Transient Absorption Spectroscopy of Semiconductor Nanoclusters

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Transient absorption spectroscopy is convenient to probe the photophysical and photochemical effects of semiconductor nanoclusters and heterogeneous charge transfer events at the semiconductor interface. The fast kinetic spectroscopy not only enables the detection of photogenerated transients in the femtosecond to microsecond time domain, but also enables understanding of the photophysical and photochemical properties that are unique to semiconductor nanoclusters. For example, this technique has provided some useful kinetic and mechanistic information of size quantization effects, non-linear optical effects, electro and photochromic effects, photocurrent generation, photocatalysis and charge rectification properties of semiconductor nanoclusters. These properties are controlled by charge separation, charge trapping and heterogeneous charge transfer at the semiconductor interface under UV and visible light irradiation. Some recent developments in this area are presented here.

Key Words: Semiconductor nanoclusters, Photosensitization, Heterogeneous electron transfer, Laser spectroscopy, Solar energy conversion

1. Introduction

There have been a burst of activities in recent years to explore the properties of semiconductor nanoclusters. Semiconductor nanoclusters have been successfully employed in the conversion of light energy^{1,2)} and photocatalytic detoxification of air and water.³⁻⁸⁾ The potential applications of semiconductor nanoclusters in the area of microelectronics, photovoltaics, imaging and display technologies, sensing devices and thin film coatings have promoted a need to understand the fundamental processes that follow the bandgap excitation.

Fast kinetic spectroscopy techniques such as laser flash photolysis have been proved to be useful in understanding the photophysical and photochemical properties of these unique class of materials. One of the early contribution in this area came from the laboratories of Henglein⁹⁾ and Grätzel¹⁰⁾ where the researchers employed colloidal semiconductor suspensions to study the photoinduced electron transfer between TiO₂ nanoclusters and an electron acceptor (*e.g.*, methyl viologen) or an electron donor (*e.g.* halide ions). The reduced methyl viologen was monitored from its absorbance around 600nm. In later years, several researchers have extended this methodology to investigate the mechanistic and kinetic details of the photoprocesses that follow the bandgap excitation. Significant progress is being made towards understanding the transformations of organic and inorganic compounds in semiconductor nanocluster systems. (see recent review articles for further details.)¹¹⁻¹⁵⁾

The photochemical activity of semiconductor nanoclusters is usually seen with direct bandgap excitation or by exciting sensitizing dyes bound to the surface (Fig.1).

In the first case, the bandgap excitation of a semiconductor particle is followed by the charge transfer at the semiconductor/electrolyte interface. However, in the second case, the semiconductor particle quenches the excited state by accepting an electron and then transfers the charge to another substrate or gener-

ates photocurrent. The energy of the conduction and valence bands of the semiconductor and redox potential of the adsorbed molecule control the reaction course of the photochemical reaction. This process which is commonly referred as photosensitization is extensively used in photoelectrochemistry and imaging science.

In earlier reviews^{2,14,15)} we have focused on the aspects of charge separation in semiconductor nanocrystallites. The efficiency of charge separation can be greatly improved by employing surface modifiers, composite systems and sacrificial donors/acceptors. One collective way to utilize these photoinduced charges in semiconductor nanoclusters is to assemble them on a conducting surface in the form of thin films. The photogenerated charges in these semiconductor nanoclusters can then be utilized collectively to generate photocurrent or carry out selective oxidative and reductive processes. The scope of transient absorption spectroscopy for probing the photochemical effects in semiconductor nanoclusters systems will be discussed here by presenting some recent research highlights.

2. Techniques

Time-resolved transient absorption measurements provide useful information on the behavior of short-lived transients such as excited states and radicals and chemical intermediates in photochemical and radiation chemical reactions. This technique which is often referred as a pump-probe method, uses the principle of inducing a chemical process by means of a short lived laser pulse or electron pulse (pulse width of few femtoseconds to nanoseconds).

In a conventional nanosecond flash photolysis (or pulse radiolysis) system a collimated beam of white light derived from a source of xenon lamp. The experiments are performed in a rectangular quartz cell of 2~10mm path length with a right angle or front face configuration between the direction of laser excita-

Fig.1 Photoinduced charge transfer processes in semiconductor nanoclusters. (a) Under bandgap excitation and (b) Sensitized charge injection by exciting adsorbed sensitizer (S). CB and VB refer to conduction and valence bands of the semiconductor and e_t and h_t refer to trapped electrons and holes respectively.

Fig.2 Schematic illustration of (a) conventional and (b) diffuse reflectance laser flash photolysis.

tion and probe light. The changes in the probe light intensity following the laser pulse (electron pulse) excitation is spectrally resolved with the aid of a monochromator and detected with photomultiplier. The photomultiplier output can be digitized with a Tektronix 7912 AD programmable digitizer and analyzed with a microprocessor or computer. For picosecond laser flash photolysis experiments a white continuum picosecond pulse generated by passing the fundamental output (1064nm) through a D₂O/H₂O solution is used as a probe. The output is fed to a spectrograph (HR-320, ISDA Instruments, Inc.) with fiber optic cables and is analyzed with a dual diode array detector (Princeton Instruments, Inc.)

Diffuse reflectance laser flash photolysis has been found to be a convenient technique in obtaining spectroscopic information of the photochemical transients generated in opaque samples in the form of powders and thin films. The reactants (*e.g.*, dyes) are immobilized on oxide powders by adsorption from solution. The dried sample is then transferred to a rectangular quartz cell that is fitted with a vacuum stopcock. The adsorbed oxygen from the sample is removed by degassing the sample for 3-5 hours. As established earlier,¹⁶⁻¹⁸ if the exciting light is totally absorbed by the sample, the intensity of the diffused probe light from the sample can be used to estimate the fractional absorption, A_d of the transient formed at the surface.

$$A_d = \ln(I_a^0/I_t) \quad (1)$$

where I_a^0 and I_t are the incident and unabsorbed fraction respectively of analyzing light intensities at the solid sample. For small fractional absorption, A_d is proportional to the concentration of the transient. This principle has been successfully applied in several recent diffuse reflectance laser flash photolysis measurements to resolve photoprocesses in fs - ms time domain (see for example, references 18-26).

