ROLE OF SURFACE STATES OF SEMICONDUCTOR NANOATERIALS IN INTERFACIAL ELECTRON TRANSFER DYNAMICS AND EFFECT OF SURFACE MODIFICATION

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Introduction

Electron transfer (ET) between molecular adsorbates and semiconductor nanomaterials has been a subject of intense research interest in recent years. This process is intimately related to the application of semiconductor nanomaterials in photography, solar energy conversion, photocatalytic waste degradation and quantum dot devices. Solar energy conversion through design and development of dye-sensitized TiO₂ semiconductor solar cell has been a subject of intense research in recent years. The most efficient cells of this type, based on Ru(dcbpy)₂(NCS)₂ [dcbpy (4,4'-dicarboxy-2,2'-bipyridine)] (or Ru N3) sensitized nanocrystalline TiO₂ thin films, can achieve a solar to electric power conversion efficiency of about 10%. The high conversion efficiency can be attributed to efficient solar energy harvesting by the sensitizer and high incident photon to current conversion efficiency (IPCE). A high IPCE requires a fast electron injection rate from the sensitizer to the semiconductor and a much slower back electron transfer.
rate to the sensitizer. A schematic of the interfacial ET processes in dye-sensitized semiconductor nanomaterials in solar cell is shown in Scheme 1. The operation of this solar cell and many devices based on nanocrystalline materials is directly related to the charge transfer and carrier relaxation/recombination dynamics. For this reason, in addition to interfacial ET, carrier relaxation and recombination dynamics in metal and semiconductor nanoparticles have also been actively studied in recent years. The mechanism of solar cell devices is based upon the injection of an electron from a photo-excited state of the sensitized dye into the conduction band of the semiconductor. The efficiency of the dye-sensitized solar cells depends critically on the rates of the forward (dye to semiconductor) and back (semiconductor to dye) electron transfer reactions. For an efficient solar energy conversion it is necessary to establish conditions for both fast electron injection and slow recombination. High yield of long-lived charge separation is expected for useful conversion of sunlight into electric charge. The basic photophysical reactions for the above process can be written as

\[ S + h\nu \rightarrow S^* \rightarrow S^+ + e^-_{\text{CB}} (\text{TiO}_2) \]

The dye (S) is excited with visible light (h\nu) to the electronically excited state S*. If this state lies energetically above the conduction band edge of the colloid, electron injection to the semiconductor can occur on a fast or ultrafast time scale.\(^6\) The energetic position of the acceptor level plays a key role for the dynamics of the injection mechanism. Most of the reports are available in the literature are the high density (conduction band continuum) of acceptor states was regarded as the main reason for the ultrafast initial charge separation. The lower lying (below conduction band) surface states can also play important role. Surface states in the nanoparticle are generated due to the intrinsic defect on the surfaces of the nanoparticles. However, one cannot investigate the role of surface states in dye sensitized TiO\(_2\) system in interfacial ET dynamics because the LUMO (lowest unoccupied molecular orbital) of most of the dye molecules are above the conduction band of TiO\(_2\). As a result the photo-excited dye molecules immediately injected into the conduction band. Higher band gap semiconductor colloids such as ZrO\(_2\) may serve as an ideal system to investigate the role of these surface states, in interfacial ET reaction. Now the question is that is it possible to observe ET reaction in ZrO\(_2\) nanoparticles by any adsorbate. The observation by many others and us reveal that most of the adsorbate do not inject electron in ZrO\(_2\). So what is the necessary condition for a dye/ ZrO\(_2\) system to realize ET process? To answer this question judiciously we have chosen a series of molecules, which can inject electron in the surface states of ZrO\(_2\). We have also address the necessary condition in dye/nanoparticle system to observe ET reaction in the surface states.

