

Femtosecond investigation of charge carrier dynamics in CdSe nanocluster films

Xicheng Ai, Rong Jin, Changbao Ge, Jingjing Wang, Yinghua Zou, Xiaowen Zhou, and Xurui Xiao

Citation: *The Journal of Chemical Physics* **106**, 3387 (1997); doi: 10.1063/1.473087

View online: <http://dx.doi.org/10.1063/1.473087>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/106/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Charge carrier transport in thin films of colloidal CdSe quantum rods](#)

J. Appl. Phys. **104**, 074306 (2008); 10.1063/1.2988136

[Auger recombination and intraband absorption of two-photon-excited carriers in colloidal CdSe quantum dots](#)

Appl. Phys. Lett. **90**, 133112 (2007); 10.1063/1.2716067

[Radiative recombination of charged excitons and multiexcitons in CdSe quantum dots](#)

Appl. Phys. Lett. **87**, 263115 (2005); 10.1063/1.2150583

[Direct carrier multiplication due to inverse Auger scattering in CdSe quantum dots](#)

Appl. Phys. Lett. **84**, 2409 (2004); 10.1063/1.1690104

[Dominant role of surface states in photoexcited carrier dynamics in CdSe nanocrystalline films prepared by chemical deposition](#)

Appl. Phys. Lett. **77**, 2352 (2000); 10.1063/1.1317536



Femtosecond investigation of charge carrier dynamics in CdSe nanocluster films

Xicheng Ai, Rong Jin, Changbao Ge, Jingjing Wang, and Yinghua Zou

Department of Physics, Mesoscopic Physics Laboratory (MPL), Peking University, Beijing, 100871, People's Republic of China

Xiaowen Zhou and Xurui Xiao

Institute of Photographic Chemistry, Academia Sinica, Beijing, 100101, People's Republic of China

(Received 10 October 1996; accepted 20 November 1996)

The charge carrier dynamics in the novel CdSe nanocluster films fabricated by a chemical deposition method was studied by the femtosecond pump-probe measurements. The intensity dependent signals can be well described by a rate equation model. The overall kinetic process is listed as follows: a rapid electron trapping (< 1 ps), the Auger recombination, the recombination of electrons in the surface states (~ 46 ps) and the long-lived trapped electron-hole recombination. When the cluster radius is as large as 27 nm, an induced transient absorption can be observed. We attribute the induced transient absorption to the formation of the biexcitons or the trapped-carrier-induced Stark effect. © 1997 American Institute of Physics. [S0021-9606(97)02008-4]

I. INTRODUCTION

Semiconductor nanostructures which are small, at least in one dimension, compared to the bulk exciton Bohr radius exhibit electron and hole confinement.¹ The confined exciton has a larger binding energy than in bulk resulting in distinct excitonic absorption resonances that shift to higher energy with small particle size. In principle, nanostructures should have enhanced nonlinear optical properties which can be applied to the design of fast optoelectronic and photonic devices.

Quantum wells and quantum wires are usually fabricated by highly sophisticated growth techniques like molecular beam epitaxy and quantum dots can be grown in relatively easy ways. These methods have been known for a long time and have been considerably improved in recent years. Now glasses and polymers doped with semiconductor clusters and semiconductor nanocluster colloids represent a new class of materials of quantum dots. In these materials the presence of the crystallite surface as a boundary and source of the surface state makes them fundamentally different in principle from epitaxial low-dimensional structures. These nanoclusters offer the largest surface area-to-volume ratio, making them suited to different applications including, for example, solar energy conversion and photocatalysis. In particular, the charge carrier dynamics in these materials are of physical and technological interest and have been studied quite extensively. It was found that the bound-edge emission is not from the excited state but from a state where carriers are trapped or localized on the surface, and the localized surface states are almost isoenergetic with the near-band-gap states.²⁻⁴ Zhang^{5,6} found that the decay dynamics were sensitive to the solvent environment in experiments of aqueous CdS colloids, which implies that the observed transient absorption should be attributed to electrons trapped at the liquid-solid interface. In all of these studies it was concluded that the majority of the trapping occurred at or near the surface and a

fraction of the trapped electrons underwent rapid recombination. Knowledge of surface carrier trapping and relaxation processes will help one to understand the possible nature of the nanocluster surface. Unfortunately, the mechanisms for surface trapping and subsequently recombination processes are not well understood now.⁶