3. Photoinduced charge separation and charge trapping effects

3.1 Trapping of charge carriers

Photoinduced charge separation in semiconductor colloids or nanoparticles is followed quickly by charge recombination and/or charge trapping at the defects (reaction 1).^{27,28}

The bench-top chemical approach employed for the synthesis of semiconductor colloids results in a high density of defect sites, usually at the semiconductor surface. The nature of these defect sites depends strongly on the experimental conditions of chemical synthesis and controls the charge trapping and recombination of photogenerated charge carriers. For example, the lack of direct recombination emission and the observation of strong red emission in CdS colloids show the dominant role of the sulfur vacancies in trapping of photogenerated charge carriers.²⁹ Trapped charge carriers, if not scavenged quickly with a suitable redox couple, can cause irreversible chemical changes at the semiconductor surface.

The trapping processes are usually fast and completed within few picoseconds. An example of electron trapping in TiO₂ nanoclusters is shown in Fig.3. Pico and femtosecond laser flash photolysis is convenient to time-resolve the chemical changes associated with trapping of charge carriers in metal oxides and metal nanoclusters.^{25,30-33} In the case of CdS colloids formation of S_{surf}^- in CdS colloids which occurs with a rate constant of $5 \times 10^8 \text{ s}^{-1}$ has been attributed to hole trapping process.³⁰ Such an accumulation of charges in the minute reaction space of a semiconductor colloid is important for improving the efficiency of interfacial redox reactions.

3.2 Non-linear optical properties

Recently, small semiconductor particles as materials for generating nonlinear optical effects have drawn the attention of many researchers.³⁴⁻³⁷ Wang and his coworkers have extensively investigated the third order optical nonlinearity in quantum confined CdS clusters.^{34,35} Photoinduced blue shifts in the absorption have also been reported for the colloids of CdS,³⁸⁻⁴⁹ Cd₃P₂,⁴⁴ In₂S₃,⁵⁰ PbS,⁵¹⁻⁵⁴ CdSe,⁵⁵⁻⁵⁷ In₂Se₃,⁵⁸ FeS₂,⁴³ TiO₂,⁵⁹ and ZnO.⁶⁰⁻⁶² Such photoinduced blue-shifts appear as a bleaching in the transient absorption spectrum.

Transient absorption spectroscopy has been employed to probe the transient bleaching in CdS^{46,47,63} and GaAs⁶⁴ colloids. Figure 4 shows the change in the absorbance as a function of wavelength at various times following a 355nm laser pulse excitation of CdS colloids in acetonitrile. The transient absorption spectra exhibit strong bleaching at wavelengths below 500nm. The bleaching appears within the laser pulse duration of 18ps and

Fig.3 Transient absorption spectra recorded following 266nm laser pulse excitation of colloidal TiO₂ show absorption in the IR as a result of electron trapping.

Fig.4 Transient photobleaching in CdS colloids. Normalized spectra recorded immediately after 355nm laser pulse (532nm) excitation. A dependence of bleaching maximum can be noted on the laser excitation intensity.⁴⁵⁾

exhibits multiexponential decay with time constants ranging into the nanosecond regime. Subpicosecond events in colloidal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ have been characterized by Ernsting *et al.*⁶³⁾ In the case of CdS/HgS/CdS colloids with a quantum dot-quantum well structure the transient photobleaching follows spectrally the newly evolving 1s-1s electronic transition of the composite particles.⁶⁵⁾

The origin of this photoinduced blue shift has been attributed to different mechanisms which included (1) band filling due to excess conduction band electrons or dynamic Burstein-Moss effect,^{66,67)} (2) a decrease in the oscillator strength of the excitonic transitions due to trapped electrons and holes,^{46,47)} (3) increase in excitonic energy due to surface-trapped electrons,^{40,41)} and (4) Coulombic screening by photogenerated free carriers.⁶⁸⁾

3.3 Photocatalytic reduction and oxidation with photoexcited semiconductor particles

Semiconductor nanoparticles have been beneficially used to carry out photocatalytic redox processes. (See for example⁶⁹⁻⁷³⁾) Both static and dynamic processes have been observed in charge transfer at the semiconductor-electrolyte interface. The static process is dominant when the acceptor molecules are adsorbed on the surface and competes directly with the charge recombination process.⁷⁴⁾ The rate constant for the interfacial electron transfer in this case is greater than $5 \times 10^{10} \text{ s}^{-1}$. However, dynamic electron transfer can also be observed when the electron trapping occurs with a high efficiency. For example heterogeneous rate constants of the order of $10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$ have been observed in the reduction of oxazine dyes in WO_3 colloidal suspensions.⁷⁵⁾

An example of one-electron reduction of fullerenes (C_{60} and C_{70}) in colloidal TiO_2 suspension is shown in Fig.5. The reduction proceeds as C_{60} reacts with photogenerated electrons at the semiconductor interface (reactions 1 and 2).^{76,77)}

The transient absorption spectrum of $\text{C}_{60}^{\cdot -}$ formed as a result of direct reduction of fullerene at the excited TiO_2 surface is shown in Fig.5 (spectrum b).

Similarly, one-electron reduction of organic dyes such as thiazine, oxazine, phenazine, squaraine and methyl orange dyes can be carried out in various colloidal semiconductors.¹⁵⁾ The values of quantum yield of reduction vary from 0.01 to 1.0. The quantum yield of reduction is dependent on both the association

Fig.5 Photocatalytic reduction of C_{60} in colloidal TiO_2 suspension with 308nm laser pulse excitation. The spectrum recorded at early times represents triplet excited C_{60} and the spectrum recorded at longer time corresponds to C_{60} anion radical. (From reference 77))

constant and the energetics of the conduction band and the redox couple. The energy difference between the two acts as a driving force for heterogeneous electron transfer at the semiconductor colloid.

