a Fermi level pinning is seen due to surface modification on the TiO₂ nanoparticles (right). The energy levels of the modified nanoparticles are pushed up in energy and thereby the effective free energy ($-\Delta G$) increases ($-\Delta G_2 > -\Delta G_1$).

injected electron and the parent cation is faster on the unmodified nanoparticle surface compared to that on the modified surface.

This interesting behavior of slow BET reaction on the modified surface can be explained following Marcus electron transfer theory. As the other factors that can affect the surface-modified nanoparticles are not operating for the present system, we are inclined to apply the semiclassical Marcus ET theory to explain the results. According to the Marcus semiclassical theory²⁴ of electron transfer, the BET rate constant (k_{BET}) can be given by the following expression (eq 1)

$$k_{BET} = \left(\frac{2\pi}{\hbar} \right) [H_{AB}]^2 \frac{1}{\sqrt{4\pi\lambda kT}} \exp \left\{ -\frac{(\Delta G^0 + \Lambda)^2}{4\lambda kT} \right\} \quad (1)$$

The BET rate constant (k_{BET}) depends on the coupling element (H_{AB}), the overall free energy of reaction ($\Delta G^0 = E_C - E_{S/S^+}$), the potentials of electrons in the conduction band of the semiconductor ($E_C = -0.49$ V),²⁵ and the redox potential of the adsorbed dye (E_{S/S^+}) (Scheme 1). We have observed earlier that surface modification does not alter the electronic coupling of the Alz/TiO₂ nanoparticle system. So we can assume that H_{AB} will be very similar in the Alz/TiO₂ system on both the unmodified and modified surface. Another parameter which can affect BET is Λ (where $\Lambda = \lambda_s + \lambda_v$), the total reorganization energy for the electron transfer reaction, where λ_v and λ_s are the internal and solvent reorganization energies, respectively. The value of λ_v depends on the frequency ν of the vibrational mode associated with the electron transfer. Here, we are discussing the ET dynamics of the same Alz/TiO₂ system in

different conditions so λ_v will be the same in all cases. However, we have changed the solvents on the modified surface; so, λ_s can vary with changing solvent. Therefore, we have carried out dye sensitization experiments on surface-modified nanoparticles in different solvents to see the effect of the dielectric constant of the medium on the BET kinetics (Figure 5, Table 1). However, we have not observed noticeable differences in the BET rate constants (Table 1) on the modified surface with changing polarity of the solvents. So, we can conclude that with changing solvent the Λ value in the above equation (eq 1) does not change in the Alz/TiO₂ system on the modified surface. Similarly, we can conclude that the Λ value on the unmodified surface and the modified surface will be very similar in the Alz/TiO₂ system. As the other parameters are not having a significant effect on the electron transfer dynamics in this system, the BET dynamics of the Alz/TiO₂ system may depend mostly on the free energy ($-\Delta G^0$) of the reaction for both the unmodified and the modified surface.

The driving force of the BET can be changed by invoking the concept of an increased pH on SM nanoparticles compared to that of the unmodified nanoparticles which thereby lifts the flat band potential,²⁶ increases the energy gap, and eventually slows down the BET rate. However, Yan and Hupp²⁷ have reported pH independent BET dynamics in dye-sensitized TiO₂ nanoparticles. This is because of the fact that changing the pH of the medium not only alters the conduction band edge but also changes the redox potential of the adsorbed dye, nullifying the overall effect of pH.²⁸

On the other hand, Dimitrijevic et al.²⁹ have observed that the position of the Fermi level in modified TiO₂ colloids is shifted by at least 0.10 V toward negative potentials as compared to that in the unmodified one. Kamat et al.³⁰ have shown that the charge distribution between semiconductor nanoparticles (TiO₂) and metal nanoparticles (Au) causes the Fermi level to shift to more negative potentials. It has been reported previously by Ellis and co-workers^{12a-c} and Natan et al.^{12d} that strong adsorption of negative counterions on the electrode surface shifts the flat band potential (V_{fb}) and also the valence band (VB) to more negative values. In the present investigation, the DBS molecule (modifier) is adsorbed strongly on the nanoparticles through the sulfonic group (SO₃H⁻). So, on surface modification the Fermi level of the modified colloids is pushed up in energy; as a result, the overall free energy of reaction increases (Scheme 1). On modification, both the flat band potential and the valence band are shifted toward negative values to the same extent¹² (Scheme 1). As a result, the band gap of the nanoparticles does not change with modification but the conduction band edge energy level shifts toward higher energies. According to Marcus ET theory, with increasing thermodynamic driving force ($-\Delta G^0$), the ET rate initially increases to reach a maximum value and then starts decreasing.¹⁴ This high exoergic region is often termed the "inverted regime". The BET processes in dye-sensitized TiO₂ nanoparticles surfaces fall in the Marcus inverted regime for its high free energy of reaction.³¹ In this region with increasing driving force ($-\Delta G^0$) of the reaction, the rate of BET decreases. As the free energy for BET for the case of SM-TiO₂ is higher than that of the unmodified TiO₂ nanoparticles, the BET rate on the modified surface is slower compared to that on the unmodified surface.

4. Conclusion

Femtosecond transient absorption spectroscopy has been carried out to study the effect of surface modification on the electron injection and back electron transfer (BET) dynamics

of Alz-sensitized TiO₂ nanoparticles capped (modified) with sodium dodecyl benzene sulfonate (DBS). Electron transfer dynamics have also been compared in the Alz/TiO₂ system on the unmodified surface. Electron injection has been confirmed by direct detection of the electron in the conduction band, cation radical of the adsorbed dye and by a bleach of the dye in real time as monitored by transient absorption spectroscopy in the visible and near-IR region. We have confirmed that the Alz molecule does not interact with the DBS molecule (surface modifier) in both the ground and excited state. We have also observed that coupling between Alz and TiO₂ nanoparticles does not change on surface modification. It has been observed that electron injection dynamics does not alter much with surface modification. We have determined the BET dynamics of the above systems by monitoring the Alz cation radical at 610 nm as well as the conduction band electron at 900 nm and found it to be multiexponential. It is very interesting to observe that the BET dynamics is slow on the modified surface as compared to that on the unmodified surface. On surface modification, the flat band potential of the nanoparticles is pushed up in energy, increasing the overall free energy of reaction ($-\Delta G^0$) for the BET reaction on the modified surface compared to the unmodified one; as a result, the BET rate decreases on the modified surface. In conclusion, we have shown that on surface modification, the rate of the BET reaction can be reduced drastically in the dye-sensitized TiO₂ nanoparticle system. This observation can, in turn, help solar energy researchers to build low-cost dye-sensitized solar cells with high photoconversion efficiency using many cheap organic dyes.

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References and Notes

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