In previous studies, the ultrafast trapping was measured either by time-correlated single-photon counting or a streak camera to determine the rising time of the particle luminescence⁷ or pump at higher energies and probe the rising time of the transient absorption at the surface states.⁸ The trapped electrons are responsible for the bleach and induced absorption features observed in the pump-probe experiments. It has been found that carriers are trapped at the surface in different semiconductor nanoclusters with trapping times varying from 100 fs to 30 ps.^{2,5,7,9-11} The measurements were contrary to general expectations, since in the quantum-mechanical confined clusters the wave function should extend to the surface region or, according to the classical diffusional trapping, the electrons generated inside the clusters should migrate to the surface within a very short time.

The ultrafast transient optical response of CdSe nanoclusters, principally in solutions, silicate glasses and polymer films, has been studied previously using a variety of techniques.^{2,8,12} At low intensity a two-component decay was observed, a fast decay in 50 ps was attributed to the recombination through surface states and the slow component with a time constant longer than 500 ps was attributed to the recombination of the deep trapped carriers.⁸ At high intensity a nonexponential and intensity dependent decay appeared which was confirmed to be an Auger recombination.¹³

In this paper, a novel CdSe nanocluster film was prepared by chemical deposition method. Compared with others, there are two advantages of our new material. First, high particle concentrations can be reached in very thin films,

because the nanoclusters are interconnected with each other in the films, and remain unchanged for about one year. This is important in practical applications. Second, the relaxation process of a pure nanocluster can be studied safely—the solvent or surrounding medium effect can be neglected. A femtosecond pump–probe technique was used in the transient absorption study with the same wavelength of the pump and probe beams. The intensity dependence of the ultrafast relaxation processes was observed for the first time in such a material. A rate equation model was proposed which can be used to explain the experimental observations.

To our knowledge, no transient transmission experiments have been performed on CdSe nanocluster films on a femtosecond time scale. In the work presented here we attempted to resolve the assignment of transient signals in CdSe nanocluster films without the influence of the ejected electrons, as observed by others.^{9,14,15} Without electrons being ejected into solutions, we can safely assign the kinetics to electrons and holes in the nanocluster.

II. EXPERIMENTS

The CdSe nanocluster films used in our experiments were prepared by a chemical deposition method¹⁶ which is similar to that reported by Hodes:¹⁷ 0.5 M CdSO₄, 0.7 M sodium nitrilotriacetate [N(CH₂COONa)₃ (NTA)] and 0.2 M sodium selenosulfate (Na₂SeSO₃) (prepared by dissolving 0.2 M Se in 0.5 M Na₂SO₃ solutions) were made up as stock solutions. The deposition solution composed of equivalent CdSO₄ and Na₂SeSO₃ solutions and NTA was used. The glass substrates were cleaned and immersed in the deposition solutions at different temperatures. By changing the deposition temperature and the post-annealing condition, CdSe nanoclusters with different size can be obtained. Samples a, b, and c were prepared at the deposition temperatures of 0, 12, 58 °C, respectively. Sample d was deposited at room temperature and subsequently annealed at 500 °C for 15 min. All nanocluster films were characterized by the transmission electron microscope (TEM) image and x-ray diffraction. From the TEM image the average radii of CdSe nanoclusters were determined to be 3.2 nm for sample a, 4.1 nm for sample b, 6.5 nm for sample c, and 27 nm for sample d. In the x-ray diffraction patterns two diffraction peaks at 42°(2θ) and 50°(2θ) corresponded to the cubic crystallite of CdSe nanoclusters. The diffraction peaks were broadened, especially for the smaller nanoclusters. The half-width of the peaks was inversely proportional to the cluster size. The films were about 1 μm thick.

