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PICOSECOND CHARGE TRANSFER PROCESSES IN ULTRASMALL CdS AND CdSe SEMICONDUCTOR PARTICLES

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Abstract The kinetic and mechanistic details of the chemical events associated with charge trapping and the interfacial charge transfer processes in colloidal CdS and CdSe systems are elucidated with picosecond transient absorption spectroscopy.

INTRODUCTION

Characterization of ultrafast electronic processes that follow the bandgap excitation of a semiconductor is important for understanding the primary photophysical and photochemical processes. Elucidation of interfacial charge-transfer processes in the sub-nanosecond time domain can yield valuable information on the kinetics of electron and hole transfer and the factors that control the charge transfer efficiency.[1-3] The use of semiconductor materials in a colloidal state facilitates the direct detection of photochemical reaction intermediates with transient absorption spectroscopy because of the transparency of colloidal systems.

Recently, photoinduced blue-shifts in the absorption spectra of metal chalcogenide semiconductor particles in Nafion films[4] and in nonaqueous medium[5,6] have been time resolved in the ps-ns time domain. Picosecond laser flash photolysis experiments that describe the kinetics of primary photochemical events in the colloidal CdS and CdSe semiconductor particles are presented here.

EXPERIMENTAL

The colloidal suspension of CdS and CdSe were prepared by exposing 0.2 mM $Cd(ClO_4)_2$ in acetonitrile to H_2S and H_2Se respectively. The reaction was carried out in the presence of 0.02% Nafion (Aldrich) at -30 °C. The colloidal particles were 40-100 Å in diameter.

The excitation source was a mode-locked 355 nm laser pulse from

Quantel YG-501DP Nd:YAG laser system (output 4 mJ/pulse, pulse width ≈ 18 ps). The white continuum picosecond probe pulse was generated by passing the residual fundamental output through a D_2O/H_2O solution. The delay in the probe pulse was introduced by varying the length of the fiber optic cable. The details of detection, operation and analysis have been reported earlier.[7] The time, $\Delta t = 0$ ps, corresponds to the time at the end of the excitation pulse. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Absorption Characteristics

The absorption spectra of the CdS and CdSe colloids prepared in acetonitrile are shown in Figure 1. Colloidal CdS exhibits an onset of absorption below 500 nm corresponding to a bandgap around 2.0 eV. Colloidal CdSe exhibits absorption below 600 nm which corresponds to a bandgap around 1.7 eV. Transmission electron microscopy of these particles suggested their diameters to be in the range of 40-100 Å. With decreasing particle size a blue shift in the absorption edge has been noted as a result of size quantization effects. The broad red emission (> 500 nm) of these particles is attributed to the sulfur (or selenide) vacancies at the semiconductor surface.

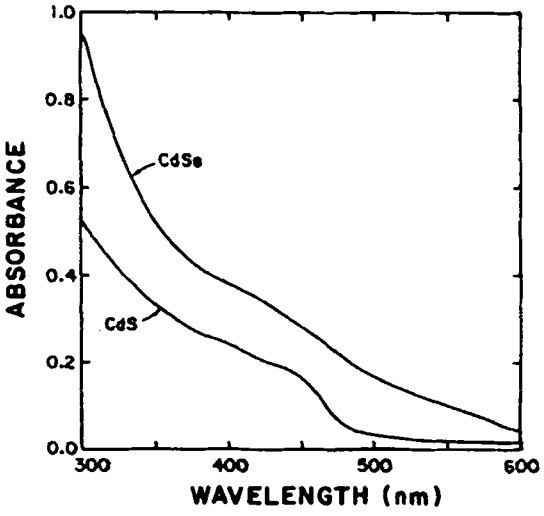

FIGURE 1 The absorption spectra of CdS and CdSe colloids in acetonitrile.

Picosecond Transient Absorption Studies

Time-resolved transient absorption measurements have been carried out by us and others to characterize the charge trapping process and investigate the reactivity of photogenerated charge carriers in colloidal CdS.[7-10] The transient absorption spectra of CdSe colloids recorded at time intervals 100 ps, 500 ps, and 1 ns following the 355 nm laser pulse excitation are shown in Figure 2. Two distinct features were observed in these spectra. i) The transient bleaching at wavelengths below 440 nm and ii) A growth in the absorption at wavelengths greater than 450 nm.

The transient bleaching which arises as a result of a photo-induced blue-shift in the absorption edge of the semiconductor, has been attributed to the dynamic Burstein-Moss effect.[5] For smaller size semiconductor particles a decrease in the oscillator strength of the excitonic transition is expected to shift the absorption edge of the semiconductor.[4] The kinetics of the recovery of transient bleaching showed a multiexponential behavior with time constants ranging into the nanosecond time regime.

