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Sensitization of TiO_2 nanoparticles in micro-emulsion by photo-excited dye molecules: A femtosecond transient absorption study

Madhab C. Rath, Dipak K. Palit, Tulsi Mukherjee, Hirendra N. Ghosh*

Radiation & Photochemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

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ABSTRACT

Photo-induced electron transfer reaction in controlled sized TiO_2 particles sensitized by catechol and quinizarin 6-sulfonate (Qz-6S) has been investigated using femtosecond transient absorption spectroscopy. Size-controlled TiO_2 nanoparticles were synthesized in reverse micelles using di-octyl sulfosuccinate (Aerosol-OT, AOT) as the surfactant stabilizer. The particle sizes of the nanoparticles were controlled by varying the water-to-surfactant molar ratio, $w_0 = [H_2O]/[AOT]$. Optical absorption measurements confirm that only strong coupling between the nanoparticles and the sensitizers can ensure sensitization the nanoparticles in the micro-emulsion media. Electron transfer process has been determined by monitoring electron in the conduction band in nanoparticle at 900 nm and parent cation in the visible region of the sensitizer molecules. Electron injection has been measured from the appearance signal of injected electron at 900 nm and it is found to be pulse-width (<50 fs) in both the systems. We have also carried out electron transfer studies of both the dye-nanoparticle systems in aqueous solutions where the particles have been prepared by sol–gel process and compared the data studied in micro-emulsion to see the effect of micro-environment.

1. Introduction

Nanocrystalline semiconductor materials [1] exhibit a wide range of novel chemical and physical properties that are finding application in devices such as solar cells [2], waste water treatment [3] and nano-electronic devices [4]. If the particle size becomes sufficiently small, quantum confinement of electrons leads to a size-dependent separation between the valence and conduction bands, which are split into discrete exciton-like states [5]. Spatial confinement of photo-generated charge carriers causes the electronic levels to be at higher energies in these particles. As a result, various optical and electronic properties of such quantum-size nanoclusters or “quantum dots” are subsequently different from those of the bulk. These quantum size (Q-size) effects have been observed for a number of different semiconductors (CdS, ZnS, Cd_3P_2, ZnO) [6–9]. Recently, we have also reported effect of particle size on the reactivity of Q-size ZnO nanoparticles and charge-transfer dynamics with adsorbed catechols [10]. Quantum Dot (QD) materials are also sometime used in solar cell for sensitization purpose where QDs like InP [11], CdSe [12–15], CdS [16,17] and PbS [18] are substituted for the dye molecules. In QD-sensitized solar cell QDs are used to sensitize another suitable semiconductor (e.g. TiO_2), which have more advantages over dye molecules due to their better tunability of optical properties by variation of sizes and better hetero-junction formation with solid hole conductors. However, no effort has been made where the sensitizers will sensitize QD itself. In this context it is necessary to study interfacial electron transfer behavior of dye-sensitized QDs, where QDs can be of TiO_2 material.

Quantum size (Q-size) effect of small size TiO_2 materials is a debatable issue. Several reports are available in the literature where the effect of size quantization reflected in the optical absorption spectra of TiO_2 particles. Kormann et al. [19] demonstrated Q-size effects in particles with a radius of 1.2 nm, prepared by the hydrolysis of titanium tetrachloride, by observing blue shift of the optical absorption edge. Kavan et al. [20] observed a shift of ~0.1 eV from particles of about 1 nm in radius prepared by oxidative hydrolysis of $TiCl_3$. However, Serpone et al. [21] argued that blue shift in the absorption edge of TiO_2 arises from direct interband transitions in an indirect band gap semiconductor instead of from size quantization. Earlier Sant and Kamat [17] reported inter-particle electron transfer behavior between CdS and TiO_2 semiconductor nanocluster synthesized in aerosol-OT/water micro-emulsion. They have demonstrated the size quantization behavior of extremely small TiO_2 colloids sensitized by CdS nanoclusters. Electron transfer from photo-excited CdS to TiO_2 particles of a size comparable to the excitonic diameter was restricted whereas ET process was allowed in bigger sized TiO_2 nanoparticles (NPs). However, the effect of size quantization of TiO_2 particles on interfacial electron transfer (IET) dynamics has not been reported in the literature. In the earlier mea-

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* Corresponding author. Tel.: +91 22 2559 0300; fax: +91 22 2550 5151.
E-mail addresses: hnghosh@barc.gov.in, hnghosh@magnum.barc.ernet.in (H.N. Ghosh).

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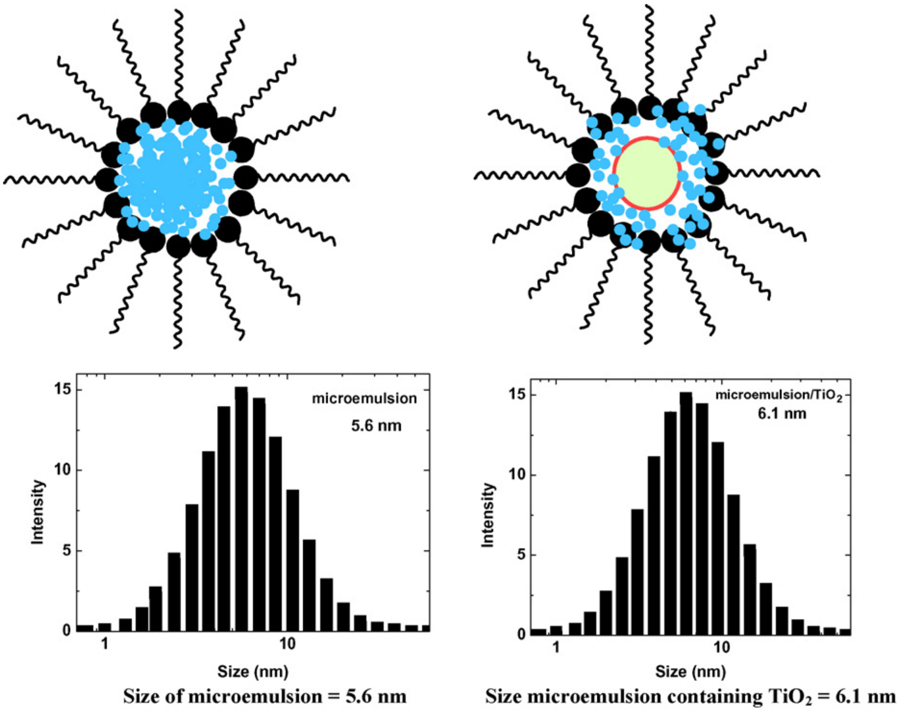