Photogenerated holes can also be simultaneously utilized to oxidize substrates at the semiconductor surface.^{14,78,79)} The holes trapped at the TiO_2 surface can survive for a duration of microseconds to milliseconds and can react with OH^- to generate $\cdot\text{OH}$ radicals in aqueous medium. These $\cdot\text{OH}$ radicals can further induce secondary oxidation. Oxidation of halide ions (X^-) has been investigated in various colloidal semiconductor suspensions by laser flash photolysis.^{80,81)}

The transient product formed in this heterogeneous process can easily be followed from the characteristic absorption in the 300-400nm region. The efficiency of halide oxidation at TiO_2 follows the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$, correlating with the decrease in the oxidation potential. Scavenging of holes by alcohol or SCN^- had a marked effect on the reduction of tetranitromethane⁸²⁾ and oxazine dyes⁸³⁾ at the TiO_2 particle. Simultaneous capture of holes and electrons at the TiO_2 surface with suitable scavengers enhanced the efficiency of interfacial charge transfer by a factor of two.

By decreasing the particle size, it is possible to shift the conduction band to more negative potentials and the valence band to more positive potentials as a result of quantization effects.⁵¹⁾ Because of the increase in the effective bandgap, the band edges of the quantized semiconductor particle attain new positions relative to the band edges of the bulk material. Hence, redox processes that cannot occur in bulk materials can be energetically favored in quantized small particles as the conduction and the valence bands become stronger reductant and oxidants respectively.

3.4 Photocatalytic applications

In aqueous solutions the holes are scavenged by surface hydroxyl groups to generate $\cdot\text{OH}$ radicals which then promote the oxidation of organics.⁸⁴⁻⁸⁸⁾ The $\cdot\text{OH}$ radical mediated oxidation has been successfully employed in the treatment of air and water by mineralizing undesirable chemical contaminants. Interestingly, the electron scavenging becomes a rate limiting factor in such oxidation processes.⁸⁹⁻⁹⁵⁾ As described in an earlier section, failure to scavenge electrons with a sacrificial electron acceptor results in the promotion of charge recombination.

Photoassisted catalytic degradation of organic materials such

as hydrocarbons, haloaromatics, phenols, halogenated biphenyls, chlorinated organics, surfactants, and diethylnitrophenyl phosphate in TiO_2 suspensions has been carried out. The reaction mechanism leading to mineralization of aromatic molecules is a multistep process and the pathways are often complex to analyze. Both laser flash photolysis and pulse radiolysis facilitate characterization of transients and reaction intermediates. The kinetic information gathered from these studies are useful in developing photocatalytic models and reactor design. A detailed discussion on this topic is beyond the scope of the present chapter. The readers can refer to recent review articles for the developments in this area.^{3-7,69,96-113)}

4. Charge injection from excited dyes into semiconductor nanoclusters

As indicated in Fig.1 (b), the semiconductor support materials are capable of interacting with the excited state of the adsorbed molecules (referred as sensitizer molecules) and participate in the interfacial charge transfer processes (see for example^{73,114-118)}). Both triplet and singlet excited states of the sensitizer are capable of injecting charges into the conduction band of the semiconductor nanocluster. Dyes such as erythrosin B, eosin, rose bengal, rhodamine B, cresyl violet, thionine, chlorophyllin, anthracene-9-carboxylate, porphyrins, phthalocyanines, carbocyanines, phenylfluorone and Ruthenium (II) polypyridyl complexes, which have high extinction coefficients in the visible, are often employed to extend the photoresponse of the semiconductor in the photoelectrochemical systems.

Fig.6 Charge injection from excited sensitizer into semiconductor nanoclusters. Fast back electron transfer is often a limiting factor in achieving higher photosensitization efficiency in these systems.

A sensitizer adsorbed on a semiconductor surface can undergo heterogeneous electron transfer in addition to the radiative and radiationless deactivation processes. The excited state processes are summarized in reactions (3-5).

Although emission lifetime of the adsorbed sensitizer serves as a good probe to estimate overall decay of the excited state, it cannot distinguish between the charge injection and any other deactivation routes that may not involve electron transfer. On the other hand transient absorption spectroscopy can be directly used to probe the electron transfer product S^{++} or $\text{SC}(e)$ and study the kinetics of heterogeneous electron transfer between the semiconductor and excited sensitizer (reaction 5).

Figure 7 shows two examples of charge injection process. The time-resolved transient absorption spectra shown in Fig.7 (A). represents the formation of a dye cation radical, $(\text{CV})^{3++}$ when cresyl violet aggregates adsorbed on colloidal SnO_2 were excited with 532nm laserpulse. Fig.7 (B) shows diffuse reflectance transient spectrum recorded following the excitation of Ru (II) polypyridyl complex coated on TiO_2 particles. The bleaching in the bleaching suggests the formation of Ru (III) while the absorption at wavelengths greater than 520nm confirms the trapping of electrons in TiO_2 nanoparticles.

The charge injection from singlet excited sensitizer into the conduction band of a large bandgap semiconductor is usually considered to be an ultrafast process occurring in the picosecond time domain. Charge injection process in the case of organic dyes such as anthracene carboxylate,¹²⁰⁾ squaraines¹²¹⁾ and cresyl violet^{122,123)} has been shown to occur in less than 20ps. Similar fast electron transfer has also been noted for $\text{Ru}(\text{H}_2\text{O})_2^{2+}$ on TiO_2 surface at very low coverage.¹²²⁾ Recent femtosecond transient spectroscopy of coumarin and perylene modified TiO_2 systems have confirmed that the sensitized charge injection is completed within few hundred femtoseconds.^{122,123)} On the contrary, relatively smaller charge injection rate constants ($10^8 - 10^9 \text{s}^{-1}$) have been reported by several research groups investigating the photophysical behavior of ruthenium complexes adsorbed on various semiconductor surfaces.^{24,124-129)} It has been