The growth in the absorption at wavelengths greater than 450 nm (spectra a in Figure 2) is due to the formation of $Se^{\bullet -}$ at the surface.[11] The photogenerated holes which are trapped at the surface undergo chemical changes to yield Se^{-}_{surf}.

$$CdSe \xrightarrow{h\nu} CdSe\ (h^{+}...e^{-}) \longrightarrow CdSe\ (h_t^{+} + e_t^{-}) \qquad (1)$$

$$(CdSe)_n + h_t^{+} \longrightarrow [(CdSe)_{n-1}\ Cd^{2+}Se_{surf}] \qquad (2)$$

The estimation of the reaction rate of trapped holes in generating Se^{-}_{surf} was made by fitting the growth in the absorption at 470 nm to a first-order kinetics. The rate constant for the Se^{-}_{surf} formation was $1.1 \times 10^{9}\ s^{-1}$.

The assignment of broad absorption in the visible to Se^{-}_{surf} was further confirmed by the laser pulse excitation of CdSe colloids in the presence of a hole scavenger such as triethanolamine. The transient absorption spectra of colloidal CdSe in a triethanolamine solution are shown in figure 2 (spectra b). The formation of Se^{-}_{surf} was greatly suppressed as the triethanolamine scavenged the trapped

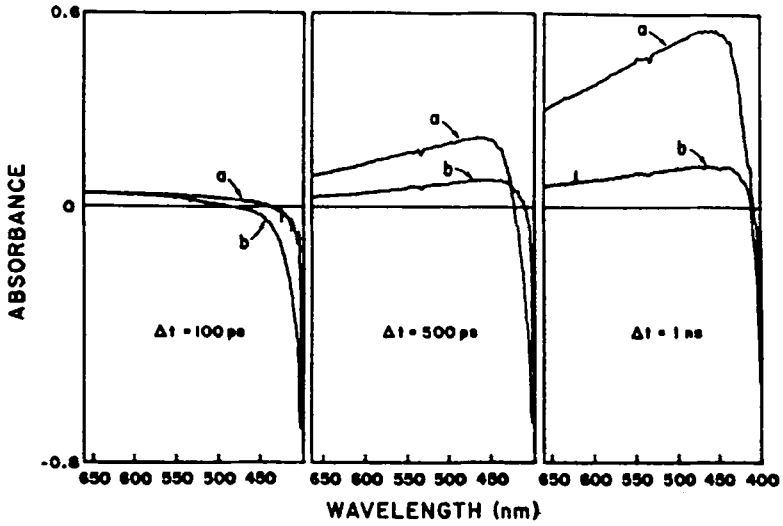

FIGURE 2 Transient absorption spectra recorded after the 355 nm laser pulse excitation of 0.2 mM colloidal CdSe in acetonitrile: (a) no scavengers; (b) in presence of 0.15 M triethanolamine.

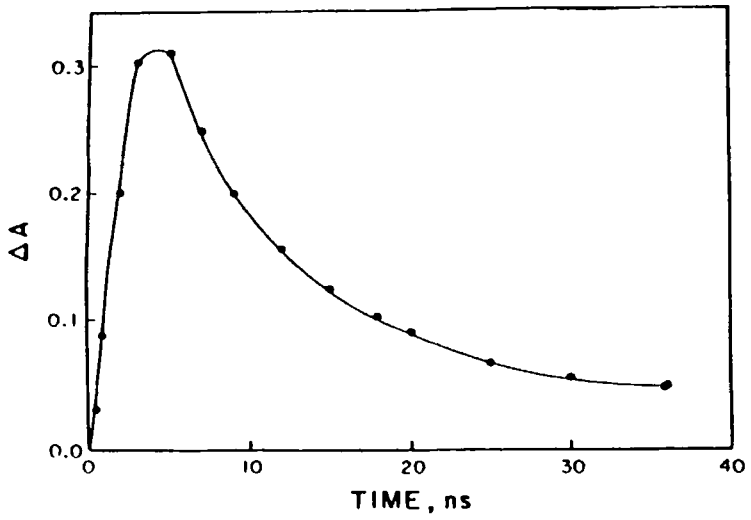

FIGURE 3 Formation and decay of S^-_{surf} in 0.2 mM colloidal CdS in acetonitrile. The absorption maximum was monitored at Δt = 5 ns following the 355 nm laser pulse excitation.

holes. The importance of hole scavenging process in preventing anodic corrosion of metal chalcogenides has been highlighted in our earlier studies.[10,11]

The trapped holes in CdS colloids undergo similar chemical changes at the semiconductor surface to generate S^-_{surf}. Figure 3 shows the formation and decay of S^-_{surf} in CdS. The rate constant for the S^-_{surf} formation in CdS colloids was found to be 5×10^8 s^{-1}. At longer timescales S^-_{surf} decayed ($k = 1 \times 10^7$ s^{-1}) as a result of its reaction with trapped electrons (reaction 3).