Scheme 1. Particle size distribution histogram of (a) micro-emulsion, (b) TiO_2 particle in micro-emulsion.

surements sensitization of semiconductor by QD material has been reported [11–18]. However, sensitization of excitonic TiO_2 materials by any adsorbate is not reported so far. However, Klimov and co-workers [22] reported photo-induced electron transfer between CdSe quantum dots and Ru–polypyridine complexes.

In the present investigation, we report the synthesis of very small size TiO_2 particles (called sub-nanoparticles, SNPs) in AOT/*n*-heptane/water micro-emulsion with $w_0 = 1$ ($w_0 = [H_2O]/[\text{surfactant}]$). Size quantization behavior of small size TiO_2 particles have been confirmed from the blue shift in the absorption band edge. Two different types of molecules, catechol (Cat) and quinizarin 6-sulfonate (Qz-6S), have been chosen to sensitize these particles. Steady-state optical measurements show that catechols interact more strongly with the nanoparticles as compared to Qz-6S. Femtosecond transient absorption spectroscopy has been carried out in Cat and Qz-6S sensitized small size TiO_2 nanoparticles in micro-emulsion, exciting with 400 nm laser pulse. Electron injection has been confirmed by direct detection of injected electron in the conduction band of TiO_2. We have also monitored back electron transfer (BET) dynamics by monitoring the kinetic decay trace of the injected electron. Experiments have also been carried out by sensitizing bigger sized TiO_2 particles as prepared by sol–gel process by the same sensitizers (Cat and Qz-6S). We have compared IET dynamics for both TiO_2 particles (NP and SNP) sensitizing both Cat and Qz-6S.

2. Materials and methods

2.1. Sample preparation

2.1.1. Materials

Titanium(IV) tetraisopropoxide $\{Ti[OCH(CH_3)_2]_4\}$ (Aldrich, 97%), and isopropyl alcohol (Aldrich) were purified by distillation process. Aerosol-OT (AOT) and *n*-heptane was also obtained from Aldrich. Nanopure water (Barnsted System, USA) was used for making aqueous solutions.

2.1.2. Preparation of semiconductor colloids in reverse micelles

Colloidal TiO_2 suspension in reverse micelles was prepared by hydrolysis of titanium (IV) isopropoxide/2-propanol solution as followed by Sant and Kamat [17]. Water-in-oil type of micro-emulsions of $w_0 = 1$ were prepared by adding 0.22 ml $HClO_4$ (0.02 M) in 30 ml solution containing 0.4 M AOT in n-heptane. An aliquot of 0.2 ml Titanium isopropoxide (0.136 M) was added drop wise to 20 ml of the above micro-emulsion under mild stirring at room temperature. The stirring was continued for about 20 min after the addition of the reagent. A clear colour less transparent solution was obtained which contains the TiO_2 nanoparticles.

2.1.3. Preparation of semiconductor colloids by sol–gel process

Nanometer-size TiO_2 was prepared by controlled hydrolysis of titanium (IV) tetraisopropoxide [23,24]. A solution of 5 mL $Ti[OCH(CH_3)_2]_4$ (Aldrich, 97%) dissolved in 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_3). The solution was continuously stirred for 10–12 h 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.

2.1.4. Dye adsorption on TiO_2 colloids in micro-emulsion and in water

It is very important to choose dye molecules, which will be adsorb on the surface of TiO_2 colloids in micro-emulsion effectively. We have observed that the dye molecules like coumarin 343 and ruthenium polypyridine complexes cannot be adsorbed on the surface of TiO_2 colloids in micro-emulsion. These kind of sensitizer molecules has good solubility in *n*-heptane. As a result the dye molecules will prefer to stay in *n*-heptane than adsorbing on the nanoparticles, which are residing in the water pool in micro-emulsion. However if the same dye molecules can interact strongly with the nanoparticles then it can sensitize the nanoparticles even in the micro-emulsion. On the other hand, if the dye molecules are water-soluble then it can reside in the water pool and easily adsorbed with the nanoparticles. In the present investigation we have chosen two sensitizer molecules, catechol and Qz-6S. Interestingly catechol can interact strongly with nanoparticles and Qz-6S is a water-soluble ionic molecules. After synthesizing the TiO_2 colloids in micro-emulsion we have added the dye molecules into it and stirred mildly for 1 h till deep red-coloured solutions were formed. The dye-nanoparticle solutions were found to be stable for couple of days.

We have sensitized the TiO_2 nanoparticles (20 g/L) by directly mixing nanoparticles and the sensitizer molecules in nanopure water and the mixed solution was stirred for 1 h. The solution turned deep red and found to be stable for many days.