Fig.7 (A) Transient absorption spectra recorded 5ns after 532nm laser pulse excitation of (a) $5\mu\text{M}$ SiO_2 ; (b) $5\mu\text{M}$ SnO_2 ; (c) $13\mu\text{M}$ $(\text{CV}^+)_2$ in $5\mu\text{M}$ SiO_2 ; and (d) $13\mu\text{M}$ $(\text{CV}^+)_2$ in $5\mu\text{M}$ SnO_2 colloidal suspensions. (B) Transient absorption spectrum recorded $45\mu\text{s}$ following 532nm laser pulse excitation of degassed sample of $\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+}$ on TiO_2 . Insert shows the absorption-time profile (650nm) of electrons trapped in TiO_2 nanoparticles. (From references 119) and 24))

suggested that electron trapping at surface defects may be a contributing factor in controlling the heterogeneous electron transfer at the semiconductor surface.¹³⁰⁾ Similarly, the charge injection from the triplet excited dyes into TiO_2 ¹³¹⁾ and ZnO ¹³²⁾ colloids has also been shown to occur on a slower timescale. The results presented here suggest that the electron transfer from the excited $\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+}$ occurs with a relatively slower rate than the singlet excited organic dyes but is comparable to the triplet excited dyes. It should be noted that the excited state of $\text{Ru}(\text{bpy})_2(\text{dcbpy})^{2+}$ involves metal to ligand charge transfer state and implications are that such an electronic configuration of the excited state plays an important role in controlling the electron injection rates. The possibility of a connection between the multiplicity of the excited sensitizer and the rate constant for charge injection deserves more careful study.

5. Spectroelectrochemical measurements

Externally applied electrochemical bias causes electron accumulation in semiconductor nanoclusters^{75,133-138)} and thus can directly influence the charge injection process discussed in the

Fig.8 Spectroelectrochemical cell employed to probe the charge injection process in a dye-modified semiconductor thin film. (From reference 140))

Fig.9 Time-resolved absorption spectra recorded following the laser pulse excitation of Ru (II) polypyridyl complex modified SnO_2 film. The applied potential was held constant at + 0.2V (left) and - 0.7V versus Ag/AgCl during the laser flash photolysis experiment (From reference 140))

previous section. The onset potential at which the electron accumulation is seen corresponds to the flat band potential of the semiconductor. Transient absorption spectroscopy is convenient to monitor the photoinduced charge transfer processes at a dye-modified nanostructured semiconductor film at positive and negative bias potentials.¹³⁹⁻¹⁴¹⁾

Spectroelectrochemical experiments can be carried out in a conventional laser flash photolysis set up by modifying the sample holder to accommodate an electrochemical cell containing OTE/ SnO_2 /Ru (II) (WE), Pt (CE) and Ag/AgCl (RE) electrodes (Fig.8).

The excitation of the Ru (II) modified SnO_2 film was carried out in a front face geometry with a 532nm laser pulse. The transparency of the OTE/ SnO_2 /Ru (II) electrode facilitated direct monitoring of the transient absorbance following laser pulse excitation. The electrode potential was maintained at a desired value during the laser flash photolysis experiment.

Time-resolved transient absorption spectra recorded at + 0.2V and - 0.7V are shown in Fig.9. The spectra recorded at early times exhibit spectral features similar to the spectrum of Ru (II)* observed on SiO_2 surface. However, the applied bias influences the spectral characteristics of transients recorded at longer times. The formation of Ru (III) is evident only with the spectrum recorded with + 0.2V bias. The absence of Ru (III) and the appearance of excited Ru (II) (Abs. Max. at 380nm) as the only observable transient at - 0.7V indicates the failure of Ru (II)* to participate in the charge injection process.

At potentials more negative than the flat band potential of SnO_2 , reaction (5) is suppressed thus extending the lifetime of Ru (II)*. On the other hand, the applied positive bias facilitates electron transfer quenching of Ru(II)* on the SnO_2 surface.

Application of external bias alters the pseudo-Fermi level of the nanocrystalline film. At negative bias the electrons are accumulated within the SnO_2 nanocrystallites thus shifting the pseudo-Fermi level to more negative potentials. Under these conditions the difference in energy (ΔE) between E_F^* and $E_{\text{Ru (II)*/III}}^0$ that acts as a driving force for the heterogeneous electron transfer decreases. These results draw further support to the conclusions that the applied potential directly controls the heterogeneous electron transfer at the semiconductor interface. Tani^{142,143)} who observed a similar dependence for the quenching of cyanine dyes on AgBr crystals has employed Marcus theory¹⁴⁴⁾ to explain the initial steep threshold in the - ΔE region. But the failure to observe the inverted region was attributed to the semi-

conducting nature of the acceptor which is composed of continuously distributed electronic energy levels. Similarly, the inverted region was not observed for the heterogeneous electron transfer between Ru (II)* and SnO₂ nanocrystallites. Although the electron transfer theory¹⁴⁴⁻¹⁴⁷ predicts that electron transfer rates should decrease with increasing thermodynamic driving force this phenomenon has been rarely demonstrated for interfacial or electrochemical processes.¹⁴⁸

5.1 Back electron transfer process

The photoinjected electrons, if not utilized quickly to generate photocurrent, undergo back electron transfer to regenerate the sensitizer (reaction 9).

Although the redox couple such as I³/I⁻ in solution reacts with the oxidized sensitizer, the competing back electron transfer can significantly decrease the efficiency of net electron accumulation within the particles. Therefore the back electron transfer plays a major role in achieving high incident photon-to-photocurrent generation efficiency (IPCE) of photochemical solar cells. For example, the high IPCE observed in the case of ruthenium polypyridyl complex/TiO₂ based photochemical cells has been attributed to the slower back electron transfer process.^{139,149-151} On the other hand, organic sensitizer based photoelectrochemical cells perform very poorly because back electron transfer processes occur at significantly higher rates than the one observed in Ru (II) polypyridyl complex/semiconductor systems. Although the back electron transfer rate for the metal oxide/Ru (II) polypyridyl complex based system is several orders of magnitude smaller than the rate constant for the charge injection process^{139,141,150,151} it can significantly increase with the excitation intensity.¹⁵²

An example of back electron transfer investigation of cresyl violet aggregate and SnO₂ nanocluster system is presented here. The decay of the sensitizer cation radical (as monitored from the transient absorption at 470nm) and the decay of injected electron (as monitored from the microwave absorption) recorded over several decades in time are compared in Figs.10 (A) & (B) respectively. It should be noted that these two sets of experiments were carried out with the same sample of nanocrystalline SnO₂ film capped with cresyl violet aggregates. An effort was also made to keep the excitation intensity relatively constant. The decay of these signal is multiexponential as is evident from the

log-log plot in Figs.10 (A) and (B). The comparable slopes (~0.5) of the linear portion of these plots suggests that both techniques are probing same process, the back electron transfer. The multiexponential behavior of the back electron transfer mainly arises from the presence of an inhomogeneous energy distribution of the trapping/detrapping sites at the semiconductor interface. Since the back electron transfer directly competes with the sensitizer regeneration process it is usually overcome by employing high concentration of redox couple.