Presence of surface states in the nano-structured materials actually brings down the efficiency of the devices. It is reported in the literature that involvement of the surface states in the interfacial ET process can actually bring down the efficiency of the solar cell. To gain higher efficiency in the devices it is very important to pacify these surface states. Modification of these states is possible using suitable modifier molecules. By this process it is possible to remove most of the lower lying surface states. Surface modification of semiconductor nanoparticles changes their optical, chemical and photo-catalytic properties significantly.\(^8\) It can lead to the following effects: i) it may enhance their excitonic and defect emission by blocking non-radiative electron/hole (e/h\(^+\)) recombination at the defect sites (traps) on the surface of the semiconductor nanoparticles, ii) it
may enhance the photo-stability of semiconductor nanoparticles\textsuperscript{19}, iii) it may create new traps on the surface of the nanoparticles leading to the appearance of new emission bands\textsuperscript{20}, iv) it may enhance the selectivity and efficiency of light-induced reactions occurring on the surface of semiconductor nanoparticles\textsuperscript{18, 21}. Overall on surface modification density of surface states (lower lying states below the conduction band) can be changed drastically. Now the question is that on surface modification is the surface states which only get affected or the energy level of conduction and valence band also changes. As we are discussing the efficiency of dye-sensitized solar cell where interfacial electron transfer plays an important role. So it is important to see the effect of surface modification on interfacial electron transfer dynamics. In the present article we are going to address the interfacial ET dynamics in the surface states of semiconductor nanoparticles. We are also going to discuss the change of optical and photo-physical of nanoparticles on surface modification by suitable modifier molecule and also the effect of surface modification on ET dynamics. To address above questions we have used Femtosecond transient absorption technique to study the ET dynamics in the surface states of ZrO\textsubscript{2} nanoparticles and also the effect of surface modification of TiO\textsubscript{2} nanoparticles on interfacial ET dynamics.

**Synthesis of Nanoparticles**

Nanometer-size ZrO\textsubscript{2} and TiO\textsubscript{2} particles were prepared by controlled hydrolysis of Zirconium (IV) isopropanol complex and Titanium (IV) isopropanol and it has been described in detail in our earlier work\textsuperscript{7, 13}. A solution of 5 ml Ti(OCH(CH\textsubscript{3})\textsubscript{3})\textsubscript{4} (Aldrich, 97%) dissolved with 95 ml isopropyl alcohol (Aldrich) was added drop-wise (1 ml/min) to 900 mL of nanopure water (2°C) at pH 1.5 (adjusted with HNO\textsubscript{3}). The solution was continuously stirred for 10-12 hours until a transparent colloid was formed. The colloidal solution was concentrated at 35-40°C with a rotary evaporator and then dried with nitrogen stream to yield a white powder. ZrO\textsubscript{2} nanoparticle was also prepared by adopting the above procedure.

**Femtosecond Spectrometer**

The femtosecond tunable absorption spectrometer has been developed in Radiation & Photochemistry Division based on a multi-pass amplified femtosecond Ti:sapphire laser system from CDP-Avesta, Russia (1 kHz repetition rate at 800 nm, 50 fs, 300 µJ/pulse)\textsuperscript{12}. 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. Typical energy of the pump pulse were kept ~6-7 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 iris size and ND filters to obtain a stable white light continuum in the 470 nm to over 1000 nm region. 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 about ~0.5 % with occasional spikes due to oscillator fluctuation. It has been 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 about <0.3 %.
Dye-Nanoparticle Interaction

To understand the mechanism of the dye-sensitized ET reaction in the dye-nanoparticles (NP) system, it is very important to know the type of interaction between the dye molecules and the NPs when they get adsorbed on the nanoparticle surface. In the present article we are going to discuss the involvement of surface states of ZrO$_2$ NP in ET dynamics. For this purpose a suitable sensitizer (quinizarin) has been identified. Steady state spectroscopic measurements of Qz molecules in TiO$_2$ and ZrO$_2$ colloidal solutions suggest that Qz molecule have strong interaction with both the NPs. It is interesting to observe that Qz molecule have stronger interaction with ZrO$_2$ NP as compared to that TiO$_2$ NP. It is interesting to observe that on adsorption of the Qz on ZrO$_2$ nanoparticle surface, a new ligand to metal CT band is formed. The formation of CT complex can be explained by the following equation

$$\text{ZrO}_2 + \text{Qz} \rightarrow [\text{ZrO}_2^{\delta-} \cdots \text{Qz}^{\delta+}]_{\text{Complex}}$$

The optical absorption spectra of Qz molecule in presence of ZrO$_2$ nanoparticles are broader and red shifted as compared to that in presence of TiO$_2$ nanoparticles. It has already been reported by Rajh et al.$^{22}$ that six-membered ring complexes are more stable on ZrO$_2$ nanoparticle surface and five-membered ring complexes are more stable on TiO$_2$ nanoparticle surface for < 20 nm particles. In the present investigation Qz forms chelating type of complex having six-membered ring with ZrO$_2$ nanoparticles (Scheme 2) forming a stronger complex as compared to that formed on TiO$_2$. 