2.2. Dynamic light scattering (DLS) measurements

Dynamic light scattering experiments were performed on a DynaPro-MS800 instrument (Protein Solutions Inc., VA) which monitors the scattered light at 90°. At least 20 measurements each of 10 s duration were collected. Experimental solutions were filtered through 0.02 mM filters (Whatman Anodisc 13, Cat. No. 6809-7003). Extreme care was taken to reduce the contamination of samples by dust. “Regularization” software provided by the manufacturer was used in analyzing the results for obtaining distribution of hydrodynamic radius of particles in the solution. In Scheme 1 we have demonstrated the structure and dynamic light scattering measurements. Our measurements it is seen that size of the micro-emulsion increases as we incorporate TiO_2 nanoparticle in the water core. In presence of nanoparticles the size of micro-emulsion swell little bit as the size of the micro-emulsion changes from 5.6 nm to 6.1 nm. However from this measurement we cannot comment on the actual size of the particles.

2.3. Femtosecond visible spectrometer

The femtosecond tunable visible spectrometer has been developed based on a multi-pass amplified femtosecond Ti:sapphire laser system from Avesta, Russia (1 kHz repetition rate at 800 nm, 50 fs, 800 μJ/pulse) and described earlier [25,26]. The 800-nm output pulse from the multi-pass 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. In the present investigation we have used 400 nm (frequency doubled in BBO [β barium borate] crystal) laser light as pump pulse to excite the samples. 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 is adjusted by iris size and ND filters to obtain a stable white light continuum from 400 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. To monitor kinetics at different wavelength we have used interference filter for different wavelength before both the photodiodes. The noise level of the white light is about ∼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 about <0.3%.

3. Results and discussion

3.1. Optical absorption spectroscopy of nanoparticles and interaction with dye molecules

We have carried out optical absorption spectroscopy of TiO_2 colloids in micro-emulsion with different w_0 (1–5). It has been observed that with decreasing w_0, optical absorption spectrum of TiO_2 colloid gets blue-shifted. This is a clear indication of decrement in their sizes. Fig. 1a shows the optical absorption spectrum of TiO_2 colloid in micro-emulsion with $w_0 = 1$. In Fig. 1b we have also shown the optical absorption spectrum of TiO_2 colloid in water as prepared by sol–gel process. It is seen clearly that the absorption onset of TiO_2 particles in micro-emulsion is noticeably blue-shifted compared to that of the particles prepared in water by sol–gel process. The size of the particles in colloids prepared in water is significantly larger (>5 nm), which has absorption onset at ∼380 nm. The absorption onset was found to be 320 nm ($E_g = 3.65$) for TiO_2 colloids in micro-emulsion with $w_0 = 1$, which matches well with that reported by Sant and Kamat [17].

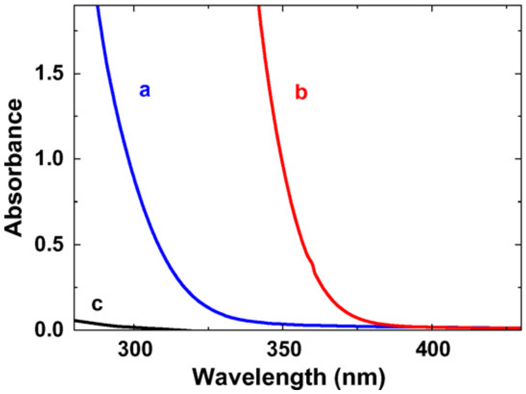


Fig. 1. Absorption spectra of (a) size quantized TiO_2 nanoparticles (SNP) in reverse micelles (micro-emulsion) with $w_0 = 1$, and (b) TiO_2 nanoparticles (NP) as prepared by sol–gel method and (c) only micro-emulsion with $w_0 = 1$.

The aim of this investigation is to study interfacial ET dynamics after sensitizing these particles in micro-emulsion. For this purpose it is necessary to monitor the dye-nanoparticle interactions. Fig. 2 shows the optical absorption spectra of free catechol (Fig. 2a), TiO_2 QDs in micro-emulsion (SNP) (Fig. 2b) and catechol-sensitized TiO_2 QDs (Fig. 2c). It is clearly seen that an additional new absorption band centered at ∼390 nm and extending up to 600 nm has appeared. This band has been attributed to a charge transfer (CT) complex of catechol-TiO_2 system [27–29]. We have also reported earlier [24,30,31] that catecholate molecules bind strongly with TiO_2 nanoparticles with the formation of a 5-membered chelating ring (Scheme 2).

We have also recorded steady-state optical absorption spectra of Qz-6S molecule on TiO_2 nanoparticles both in micro-emulsion and in water. In our earlier studies, we have already reported that the parent molecule, i.e. quinizarin (Qz), can effectively bind with TiO_2

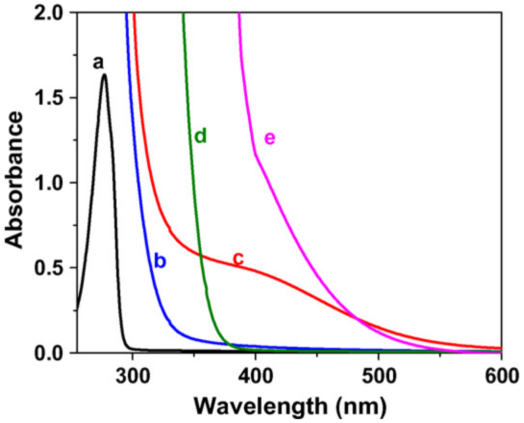
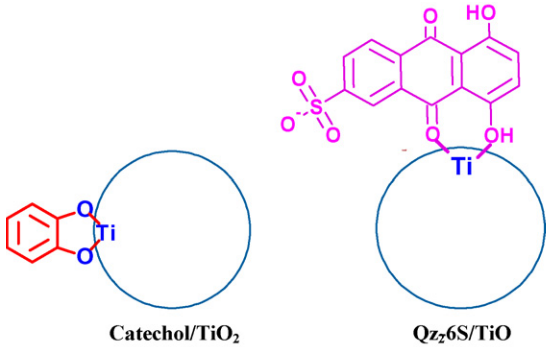


Fig. 2. Absorption spectra of (a) free catechol, (b) SNP TiO_2, (c) catechol-sensitized SNP TiO_2, (d) TiO_2 (sol–gel) and (e) catechol-sensitized TiO_2 (sol–gel).