Detrapping of electrons from shallow traps is thermodynamically and kinetically favorable and is a rate determining step in the back electron transfer. Hence it plays an important role in controlling the kinetics of back electron transfer. On the other hand the activation energy needed to detrapp electrons from deeper traps is significantly higher, and hence their role in the back electron transfer is considered to be negligible. These effects can be studied by monitoring the dependence of back electron transfer rate on the excitation intensity or altering the surface states that control the trapping sites. The example discussed above shows the usefulness of transient absorption measurements in providing fundamental information of the heterogeneous charge transfer in semiconductor nanocluster systems.

6. Concluding remarks

During the last decade we witnessed a phenomenal growth in the basic research of semiconductor nanoclusters and other nanomaterials. A great number of research laboratories have engaged in the development, characterization and utilization of nanocrystalline semiconductor materials of particle diameter 1~100nm. The use of particulate semiconductor photocatalysis as a method for converting light energy into electricity and destroying many pollutants attracted the attention of both scientific and industrial communities. Transient absorption studies is a useful technique that is useful in elucidating photophysical and photochemical effects of semiconductor nanoclusters. Many issues in the understanding of semiconductor nanocluster properties are still open and need to be actively pursued.

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Fig.10 Log-log plot of (A) transient absorbance decay at 470nm and (B) microwave absorption as a function of time (slope = 0.53 and 0.46 respectively). The absorption-time profiles of OTE/SnO₂/(CV)₂²⁺ film were recorded over several decades in time following 532nm laser pulse excitation. (From reference 152))