Scheme 2: Molecular structure of quinizarin coupled with ZrO$_2$
nanoparticle surface. In this scheme, it can be seen that oxygen bonded to the central ring in keto (quinoid) form along with one OH group binds to the Zr (IV) atom, which is sitting on the surface of the nanoparticle. This binding mode results in a six membered ring chelate type of complex with the surface Zr atoms. A six membered ring has larger bond angles that can accommodate the cubic structure of ZrO$_2$.

**Electron Transfer (ET) Dynamics into the Surface States of ZrO$_2$ Nanoparticles and its Mechanism**

The main aim of this article is to study IET dynamics in the surface states of ZrO$_2$ nanoparticles. It has been observed that all the sensitizers, which inject electron into the conduction band of TiO$_2$ not necessarily will inject electron in to the surface states of ZrO$_2$. As the chemical nature of ZrO$_2$ and TiO$_2$ nanoparticle surfaces are very similar$^{23}$ to understand the photophysics of the dye molecule on a non-injecting nanoparticle surface, we have used ZrO$_2$ nanoparticles surface, where electron injection was not possible from photoexcited dye. In those systems$^{7,8}$ excited state properties of the dye molecules on ZrO$_2$ nanoparticles surface were very similar to that in bulk solvents. However, in Qz/ZrO$_2$ system interesting behavior has been observed in photo-excited condition. Fig.2 shows the time resolved transient absorption spectra of Qz/ZrO$_2$ system in water. The spectrum at each time delay consists of a bleach in 475-585 nm wavelength region centered around 510 nm, a positive peak at ~660 nm and broad positive feature in the whole spectral region (750 - 1000 nm). From the transient spectrum it is clearly visible that photophysics of Qz molecules on ZrO$_2$ nanoparticles surface is very different from that in methanol$^{13}$. Temporal characteristics of the transients in the entire wavelength region are also dissimilar to that of free Qz in solution$^{13}$. The positive peak at 660 nm has been attributed to the combination of cation radical of Qz molecule as well as the injected electron in ZrO$_2$ nanoparticles and broad absorption band in the region of 750-1000 nm has been attributed to the injected electrons in the nanoparticles. Since the excited singlet state (S1) of Qz molecule is well below the conduction band of ZrO$_2$ (Scheme II), photo excited Qz molecule will be unable to inject electron in the conduction band of ZrO$_2$ nanoparticles. Thus, this injection process has been attributed to the injection in the surface states of nanoparticles. The bleach peak appears due to disappearance of ground state of the dye-ZrO$_2$ complex, on excitation by the laser pulse. The appearance time of the above signal is pulse width limited (<50 fs), it can be attributed to electron injection time into the surface states of ZrO$_2$ nanoparticles. The electron injection in ZrO$_2$ nanoparticles can be explained by the equation given below.

The kinetic decay of both electron in the conduction band as well as the parent cation radial and also the recovery kinetics of the bleach can provide the recombination dynamics of the injected electrons and the parent cation. Fig.1 inset shows the bleach recovery kinetics at 570 nm wavelength. The recovery kinetics has been best fitted with a multi-exponential function with the time constants of 0.6 ps (76.2%), 4.5ps (10.8%) and >200 ps (13%). Recombination dynamics of the above reaction can also be determined by both monitoring the cation radical at 660 nm and also the electron in the nanoparticle at 900 nm. It has been discussed earlier that Qz forms a strong complex with ZrO$_2$ nanoparticles than with TiO$_2$.
nanoparticles. Time-resolved absorption studies reveals that electron injection time for both TiO$_2$ and ZrO$_2$ nanoparticles is pulse width limited (<50 fs). Although, the density of acceptor states in the surface sates of ZrO$_2$ nanoparticles is much smaller compared to that in the conduction band of TiO$_2$ nanoparticles, still we have observed that electron injection is ultrafast in both the cases. Rego et al.$^{24}$ and Wang et al.$^{25}$ have already explained the direct electron injection into the nanoparticles through charge transfer mechanism. In the present investigation we have observed that Qz forms strong CT complex with ZrO$_2$ nanoparticles, which can facilitate direct electron injection into the surface states of the nanoparticles. As the LUMO in the case of a CT complex is located on the metal center (Zr), on excitation with light, the electron gets directly localized on the metal center from where diffusion into either the continuum of conduction band states or surface states of the nanoparticle takes place depending on the semiconductor. However, we have shown in the Scheme 3 that electron injection in Qz/ZrO$_2$ system can be possible both via photo-excited Qz molecules (kinj) and also direct injection (k’ inj) to metal centers (Zr).