Scheme 2. Molecular structure of catechol (Cat) and quinizarin 6-sulfonate (Qz-6S) coupling with TiO_2 nanoparticles.

nanoparticles with the formation of 6-membered chelating ring. Fig. 3 shows the optical absorption spectra of Qz-6S in water (curve a), in micro-emulsion (curve b), on TiO_2 nanoparticles in water (NP) (curve c) and on TiO_2 particles in micro-emulsion (SNP) (curve d). The optical absorption spectrum of Qz-6S in water (Fig. 3, curve a) shows a peak at 474 nm with a shoulder at 520 nm. In micro-emulsion ($w_0 = 1$), the optical absorption spectra of Qz-6S also show a peak at 474 nm with a sharper shoulder at 520 nm (Fig. 3, curve b). The structure in the absorption spectra recorded in micro-emulsion is different as compared to that in bulk water. This structural behavior of Qz-6S molecules has been observed because the molecules are confined in the water pool of micro-emulsion. On addition of TiO_2 nanoparticles in an aqueous solution, the colour of Qz-6S solution changes from violet to dark pink. With increasing concentration of TiO_2 nanoparticles optical absorption of Qz-6S is gets red-shifted gradually with an increase of absorbance. Qz-6S shows a peak at 520 nm with a shoulder at 570 nm (Fig. 3, curve c) as it is adsorbed on TiO_2 nanoparticles (20 g/L). However the optical absorption of Qz-6S on TiO_2 nanoparticles in micro-emulsion (Fig. 3, curve d) shows a broad peak at 500 nm with a sharp shoulder at 575 nm. The optical absorption spectra of Qz-TiO_2 system look quite different in micro-emulsion. This may be due to micro-heterogeneity of the medium. From this measurement, it was clear that Qz-6S could also sensitize the TiO_2 QDs in micro-emulsion. Now it will be quite interesting to compare the electron transfer behavior in different particles in different media.

3.2. *Transient absorption measurements in catechol/TiO_2 system*

It has been demonstrated by many workers including us that, optical excitation of dye molecules adsorbed on TiO_2 nanoparticle surface inject electron into the conduction band of the nanoparticle [23–33]. In the present investigation, we have carried out femtosecond laser flash photolysis experiments exciting the Cat/TiO_2 system in micro-emulsion with 400 nm laser light to study the ET dynamics on semiconductor surface where particles are synthesized in the water pool of micro-emulsion. Fig. 4 shows the time-resolved transient absorption spectra of Cat/TiO_2 system in micro-emulsion at 0.2, 0.5, 1, 2, and 10 ps after exciting at 400 nm. The spectrum at each delay time consists of bleach in the 470–500 nm regions and a transient absorption band in the 500–900 nm region. The transient absorption and the bleach are separated by a well-defined isosbestic point at ~500 nm. The transient spectra show a transient absorption band in the 500–700 nm region with a peak at 610 nm and a flat absorption band in the 700–900 nm region. The positive absorption band can be attributed to the charge-separated species, i.e. catechol cation radical and injected electron in the nanoparticles. However, catechol cation radical does not have any absorption beyond 500 nm [34]. So the transient absorption signal at 500–900 nm can be attributed to the injected electrons in TiO_2. Lian and co-workers have also assigned this transient band in catechol-sensitized TiO_2 nanoparticles in water as injected electrons in nanoparticles. However, in earlier measurements we [24–26,30–32] have shown that the transient spectra of the injected electron in the visible region are quite broad and structure-less. It is also interesting to see that at longer time delay (Fig. 4) the transient peak at 610 nm gets smeared off with the flat absorption band (700–900 nm). In the case of Cat-TiO_2 SNP system, on excitation by 400 nm laser light, only the CT band is excited. On excitation of the CT band electron is directly injected to the Ti metal ion. From the Ti ion the electron gets de-localized from the metal ion to the conduction band of the nanoparticles [29]. So, at the end of the laser pulse in the transient absorption spectra of Cat/TiO_2 SNP system we have observed charge-separated CT state, where electron is localized in the metal ion. Hence, in the present investigation transient absorption band peaking at ~610 nm can be attributed to the excited CT state of Cat/TiO_2 SNP system, where electrons are localized in the metal ion. To determine the electron injection we have monitored the appearance signal of the transients at both 610 nm and 900 nm. We have observed that both the kinetic trace looks very similar. The transient signal at 900 nm can be attributed to the injected electron in the conduction band of semiconductor nanoparticles and it is shown in Fig. 5a for Cat/TiO_2 SNP system. Time constant for the appearance signal has been fitted and found

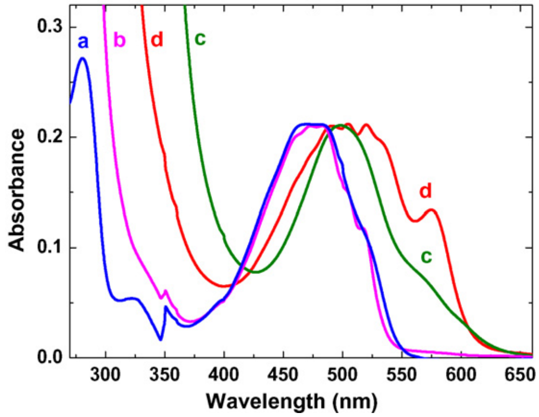


Fig. 3. Normalized absorption spectra of (a) Qz-6S in water, (b) Qz-6S in micro-emulsion, (c) Qz-6S sensitized TiO_2 NP in water and (d) Qz-6S sensitized TiO_2 SNP in micro-emulsion.