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References

- 1) A. Hagfeldt and M. Grätzel: *Chem. Rev.* **95** (1995) 49.
- 2) P. V. Kamat: *Native and Surface Modified Semiconductor Nanoclusters* (Vol.44, ed. P. V. Kamat, John Wiley & Sons, Inc., New York, 1997) pp.273.
- 3) D. F. Ollis: *Environ. Sci. Technol.* **19** (1985) 480.
- 4) M. A. Fox: *Chemtech* **22** (1992) 680.
- 5) N. Serpone, D. Lawless, R. Terzian, C. Minero, and E. Pelizzetti: *Heterogeneous Photocatalysis; Photochemical Conversion of Inorganic Substances in The Environment; Hydrogen Sulfide, Cyanides, and Metals* (ed. N. Serpone, D. Lawless, R. Terzian, C. Minero, and E. Pelizzetti (Kluwer Acad. Publ., Dordrecht, The Netherlands, 1991).
- 6) K. Rajeshwar: *J. Appl. Electrochem.* **25** (1995) 1067.
- 7) U. Stafford, K. A. Gray, and P. V. Kamat: *Heterogeneous Chemistry Reviews* **3** (1996) 77.
- 8) K. Vinodgopal and P. V. Kamat: *CHEMTECH* April (1996) 18.
- 9) A. Henglein and Ber. Bunsenges: *Phys. Chem.* **86** (1982) 241.
- 10) M. Grätzel and A. J. Frank: *J. Phys. Chem.* **86** (1982) 2964.
- 11) P. V. Kamat and D. Meisel: *Semiconductor Nanoclusters-Physical, Chemical and Catalytic Aspects* (Elsevier Science: Amsterdam, 1997).
- 12) A. Henglein: *Chem. Rev.* **89** (1989) 1861.
- 13) A. Henglein and H. Weller: *Photochemical Energy Conversion*, (ed. J.R. Norris, Jr. and D. Meisel, Elsevier, New York, 1989) .
- 14) P. V. Kamat: *Chem. Rev.* **93** (1993) 267.
- 15) P. V. Kamat: *Progr. React. Kinetics* **19** (1994) 277.
- 16) R. W. Kessler, G. Krabichler, S. Uhl, D. Oelkrug, W. P. Hagan, J. Hyslop, and F. Wilkinson: *Optica Acta* **30** (1983) 1099.
- 17) F. Wilkinson: *J. Chem. Soc., Faraday Trans.* **282** (1986) 2073.
- 18) D. Oelkrug, H. Wolfgang, F. Wilkinson, and C. J. Willsher: *J. Chem. Soc., Faraday Trans.* **283** (1987) 2081.
- 19) F. Wilkinson and C. Willsher: *J. Chem. Soc., Chem. Commun.* **3** (1985) .
- 20) P. V. Kamat, K. R. Gopidas, and D. Weir: *Chem. Phys. Lett.* **149** (1988) 491.
- 21) K. R. Gopidas and P. V. Kamat: *J. Phys. Chem.* **93** (1989) 6428.
- 22) M. A. Fox, R. B. Draper, M. Dulay, and K. O'Shea: *Control of Photocatalytic Oxidative Selectivity on Irradiated TiO₂ Powders: A Diffuse Reflectance Kinetic Study* (ed. M. A. Fox, R. B. Draper, M. Dulay, and K. O'Shea, Kluwer Acad. Publ., Dordrecht, The Netherlands, 1991).
- 23) R. B. Draper and M. A. Fox: *J. Phys. Chem.* **94** (1990) 4628.
- 24) K. Vinodgopal, X. Hua, R. L. Dahlgren, A. G. Lappin, L. K. Patterson, and P. V. Kamat: *J. Phys. Chem.* **99** (1995) 10883.
- 25) D. P. J. Colombo and R. M. Bowman: *J. Phys. Chem.* **99** (1995) 11752.
- 26) D. P. J. Colombo and R. M. Bowman: *J. Phys. Chem.* **100** (1996) 18445.
- 27) H. Weller, M. Haase, L. Spanhel, and A. Henglein: *Prog. Colloid Polym. Sci.* **76** (1988) 24.
- 28) A. Henglein Ber. Bunsenges: *Phys. Chem.* **99** (1995) 903.
- 29) J. J. Ramsden, S. E. Webber, and M. Grätzel: *J. Phys. Chem.* **89** (1985) 2740.
- 30) P. V. Kamat, T. W. Ebbesen, N. M. Dimitrijevic, and A. J. Nozik: *Chem. Phys. Lett.* **157** (1989) 384.
- 31) N. Serpone, D. Lawless, R. Khairutdinov, and E. Pelizzetti: *J. Phys. Chem.* **99** (1995) 16655.
- 32) J. E. Evans, K. W. Springer, and J. Z. Zhang: *J. Chem. Phys.* **101** (1994) 6222.
- 33) D. P. J. Colombo, K. A. Rousal, J. Saeh, D. E. Skinner, and R. M. Bowman: *Chem. Phys. Lett.* **232** (1995) 207.
- 34) L.-T. Cheng, N. Herron, and Y. Wang: *J. Appl. Phys.* **66** (1989) 3417.
- 35) Y. Wang, N. Herron, W. Mahler, and A. Suna: *J. Opt. Soc. Am. B* **6** (1989) 808.
- 36) L. Brus: *Appl. Phys.* **A53** (1991) 465.
- 37) O. A. Aktsipetrov, P. V. Elyutin, A. A. Fedyanin, A. A. Nikulin, and A. N. Rubtsov: *Surface Science* **325** (1995) 343.