$$[(CdS)_{n-1}\ Cd^{2+}\ S^-] + e_t^- \longrightarrow (CdS)_n \qquad (3)$$

In a similar way, Se^-_{surf} decayed with a rate constant of 5×10^7 s^{-1} in acetonitrile solutions. The variations in the nature of traps and trap depths could influence the kinetics of recombination. Only a small fraction (<10%) which failed to participate in the regeneration process led to the anodic corrosion of the semiconductor. The longer life of trapped charge carriers has also been independently confirmed from the emission lifetime measurements.[12]

The trapped electrons also undergo chemical changes at the semiconductor surface by reacting with Cd^{2+} sites. The chemical changes associated with this process cannot be detected from the absorption in the visible region. However, the formation of Cd^0 has been indirectly confirmed in the steady state photolysis of CdS.[13]

Interfacial Charge Transfer in Colloidal CdS System

In our earlier study[12] we have demonstrated that diethyldithiocarbamate ($NCEt_2S_2^-$) strongly complexes with CdS colloids and reacts with the photogenerated holes to form the radical $NCEt_2S_2^{\bullet}$. This radical can be easily monitored with transient absorption spectrophotometry as it exhibits absorption in the visible (λ_{max} = 580 nm, ϵ = 1800 M^{-1} cm^{-1}).[12] We have now used this oxidation process to time resolve the reaction of photogenerated holes. Figure 4 shows time-resolved transient absorption spectra of $NCEt_2S_2^{\bullet}$ formation in colloidal CdS suspension. The major fraction of $NCEt_2S_2^{\bullet}$ is formed within the laser pulse duration of 18 ps. This ultrafast process is attributed to the reaction of $NCEt_2S_2^-$ with the valence band holes.

The second component of $NCEt_2S_2^{\cdot}$ formation which is completed within 250 ps is attributed to the oxidation of $NCEt_2S_2^{-}$ by trapped holes. These two processes can be described by the reactions (4) and (5).

$$(h^+_{VB}) + NCEt_2S_2^{-} \longrightarrow NCEt_2S_2^{\cdot} \quad (k > 5 \times 10^{10}\ s^{-1}) \qquad (4)$$

$$(h_t^+) + NCEt_2S_2^{-} \longrightarrow NCEt_2S_2^{\cdot} \quad (k \approx 10^{10}\ s^{-1}) \qquad (5)$$

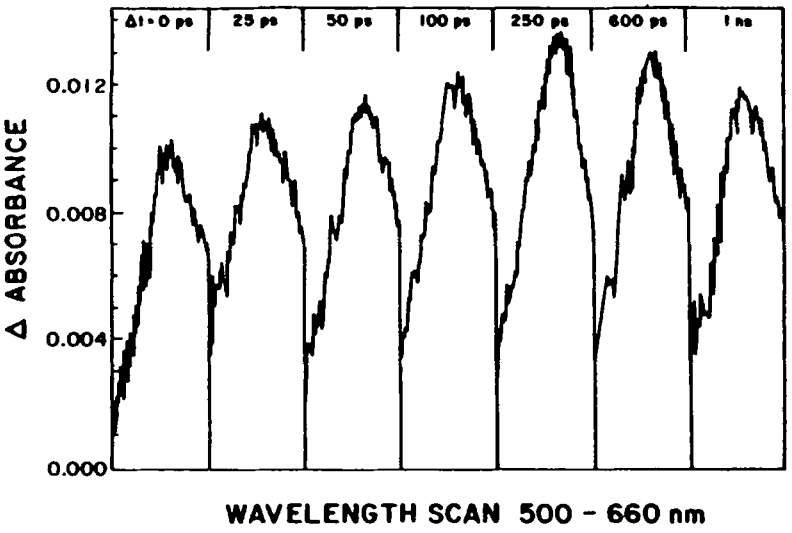

FIGURE 4 Formation of $NCEt_2S_2^{\cdot}$ in colloidal CdS suspension. The transient spectra were recorded at different time intervals following the 355 nm laser pulse excitation of 0.2 mM colloidal CdS in acetonitrile containing 2.5 mM $NCEt_2S_2^{-}$.

Time resolution of these two processes can give a kinetic estimate for the reactivity of holes from the valence band and trapped sites. The rate constants for reactions (4) and (5) were estimated to be $> 5 \times 10^{10}\ s^{-1}$ and $\sim 10^{10}\ s^{-1}$ respectively. Only a small fraction (~ 15%) of $NCEt_2S_2^{\cdot}$ decayed during the time period of 1 ns, probably by reacting with trapped electrons. The maximum quantum yield for the production of $NCEt_2S_2^{\cdot}$ was 0.28. This shows that majority of the photogenerated holes are not accessible for the charge transfer at

the semiconductor surface. Efforts are currently being made to employ surface modifiers to enhance the efficiency of charge transfer process.

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