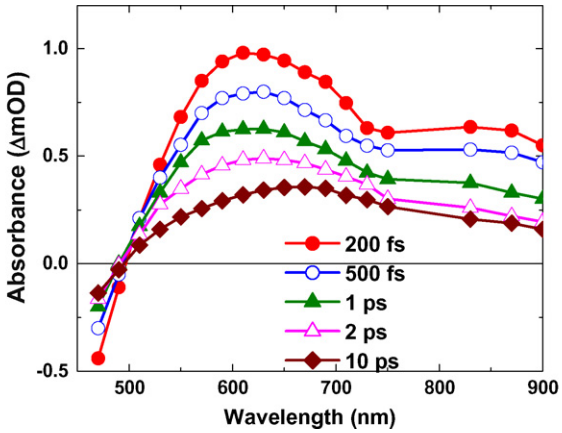


Fig. 4. Transient absorption spectra of catechol/SNP TiO_2 complex in micro-emulsion at 0.2, 0.5, 1, 2, and 10 ps after 400 nm excitation. The spectrum at each delay time constants of a bleach signal, an absorption peak at 610 nm and a broad absorption feature in the whole spectral region (700–900 nm). These features are assigned to the depletion of the CT transition, excited CT state and absorption of injected electrons in TiO_2 SNP, respectively.

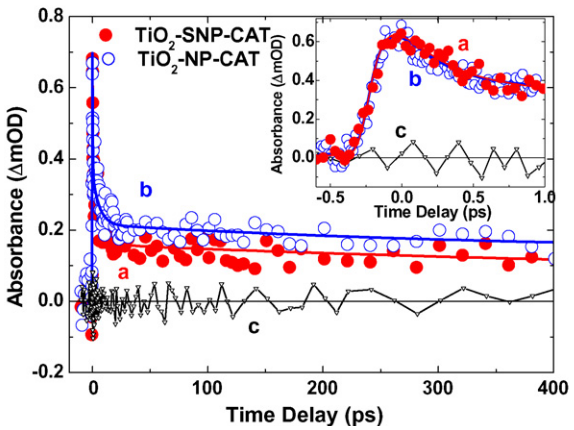
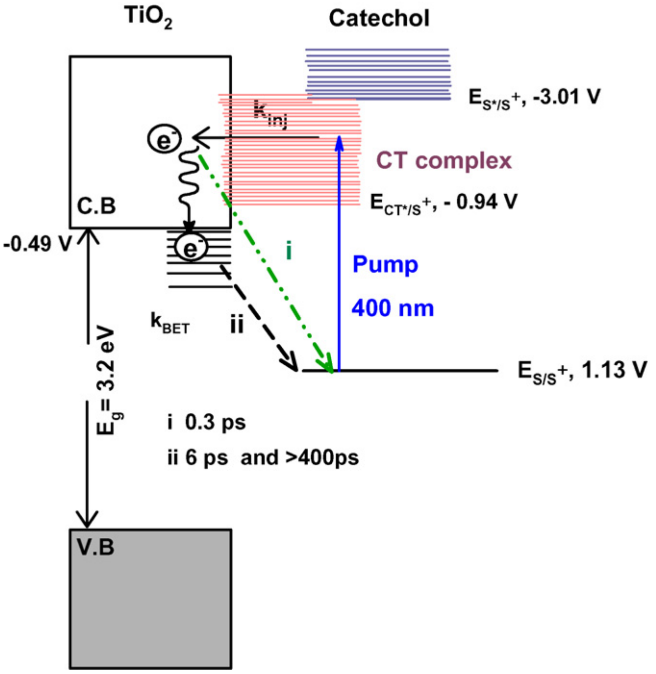


Fig. 5. Normalized transient absorption decay profiles at 900 nm after 400 nm excitation for (a) catechol sensitized SNP TiO_2 (●) in micro-emulsion, (b) catechol sensitized NP TiO_2 (○) in water and (c) NP TiO_2 (▽) in water. The solid lines are best fits to the data. Fitting parameters are shown in Table 1. Inset: same kinetic decay trace is plotted in a shorter time scale.



Scheme 3. Mechanistic scheme of electron transfer for the catechol (Cat) sensitized TiO_2 nanoparticles. Here S^*/S^+ is the excited sensitized dye/cation radical couple, and CT^*/S^+ is the excited CT state/cation radical couple. On 400 nm excitation, CT complex of Cat/TiO_2 gets excited and electron injection to the conduction band takes place. $E_{S/S}+$ and $E_{S^*/S}+$ is the ground and excited state redox potential of catechol and $E_{CT^*/S}+$ excited state potential of the CT complex.