- 38) W. J. Albery, G. T. Brown, J. R. Darwent, and E. Saivar-Iranizad: *J. Chem. Soc., Faraday Trans.* **1** **81** (1985) 1999.
- 39) J. P. Kuczynski, B. H. Milosavljevic, and J. K. Thomas: *J. Phys. Chem.* **88** (1984) 980.
- 40) A. Henglein, A. Kumar, E. Janata, and H. Weller: *Chem. Phys. Lett.* **132** (1986) 133.
- 41) M. Haase, H. Weller, and A. Henglein: *J. Phys. Chem.* **92** (1988) 4706.
- 42) C. Liu and A. J. Bard: *J. Phys. Chem.* **93** (1989) 3232.
- 43) C. Liu and A. J. Bard: *J. Phys. Chem.* **93** (1989) 7047.
- 44) M. Haase, H. Weller, and A. Henglein: *Ber. Bunsenges. Phys. Chem.* **92** (1988) 1103.
- 45) P. V. Kamat, N. M. Dimitrijevic, and A. J. Nozik: *J. Phys. Chem.* **93** (1989) 2873.
- 46) E. F. Hilinski, P. A. Lucas, and Y. Wang: *J. Chem. Phys.* **89** (1988) 3435.
- 47) Y. Wang, A. Suna, J. McHugh, E. F. Hilinski, P. A. Lucas, and R. D. Johnson: *J. Chem. Phys.* **92** (1990) 6927.
- 48) T. Rajh, O. I. Micic, D. Lawless, and N. Serpone: *J. Phys. Chem.* **96** (1992) 4633.
- 49) A. V. Barzykin and M. A. Fox: *Isr. J. Chem.* **33** (1993) 21.
- 50) P. V. Kamat, N. M. Dimitrijevic, and R. W. Fessenden: *J. Phys. Chem.* **92** (1988) 2324.
- 51) O. I. Micic, M. T. Nenadovic, T. Rajh, N. M. Dimitrijevic, and A. J. Nozik: *Nato Asi Ser., Ser. C* **26** (1986) .
- 52) J. M. Nedeljkovic, M. T. Nenadovic, O. I. Micic, and A. J. Nozik: *J. Phys. Chem.* **90** (1986) 12.
- 53) M. T. Nenadovic, M. I. Comor, V. Vasic, and O. I. Micic: *J. Phys. Chem.* **94** (1990) 6390.
- 54) R. Tassoni and R. R. Schrock: *Chem. Mater.* **6** (1994) 744.
- 55) N. M. Dimitrijevic and P. V. Kamat: *J. Phys. Chem.* **91** (1987) 2096.
- 56) K. R. Gopidas and P. V. Kamat: *Mater. Lett.* **9** (1990) 372.
- 57) N. M. Dimitrijevic: *J. Chem. Soc., Faraday Trans.* **1** **83** (1987) 1193.
- 58) N. M. Dimitrijevic and P. V. Kamat: *Langmuir* **3** (1987) 1004.
- 59) C. Kormann, D. W. Bahnemann, and M. R. Hoffmann: *J. Phys. Chem.* **92** (1988) 5196.
- 60) M. Haase, H. Weller, and A. Henglein: *J. Phys. Chem.* **92** (1988) 482.
- 61) P. V. Kamat and B. Patrick: *J. Phys. Chem.* **96** (1992) 6829.
- 62) G. Redmond, A. O'Keeffe, C. Burgess, C. MacHale, and D. Fitzmaurice: *J. Phys. Chem.* **97** (1993) 11081.
- 63) N. P. Ernsting, M. Kaschke, H. Weller, and L. Katsikas: *J. Opt. Soc. Am. B, Opt. Phys.* **7** (1990) 1630.
- 64) H. Uchida, C. J. Curtis, P. V. Kamat, K. M. Jones, and A. J. Nozik: *J. Phys. Chem.* **96** (1992) 1156.
- 65) A. Eychmueller, T. Vobmeyer, A. Mews, and H. Weller: *J. Lumin.* **58** (1994) 223.
- 66) T. S. Moss: *Proc. Phys. Soc. (London) B* **67** (1954) 775.
- 67) B. E. Burstein: *Phys. Rev.* **93** (1954) 632.
- 68) L. Banyai and S. W. Koch: *Phys. Rev. Lett.* **57** (1986) 2722.
- 69) M. A. Fox and M. T. Dulay: *Chem. Rev.* **93** (1993) 341.
- 70) Y. Li and L. Wang: *Semiconductor-Mediated Photocatalysis for Organic Synthesis* (ed. Y. Li and L. Wang, Elsevier Science, Amsterdam, 1997) pp.391.
- 71) M. Kanemoto, K. Ishihara, Y. Wada, T. Sakata, H. Mori, and S. Yanagida: *Chem. Lett.* **6** (1992) .
- 72) T. Shiragami, S. Fukami, C. Pac, and S. Yanagida: *J. Chem. Soc., Faraday Trans* **89** (1993) 1857.
- 73) K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, and S. Murasawa: *J. Electroanal. Chem.* **396** (1995) 27.
- 74) P. V. Kamat and M. A. Fox: *Primary Photophysical and Photochemical Processes of Dyes in Polymer Solutions and Films* (ed. P. V. Kamat and M. A. Fox, CRC Press, Boca Raton, FL, Vol. II, (1990) p.185.
- 75) I. Bedja, S. Hotchandani, and P. V. Kamat: *J. Phys. Chem.* **97** (1993) 11064.
- 76) P. V. Kamat: *J. Am. Chem. Soc.* **113** (1991) 9705.
- 77) P. V. Kamat, I. Bedja, and S. Hotchandani: *J. Phys. Chem.* **98** (1994) 9137.
- 78) A. Henglein: *J. Phys. Chem.* **97** (1993) 5457.
- 79) M. Grätzel: *Nato: Asi Ser. Ser. C* **174** (1986) 91.