**Modification of Surface States of Nanoparticles**

It is quite clear that surface states play an important role in interfacial ET reaction. Surface states directly involved in the ET process for dye/NP systems where dye molecules couple strongly with the formation CT complex. To make an efficient solar cell devices it is always expected that surface states nano-structured materials should not take part. However SS are the unavoidable intrinsic property of nano-structured material. However, these SS of nano-materials can be modified by using suitable capping agent (modifier molecule)$^{26}$. Where modifier molecules directly interact with the lower lying surface states. As a result density of SS can be changed.
drastically in the modified particles as compared to the bare one. DBS \((C_{12}H_{25}C_6H_4SO_3Na, \text{ sodium dodecyl benzene sulphonate})\) is one of the modifier molecules, which can be dissolved only in water, because it’s ionic nature. As TiO\(_2\) nanoparticle is important material for the development of dye-sensitized solar cell, it would be interesting effect of surface modification of it. As the surface of the TiO\(_2\) nanoparticles is positively charged, DBS molecules can easily bind through sulphonic group (SO\(_3^-\)) with the nanoparticles. The newly capped TiO\(_2\) nanoparticles looks like reverse micelle (Scheme 4) and can be dissolved in organic solvent. In this situation TiO\(_2\) nanoparticles migrate from water to organic phase (toluene). Now with the help of a separating funnel the organic phase was separated out. At this stage the organic phase looks little cloudy. The organic phase was dried in CaCl\(_2\) and transformed to an optically clear solution. The organic phase was then refluxed for 2 hours and the solvent was taken out with the help of a rotary evaporator in N\(_2\) atmosphere. Dry TiO\(_2\) particles capped by DBS, which were left in the flask, can be dissolved in many non-aqueous solvents to get colloidal solution in that particular solvent. Similarly ZrO\(_2\) nanoparticles can be modified by DBS molecule as the surface nature of ZrO\(_2\) nanoparticles as similar to TiO\(_2\) nanoparticles.

**Effect of Surface Modification on Interfacial Electron Transfer Dynamics**

The central theme of this article is to demonstrate the effect of surface modification on interfacial electron transfer dynamics in dye-sensitized TiO\(_2\) nanoparticles. For that purpose alizarin (Alz) molecule had been chosen for sensitization of semiconductor nanoparticles, which adsorb on the semiconductor surface very strongly with or without the presence of the modifier molecule (DBS). Interestingly Alz does not interact with DBS molecule both in the ground and excited state, this is an ideal system to study the effect of surface modification on dye-sensitized semiconductors. It is seen that Alz and TiO\(_2\) nanoparticles interact strongly and similarly both on unmodified and modified surface. It indicates that electronic coupling between Alz and TiO\(_2\) in the ground states is very similar in both cases. Electronic coupling is an important parameter for forward electron transfer (electron injection) process in dye/nanoparticle system. The above observations may lead us to speculate that there will be negligible effect of surface modification on electron injection on Alz/TiO\(_2\) nanoparticle systems. To verify the above speculation electron injection experiments has been carried out in Alz/TiO\(_2\) system on both unmodified and modified surface by changing the solvent. Figure 2 shows the comparison of electron injection dynamics in Alz/TiO\(_2\) system on both unmodified and modified surface in different solvents after monitoring the appearance signal of 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 initially populated electronic state in the molecular adsorbate and the delocalized electronic states of similar energy in the semiconductor. Although electron injection dynamics is found to be unaffected by surface modification, however, charge recombination (BET) dynamics found to be affected substantially on surface modification. Figure 3 shows the transient absorption decay of conduction band electron (eCB-) at 900 nm in Alz/TiO$_2$ system on both unmodified and modified surface in different solvents. The decay of the observed signals can be fitted by multi-exponential functions with time constants of 0.6 ps (75%), 7 ps (10%) and > 400 ps (15%) for Alz/unmodified-TiO$_2$ system and 1.9 ps (45.3%), 35 ps (12.9%) and > 400 ps (41.8%) for Alz/SM-TiO$_2$ system. It is striking to see that BET reaction between the 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 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 towards applying the semi-classical Marcus ET theory for explaining the results by following expression