to be pulse width limited, i.e. <50 fs (Fig. 5a inset). Electron injection time in strong coupling dye-nanoparticle system is an adiabatic process. Which indicate that on photo-excitation electron transfer takes place from the sensitizer to nanoparticle very fast. It is reported by Schnadt et al. [35] that electron injection can take place as fast as sub-3 fs from aromatic adsorbate to TiO_2. Similarly in the present investigation also we have observed that injection time is too fast to measure by our laser pulse (pulse width $\sim$50 fs). In our earlier work [32] we have shown there that pulse width limited injection means that the data can be fitted with time constant between 1 fs and 25 fs. We had seen that 50 fs rise time showed bad fitting and we had attributed that injection is pulse width limited. Similarly in the present investigation also we have fitted the data in all the systems with 1–25 fs rise time, which clearly indicate pulse-width limited injection. To determine back electron transfer dynamics we have monitored the kinetic decay trace at 900 and it is shown in Fig. 5a. The kinetics at 900 nm can be fitted multi-exponentially with time constants of 300 fs (74.0%), 6 ps (11.3%) and >400 ps (14.7%) (Table 1). Charge recombination dynamics in dye-sensitized TiO_2 nanoparticles is multi-exponential in nature. To understand the multi-exponential nature of BET dynamics we have drawn Scheme 3. We have depicted the electron transfer process in Scheme 3 where $E_{S/S}+$ and $E_{S^*/S}+$ is the ground and excited state redox potential of catechol and $E_{CT^*/S}+$ excited state potential of the CT complex. $E_{S/S}+$ is found to be +1.13 V [29]. $E_{S^*/S}+$ has been determined from ground state redox potential ($E_{S/S}+$) subtracting the $S_1 \leftarrow S_0$ transition (Fig. 2a) of catechol molecule and found to be −3.01 V. Similarly $E_{CT^*/S}+$ has been determined from ground state redox potential ($E_{S/S}+$) subtracting the $S_{CT} \leftarrow S_0$ transition (Fig. 2c) of CT complex of catechol/TiO_2 e and found to be −0.94 V. Catechol is a tricky molecule and it absorbs light below 300 nm. So on excitation by 400 nm light pure catechol molecule cannot be excited. However it is interesting to see that on 400 nm laser excitation electron injection takes place into the TiO_2 nanoparticles. In the present investigation we can excite only the CT band of catechol/TiO_2 system and observe electron injection. Theoretical calculations [36–38] also confirmed that in catechol/TiO_2 system electron injection takes place directly into the conduction band. To find out back ET dynamics we have fitted the data in Lab-view programme that yielded best-fitted three exponential time constants. These data could not be fitted bi-exponentially rather we could fit three exponentially with very good χ^2. These three different time constants do not appear arbitrarily, they always carry physical meaning. The fastest component, i.e. 300 fs can be attributed to the recombination dynamics of hot electron and parent cation (process *i* in Scheme 3), which recombines just after injection due to strong coupling in nature. The second time constants 6 ps component might be the recombination time constant of injected electron in the conduction band edge or shallow trapped electron and parent cation. On the other hand the longer component (>400 ps) is the recombination time constant between deeper trapped electron and parent cation. The longer components we have attributed to process *ii* in Scheme 3. We have also carried out intensity dependence measurements on back ET dynamics in the present studies. However we did not observe and difference in back ET dynamics like our earlier observation [30].

Table 1
Parameters for the multi-exponential fits to the back-ET kinetics of catechol and quinizarin 6-sulfonate (Qz-6S) sensitized TiO_2 SNP and NP particles.

System	$1/k_1$ (A_1)	$1/k_2$ (A_2)	$1/k_3$ (A_3)
Cat-SNP	0.3 ps (74%)	6 ps (11.3%)	>400 ps (14.7%)
Cat-NP	0.3 ps (67.3%)	6 ps (13.2%)	>400 ps (19.5%)
Qz-6S-SNP	0.75 ps (66.1%)	7 ps (15.4%)	>400 ps (18.5%)
Qz-6S-NP	0.75 ps (67.7%)	7 ps (9.7%)	>400 ps (22.6%)

Although interfacial electron dynamics in catechol-sensitized TiO_2 nanoparticles (NPs) (prepared from sol–gel process) in water has been carried out by Wang et al. [25], for the sake of comparison of the ET dynamics in the above system in two different types of particles in different media we have also carried out sensitization experiments in Cat/TiO_2 NP system in water. We have monitored the kinetic decay trace at 900 nm and shown in Fig. 5b. The kinetic decay trace can be fitted multi-exponentially with the time constants of 300 fs (67.3%), 6 ps (13.2%) and >400 ps (19.5%) (Table 1). We have also monitored the appearance signal at 900 nm which is due to injected electron in the conduction band of TiO_2 (Fig. 5b inset). It is interesting to see that electron injection time in both the particles is similar (pulse-width limited). We tried to fit both

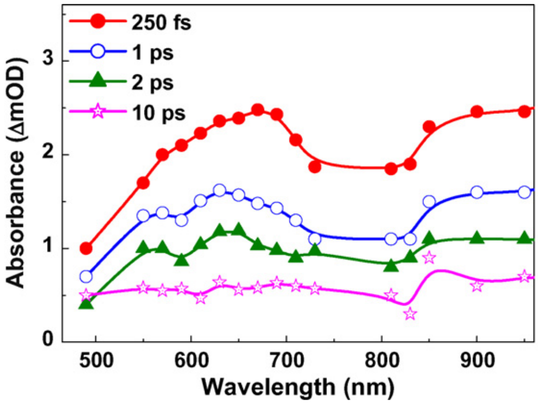


Fig. 6. Transient absorption spectra of quinizarin-6-sulfonate (Qz-6S) sensitized TiO_2 in micro-emulsion at 0.25, 1, 2, and 10 ps after 400 nm excitation. The spectrum at each time delay consists of an absorption peak at 650 nm and a broad positive absorption feature in the whole spectral region (700–1000 nm). These features are assigned to cation radical of Qz-6S dye and injected electron in nanoparticles, respectively.