- 80) J. Moser and M. Grätzel *Helv. Chim. Acta* **65** (1982) 1436.
- 81) P. V. Kamat and B. Patrick: *Photochemistry and Photophysics of ZnO Colloids* (Symp. Electron. Ionic Prop. Silver Halides, The Society for Imaging Science and Technology, Springfield, Va, 1991) p.293.
- 82) D. Bahnemann, A. Henglein, J. Lilie, and L. Spanhel: *J. Phys. Chem.* **88** (1984) 709.
- 83) P. V. Kamat: *Langmuir* **1** (1985) 608.
- 84) B. Krautler, C. D. Jaeger, and A. J. Bard: *J. Am. Chem. Soc.* **100** (1978) 4903.
- 85) M. Anpo, T. Shima, and Y. Kubokawa: *Chem. Lett.* (1985) 1799.
- 86) R. F. Howe and M. Grätzel: *J. Phys. Chem.* **89** (1985) 4495.
- 87) O. I. Micic, Y. Zhang, K. R. Cromack, A. D. Trifunac, and M. C. Thurnauer: *J. Phys. Chem.* **97** (1993) 13284.
- 88) O. I. Micic, Y. Zhang, K. R. Cromack, A. D. Trifunac, and M. C. Thurnauer: *J. Phys. Chem.* **97** (1993) 7277.
- 89) H. Gerischer and A. Heller: *J. Phys. Chem.* **95** (1991) 5261.
- 90) C. M. Wang, A. Heller, and H. Gerischer: *J. Am. Chem. Soc.* **114** (1992) 5230.
- 91) H. Gerischer and A. Heller: *J. Electrochem. Soc.* **139** (1992) 113.
- 92) M. W. Peterson, J. A. Turner, and A. J. Nozik: *J. Phys. Chem.* **95** (1991) 221.
- 93) K. Vinodgopal, S. Hotchandani, and P. V. Kamat: *J. Phys. Chem.* **97** (1993) 9040.
- 94) J. M. Kesselman, A. Kumar, and N. S. Lewis: *Fundamental Photoelectrochemistry of TiO₂ and SrTiO₃ Applied to Environmental Problems*, ed. J. M. Kesselman, A. Kumar, and N. S. Lewis (Elsevier Science Publishers B. V, Amsterdam, 1993) p.19.
- 95) J. M. Kesselman, G. A. Shreve, M. R. Hoffmann, and N. S. Lewis: *J. Phys. Chem.* **98** (1994) 13385.
- 96) A. J. Bard: *J. Photochem* **10** (1979) 59.
- 97) M. A. Fox: *Acc. Chem. Res.* **16** (1983) 314.
- 98) P. Pichat: *Nato Asi Ser., Ser. C* **174** (1986) 533.
- 99) R. W. Matthews: *Sol. Energy* **38** (1987) 405.
- 100) N. Serpone and E. Pelizzetti: *Photocatalysis Fundamentals and Applications* (John Wiley and Sons, New York, 1989).
- 101) M. Anpo: *Res. Chem. Intermed.* **11** (1989) 67.
- 102) D. F. Ollis, E. Pelizzetti, and N. Serpone: *Heterogeneous Photocatalysis in The Environment, Application to Water Purification*, ed. D. F. Ollis, E. Pelizzetti, and N. Serpone, (Wiley, New York, 1989) p.603.
- 103) M. Grätzel: *Colloidal Semiconductors*, ed. M. Grätzel (Wiley, New York) 1989.
- 104) P. Pichat: *Photochemical Conversion and Storage of Solar Energy*, ed. E. Pelizzetti and M. Schiavello (Kluwer Acad. Publ., Dordrecht, The Netherlands 1991).
- 105) N. Serpone, D. Lawless, R. Terzian, and D. Meisel: *Redox Mechanisms in Heterogeneous Photocatalysis. The Case of Holes versus OH. Radical Oxidation and Free versus Surface Bound OH. Radical Oxidation Processes*, ed. N. Serpone, D. Lawless, R. Terzian, and D. Meisel, (VCH Publishers, New York, 1992) p.399.
- 106) J. M. Herrmann, C. Guillard, and P. Pichat: *Catal. Today* **17** (1993) 7.
- 107) D. F. Ollis, E. Pelizzetti, and N. Serpone: *Environ. Sci. Technol.* **25** (1991) 1523.
- 108) D. F. Ollis and E. H. Al: *Photocatalytic Purification and Treatment of Water and Air* (Elsevier Science Publishers B. V., Amsterdam, 1993).
- 109) O. Legrini, E. Oliveros, and A. M. Braun: *Chem. Rev.* **93** (1993) 671.
- 110) A. Wold: *Chem. Mater.* **5** (1993) 280.
- 111) D. Bahnemann, J. Cunningham, M. A. Fox, E. Pelizzetti, P. Pichat, and N. Serpone: *Photocatalytic Treatment of Waters*, ed. D. Bahnemann, J. Cunningham, M. A. Fox, E. Pelizzetti, P. Pichat, and N. Serpone (Lewis Publishers, Boca Raton, Florida, 1994) p.261.
- 112) W. A. Zeltner, C. G. Hill, Jr., and M. A. Anderson: *Chem. Tech.* (1994) 21.
- 113) M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann: *Chem. Rev.* **95** (1995) 69.
- 114) H. Gerischer: *Photochem. Photobiol.* **16** (1972) 243.
- 115) H. Meier: *J. Photochem. Photobiol.* **16** (1972) 219.
- 116) M. Grätzel: *Comments Inorg. Chem.* **12** (1991) 93.
- 117) B. A. Parkinson and M. T. Spitler: *Electrochim. Acta* **37** (1992) 943.
- 118) P. V. Kamat: *Chemtech* June (1995) 22.
- 119) D. Liu and P. V. Kamat: *J. Chem. Phys.* **105** (1996) 965.
- 120) P. V. Kamat: *Langmuir* **6** (1990) 512.
- 121) P. V. Kamat, S. Das, K. G. Thomas, and M. V. George: *Chem. Phys. Lett.* **178** (1991) 75.
- 122) R. Eichberger and F. Willig: *Chem. Phys. Lett.* **141** (1990) 159.
- 123) F. Willig, R. Eichberger, N. S. Sundaresan, and B. A. Parkinson: *Am. Chem. Soc.* **112** (1990) 2702.
- 124) I. Bedja, S. Hotchandani, and P. V. Kamat: *J. Phys. Chem.* **98** (1994) 4133.
- 125) W. E. Ford and M. A. J. Rodgers: *J. Phys. Chem.* **98** (1994) 3822.
- 126) H. Takemura, T. Saji, M. Fujihira, S. Aoyagui, K. Hashimoto, and T. Sakata: *Chem. Phys. Lett.* **122** (1985) 496.
- 127) K. Hashimoto, M. Hiramoto, T. Kajiwarra, and T. Sakata: *J. Phys. Chem.* **92** (1988) 4636.
- 128) K. Hashimoto, M. Hiramoto, A. B. P. Lever, and T. Sakata: *J. Phys. Chem.* **92** (1988) 1016.
- 129) K. Hashimoto, M. Hiramoto, T. Sakata, H. Muraki, H. Takemura, and M. Fujihira: *J. Phys. Chem.* **91** (1987) 6198.
- 130) K. Schwarzburg and F. Willig: *Appl. Phys. Lett.* **58** (1991) 2520.
- 131) M. A. Ryan, E. C. Fitzgerald, and M. T. Spitler: *J. Phys. Chem.* **93** (1989) 6150.
- 132) B. Patrick and P. V. Kamat: *J. Phys. Chem.* **96** (1992) 1423.
- 133) B. O'Regan, M. Grätzel, and D. Fitzmaurice: *Chem. Phys. Lett.* **183** (1991) 89.
- 134) B. O'Regan, M. Grätzel, and D. Fitzmaurice: *J. Phys. Chem.* **95** (1991) 10525.
- 135) G. Redmond, D. Fitzmaurice, and M. Grätzel: *J. Phys. Chem.* **97** (1993) 6951.
- 136) G. Redmond and D. Fitzmaurice: *J. Phys. Chem.* **97** (1993) 1426.
- 137) S. Hotchandani, I. Bedja, R. W. Fessenden, and P. V. Kamat: *Langmuir* **10** (1994) 17.
- 138) A. Hagfeldt, N. Vlachopoulos, and M. Grätzel: *J. Electrochem. Soc.* **141** (1994) L82.
- 139) B. O'Regan, J. Moser, M. Anderson, and M. Grätzel: *J. Phys. Chem.* **94** (1990) 8720.
- 140) I. Bedja, S. Hotchandani, and P. V. Kamat: *J. Electroanal. Chem.* **401** (1996) 237.
- 141) S. G. Yan and J. T. Hupp: *J. Phys. Chem.* **100** (1996) 6867.
- 142) T. Tani, T. Suzumoto, and K. Ohzeki: *J. Phys. Chem.* **94** (1990) 1298.
- 143) T. Tani: *J. Imag. Sci.* **34** (1990) 143.
- 144) R. A. Marcus: *J. Chem. Phys.* **43** (1993) 679.
- 145) Marcus: *J. Phys. Chem.* **94** (1990) 1050.
- 146) J. J. Jortner: *J. Chem. Phys.* **64** (1976).
- 147) B. S. Brunswig and N. Sutin: *Comments Inorg. Chem.* **6** (1987) 209.
- 148) H. Lu, J. N. Prieskorn, and J. T. Hupp: *J. Am. Chem. Soc.* **115** (1993) 4927.
- 149) B. O'Regan and M. Grätzel: *Nature (London)* **353** (1991) 737.
- 150) M. K. Nazeeruddin, A. Kay, I. Rodicio, B. R. Humphry, E. Mueller, P. Liska, N. Vlachopoulos, and M. Grätzel: *J. Am. Chem. Soc.* **115** (1993) 6382.
- 151) P. V. Kamat, I. Bedja, S. Hotchandani, and L. K. Patterson: *J. Phys. Chem.* **100** (1996) 4900.
- 152) D. Liu, R. W. Fessenden, G. L. Hug, and P. V. Kamat: *J. Phys. Chem. B* **101** (1997) 2583.