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

BET rate constant ($k_{BET}$) depends on the coupling element (HAB), the overall free energy of reaction ($\Delta G^0 = EC - E_{S/S}^+$), the potentials of electrons in the conduction band of the semiconductor ($EC=-0.49V$), and the redox potential of the adsorbed dye ($E_{S/S}^+$) (Scheme 5). It has been observed that on surface...
modification both electronic coupling (HAB) and the solvent reorganization parameter (L) of Alz/TiO$_2$ nanoparticle system do not alter. As a result BET dynamics of Alz/TiO$_2$ system may depend mostly on free energy (-$\Delta G^0$) of the reaction for both unmodified and modified surface. Ellis et al.$^{27}$ reported that strong adsorption of negative counter ions on the electrode surface shifts the flat band potential (Vfb) and also the valence band (VB) to more negative values. On TiO$_2$ nanoparticle DBS molecule (modifier) is adsorbed strongly through sulphonic group (SO$_3$H). 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. On modification, both flat band potential and valence band is shifted towards negative values with same extent.$^{28}$ (Scheme 5). As a result the band gap of 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.$^{29}$ This high exoergic region is often termed as “inverted regime”. BET processes in dye-sensitized TiO$_2$ nanoparticles surfaces fall in the Marcus inverted regime for its high free energy of reaction$^{10,31}$. 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-TiO$_2$ is higher than that of the unmodified TiO$_2$ nanoparticles, BET rate on the modified surface is slower as compared to that on the unmodified surface.

**Conclusions**

Electron injection has been demonstrated in the forbidden energy states i.e. surface states of semiconductor nanoparticles by time-resolved Femto-second transient absorption studies. It is shown that quinizarin (Qz) an adsorbate that can couple very strongly with ZrO$_2$ nanoparticles can inject electron in the surface states of NP although energy level of photo-excited Qz lies far below the conduction band of ZrO$_2$ NP. Steady-state absorption studies revealed that quinone moiety of Qzs, form six-membered strong charge transfer (CT) complex with ZrO$_2$ nanoparticles. It has been observed that CT complex formation facilitates electron injection in the surface states of ZrO$_2$ nanoparticles. Surface states of NP has been modified by a suitable
modifier molecule namely DBS. Upon surface modification it has been observed that optical and photochemical properties of NP changed. Effect of surface modification on interfacial electron transfer dynamics in surface modified TiO₂ nanoparticles using suitable sensitizer molecule like alizarin (Alz). Electron injection dynamics has been found unaffected by surface modification, however, charge recombination (BET) dynamics is found to be slow on modified surface as compared to that on bare surface. The flat band potential of the modified nanoparticles is pushed up in energy, increasing the overall free energy of reaction (-ΔG) for BET; as a result BET rate decreases on modified surface. In conclusion, electron injection into the forbidden states of semiconductor nanoparticles have demonstrated and also it is shown that on surface modification, the rate of BET reaction can be reduced drastically in dye-sensitized nanoparticle system. This observation can, in turn, help the solar energy researchers to build low cost dye-sensitized solar cell with high photo-conversion efficiency.

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References


After obtaining his M. Sc. In Chemistry from IIT, Kharagpur, in 1989, Dr. Ghosh joined Chemistry Division, BARC, in 1990, through BARC Training School Course (33rd batch, 1989-90). Dr. Ghosh obtained his Ph.D. degree in 1996 from Bombay University for his work on fast photochemical processes in liquid and microheterogeneous media. He did his Post-doctoral studies for the period of 1997-1998, with Prof. Tim Lian at the Chemistry Department of Emory University, Atlanta, USA, in femtosecond infrared spectroscopy. Dr. Ghosh was awarded the “INSA Young Scientist” Medal for the year of 1998 for his outstanding Ph.D. work. He has also received the prestigious “Anil Kumar Bose Memorial Award” in 2000 for the best output during the year after INSA Young Scientist Award by the Indian National Science Academy, New Delhi. Dr. Ghosh has published more than 50 research papers in highly reputed International Journals, and his research papers have been cited by peers and experts in his field of research for more than 1000 times. He has developed Femtosecond laser spectrometer detecting both invisible and infrared region. His current research interest includes ultrafast interfacial electron transfer and charge carrier relaxation dynamics in semiconductor nanoparticles and quantum dot materials as also development of Femtosecond terahertz spectrometer.