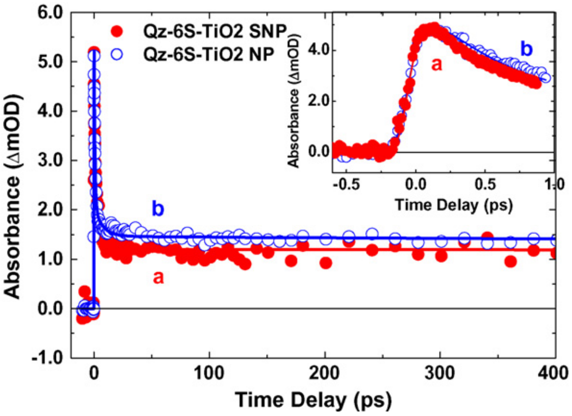


Fig. 7. Normalized transient decay kinetics at 900 nm after 400 nm excitation for (a) quinizarin 6-sulfonate (Qz-6S) sensitized SNP TiO_2 in micro-emulsion (●) and (b) Qz-6S sensitized NP TiO_2 in water (○). The solid lines are best fits to the data. Fitting parameters are shown in Table 1. Inset: same kinetic decay traces are plotted in shorter time scale.

colloidal data and micro-emulsion data for both the dye/TiO_2 system with similar time constants as the kinetic decay traces are very similar and also tried to fit to the model. However we can see clearly the contribution of the components are different.

3.3. *Transient absorption measurements in quinizarin 6-sulfonate/TiO_2 system*

Optical absorption measurements and Scheme 2 shows that Qz-6S molecule can be adsorbed quite effectively on TiO_2 surface with the formation of a 6-membered chelating ring. Fig. 6 shows the time-resolved transient absorption spectra of Qz-6S sensitized TiO_2 nanoparticles in micro-emulsion. The spectrum at each time delay consists of an absorption band with a peak at ~660 nm and also a broad absorption band in the 700–1000 nm region. The latter can be attributed to the conduction band electrons in the nanoparticles (e_{CB}^-) [24–26]. In our earlier studies, we have shown sensitization of TiO_2 nanoparticles by quinizarin (Qz) where photo-excited Qz injects electron with pulse width limited time. The oxidized Qz was found to have a peak at 650 nm [26]. In the present investigation the transient peak at 660 nm can be attributed to Qz-6S$^+$. We have measured the electron injection time in the nanoparticles by monitoring the appearance signal of Qz-6S$^+$ at 650 nm as well as the conduction band electron (e_{CB}^-) at 900 nm (inset, Fig. 7a) and has been found to be <50 fs. We have determined the charge recombination time (BET) by monitoring the decay of the injected electron at 900 nm as shown in curve a Fig. 7. The kinetic decay trace can be fitted multi-exponentially with the time constants of 750 fs (66.1%), 7 ps (15.4%) and >400 ps (18.5%) (Table 1). We have also carried out sensitization experiments in Qz-6S/TiO_2 nanoparticles in water. Electron injection has been confirmed by monitoring the injected electron in the conduction band (e_{CB}^-) at 900 nm (Fig. 7b). Here also electron injection time was also found to be pulse-width limited. The kinetic decay trace at 900 nm (Fig. 7b) can be fitted multi-exponentially with time constants of 750 fs (67.7%), 7 ps (9.7%) and >400 ps (22.6%) (Table 1).

3.4. *Effect of micro-environment in interfacial electron transfer dynamics*

One of the main aims of this investigation is to monitor interfacial ET dynamics of exciton like TiO_2 particles synthesized in micro-emulsion. We had to choose to synthesis particles in micro-emulsion method as it gives good control over size of the particles. Which we have easily synthesized by controlling the size of the water pool with $w_0 = 1$. Electron injection and BET dynamics has been monitored by directly detecting the electron in the conduction band and/or cation radical of the adsorbates. To see the effect of micro-environment and size quantization of the particles, the above experiments were also carried out using bigger size particles as synthesized by sol–gel process. Now let us discuss the ET dynamics of Cat/TiO_2 system. Earlier, we have discussed that Cat/TiO_2 system is a strong coupling system and catechol forms strong CT complex with TiO_2 nanoparticles irrespective of the medium and environment. It is interesting to observe that in both the cases, electron injection is pulse-width limited as Lian and co-workers [25] observed in catechol/TiO_2 system. Recently, Rego and Batista [36] have studied the interfacial ET dynamics in catechol/TiO_2 nanoclusters after combining *ab initio* DFT molecular dynamics simulations and quantum dynamics calculations. They have found that the primary process that localizes the charge in the Ti^{4+} surface ions next to the catechol adsorbate. As in both micro-emulsion and in water, catechol forms strong CT complex and on excitation of this CT complex at 400 nm, the electron will be first localized in Ti(IV) ion, which is basically the electron injection into the nanoparticles. Electron injection time found to be similar in both the systems. The primary event is followed by charge delocalization (i.e. charge diffusion) through the nanocrystalline material. This process of localization of the electron at the metal center is only possible when the dye molecules form a strong CT complex with the nanoparticles. However, the injected electrons can also rapidly delocalize and diffuse out and get trapped in different trapping positions with a distribution of trap energy and distance from the adsorbate. As a result, multi-exponential recombination (BET) dynamics is expected and this has really been observed by us [24–26,30–32] and many other authors [29] earlier. Ultrafast BET reaction in catechol-sensitized TiO_2 nanoparticles has been reported by Wang et al. [29]. They have reported that majority of the injected electrons recombine with the parent cation with time constant ~400 fs. Our kinetic data traces for the charge recombination reaction can be fitted multi-exponentially with time the constants of 300 fs (74.0%), 6 ps (11.3%) and >400 ps (14.7%) for smaller size nanoparticles (SNP) and 300 fs (67.3%), 6 ps (13.2%) and >400 ps (19.5%) for the bigger size nanoparticles (NP). It is clear from the kinetic decay traces in Fig. 5 and Table 1 that early dynamics (faster components) for both systems is very similar and longer dynamics is marginally slower on NP surface.

It is well known [5] that on size quantization, the energy level of the conduction band moves up. As a result, the effective free energy of BET reaction will be more in smaller size particle for the same dye-nanoparticle system, so it is expected that BET rate will be slower on smaller size particles (SNP) as compared to that on NP. As BET processes in dye-sensitized TiO_2 nanoparticles surfaces fall in the Marcus inverted regime for its high free energy of reaction [39,40]. In this region, with increasing driving force ($-\Delta G^\circ$) of the reaction, the rate of BET decreases. However we did not observe much difference in the dynamics in early time domain. This can be explained, as catechol/TiO_2 system is a strongly coupled system where we excite mainly the CT complex. Now on excitation CT complex by 400 nm initially the electron will be localized in the Ti(IV) metal ion center. After localization a majority of the electrons will recombine with the parent catechol cation, which is reflected in Table 1 a fast 300 fs component for both SNP and NP system. So in early time domain strong coupling in the charge-separated species in the CT complex actually dominates the recombination dynamics rather than size quantization of the particles. However we have observed that in longer time scale BET dynamics on TiO_2 particles in micro-emulsion is marginally faster. This can be explained as small size nanoparticles are synthesized in micro-emulsion environment where surfactant molecules (AOT) can act as surface modifier. These AOT molecules can remove lots of trap states particularly the deeper trap states. So the injected electrons in SNP which avoid ultrafast recombination in early time scale will reside in relatively shallower trap states as compared to that in NP. As recombination reaction of the parent cation and shallower trap electrons will be faster as compared to the deeper one, for the same dye-semiconductor pair charge recombination reaction is expected to be faster for SNP (AOT modified) as compared to NP (bare). We made similar observation in our earlier studies in dibromo fluorescein (DBF) sensitized TiO_2 nanoparticles for modified (by sodium dodecyl benzene sulfonate, DBS) and bare particles [41]. As a result in longer time domain we have observed relatively faster recombination on TiO_2 surface in micro-emulsion. In our earlier investigation [25] we have observed that on surface modification back ET reaction becomes slow due to pining of conduction band and modification of surface states. However, in the present investigation although we have used two different type particles still we have not observed very different BET dynamics. This is due to the fact that the surface modified particles are smaller as result there will be shorter distance between injected electron and parent cation as compared to those bigger particles (sol–gel particles) so back ET dynamics will be faster on smaller particle surface due to better electronic overlap between injected electron and parent cation. So two opposite effects are acting together on surface modified particles in micro-emulsion, as a result we observe marginally different back ET dynamics on both the particle surface.

Now let us discuss BET dynamics in Qz-6S/TiO_2 system on both particle surfaces. We have chosen Qz-6S molecule, which can couple with TiO_2 nanoparticles with the formation six-membered ring (Scheme 2). It is reported [42] that six-membered ring on TiO_2 surface forms weaker complex as compared to five-membered complex of Cat/TiO_2 system. In ultrafast transient absorption measurements, we expected different mechanism for BET reaction for two different dye-nanoparticle systems. However, it is clear from optical absorption spectra and our earlier studies [26] revealed that quinizarin and TiO_2 nanoparticles interact quite strongly, although the interaction may be little weaker as compared to Cat/TiO_2 system. Transient absorption studies revealed that majority of the injected electrons in Qz-6S/TiO_2 system recombines with 600 fs component in both nanoparticles surfaces. In our earlier studies [22] also we have observed that in Qz/TiO_2 system BET reaction takes place multi-exponentially with 650 fs as major component. The sub-picosecond major component clearly indicates that Qz-6S and TiO_2 particles are coupled quite strongly for BET reaction. So the recombination dynamics in Qz-6S/TiO_2 system also follow similar mechanism as in the case of Cat/TiO_2 system on both the particle surfaces as reflected in Table 1. In Qz-6S/TiO_2 system also strong coupling between dye molecule and nanoparticle dominates in charge recombination dynamics over size quantization of the particles. However we are on our way to find a suitable sensitizer molecule, which can sensitize TiO_2 nanoparticles in micro-emulsion with relatively weaker binding group like carboxylic, where effect of size quantization on ET dynamics can be easily monitored.

4. Conclusions

We have synthesized TiO_2 semiconductor particles of very small size (~1 nm) (SNP) in AOT/water micro-emulsion with $w_0 = 1$. Size quantization behavior of TiO_2 particles of small size has been confirmed from blue shift in the absorption band edge. We have also used these particles in micro-emulsion along with suitable sensitizer molecules like catechol (Cat) and quinizarin 6-sulfonate (Qz-6S). Optical measurements indicate that catechols interact more strongly with these particles as compared to Qz-6S. We have also sensitized TiO_2 nanoparticles (NP) by Cat and Qz-6S molecules as synthesized by sol–gel process. In the catechol/TiO_2 systems 400 nm excitation of the CT bands promotes an electron from catechol ligand to Ti(IV) centers. Electron injection has been found to be pulse-width limited. In both SNP and NP surfaces, just after injection a major portion of the injected electron recombines with an ultrafast component (300 fs) with multiple slower components. Similarly sensitization of SNP and NP has also been carried out using Qz-6S, which is a relatively weaker coupling adsorbate as compared to catechol. However, in Qz-6S/TiO_2 systems, electron injection also was found to be pulse-width limited. Charge recombination dynamics was found to be very similar on both the particle surfaces for both the dye/nanoparticle pairs. Strong coupling between the dye-nanoparticle systems dominates the charge recombination dynamics in early time scale and found to be similar in different type particles. However the overall recombination reaction is marginally faster on TiO_2 surface in micro-emulsion, which may due to modification of the surface states by AOT molecules.

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