A pump–probe method was used to detect the ultrafast response of the sample. The pulses were generated from a femtosecond dye laser (Coherent Satori model 774) synchronously pumped by a cw mode-locked Nd:YAG laser (Coherent Antares 76-S) operating at 76 MHz. The wavelength of the dye laser was 647 nm. The pump and probe pulses were split from the dye laser output ($I_{\text{pump}}:I_{\text{probe}}=10:1$) and polarized perpendicularly to each other to avoid coherent effects from the pump and probe beams. The pump beam was chopped at 2770 Hz and the probe beam went through a

motorized delay line controlled by a computer. The two beams were then focused tightly on the same spot on the sample with a spot size of about 20 μm by a lens of focal length 10 cm. The full width at half-maximum (FWHM) of the pulses was about 165 fs which was deduced from a pump–probe autocorrelation curve measured by the second-harmonic generation in KDP at the sample position. The transmitted probe beam was sent through a polarizer to filter out the scattering light of the pump beam and then was detected by a photodiode connected to channel A of the lock-in amplifier. In order to improve the final signal-to-noise ratio, a reference beam was split from the pump beam before chopping and detected by another photodiode connected to channel B of the lock-in amplifier. By adjusting the intensity of the reference beam we can record the signals with better signal-to-noise ratios. Finally the signals were collected and stored in the computer equipped with an A/D card.

III. DECAY KINETICS: MODELING

In our pump–probe experiments the probe beam is in the same wavelength as the pump beam. Usually, in a semiconductor the free charge carriers excited by the pump pulse are responsible for the transient transmission signals. The phase-space filling and the Coulomb interaction between the electron–hole pairs are the dominant mechanisms for bleaching. In contrast, in semiconductor nanoclusters, it is generally believed that the carriers are trapped very rapidly at the surface. The contribution of free carriers and excitons to the transient transmission signals can exist only in the initial subpicosecond time domain. Thereafter the trapped carriers at the surface state result in the observed signals.

As pointed out in many articles,^{10,14,18} the evolution of the surface trapped electrons involves several important processes: (i) Auger process.¹³ The Auger process involves three-body collisions (two electrons and one hole or two holes and one electron). When an electron recombines with a hole, the energy released is immediately absorbed by another electron (or a hole). The high energetic electron (or hole) can dissipate its excess energy in many ways including through phonon emission, electron ejection or diffusion to some long-lived trap sites which have a substantial barrier. (ii) Trapped electron–hole recombination, including geminate and non-geminate ones.^{5,6} (iii) Diffusion from the near band surface state (shallow trap states) to the deep trap states.^{7,11} All the processes can contribute to the relaxation.

The transient transmission signal in a CdSe nanocluster is composed of four parts, three intensity independent components (<1 ps, ~46 ps and a much longer time constant) and one intensity dependent component. We attribute the very early decay (<1 ps) to the ultrafast surface trapping. As for the intensity dependent component, we found that our experimental data can be treated very well if we use third-order kinetics to fit this part. So we attribute it to the Auger process. At last, we found two relatively slow parts coming from the recovery of shallowly trapped electrons and deep trapped carriers respectively. We can describe the whole process with the following equation group:

$$\frac{dn_i}{dt} = -\frac{n_i}{\tau_i}, \quad (1)$$

$$\frac{dn_s}{dt} = b\frac{n_i}{\tau_i} - cn_s^3 - \frac{n_s}{\tau_s}, \quad (2)$$

where n_i refers to the electron density in the initial exciting states, n_s refers to the population of the surface states which shallowly trap electrons. Bawendi *et al.*² have confirmed that luminescence from the band edge was from the surface trapped states, and it is generally believed that electron–holes are trapped very rapidly at the surface in semiconductor nanoclusters.¹¹ Thus the radiative decay from the excited electron–hole state to the ground state due to the ultrafast surface trapping rate is reasonably neglected. The parameters, $1/\tau_i$, $1/\tau_s$, c refer to the rate of electron trapping due to surface states or defect sites, the recombination rate of electrons staying at surface states, and the Auger constant, respectively. Factor b in Equation (2) is introduced to express that only a fraction of free carriers is shallowly trapped by the surface states, because some of them can be trapped by interstitial defects as they diffuse to the surface.¹⁴ The item cn_s^3 in Equation (2) represents Auger recombination.¹³ The decay rate right after the ultrafast trapping is relatively quick because there is a very high density of electrons (holes) on surface and the Auger process plays a very important role in the relaxation. With the decrease of the density of electrons (holes), the Auger process becomes less and less important and the first-order decay shows its importance. The decay rate becomes slower and slower, then reaches a constant decay which represents itself in Equation (2) as n_s/τ_s . We have ignored non-geminate electron–hole recombination because the band edge luminescence quantum yield is very low in our samples.

According to previous studies the effective mass of the hole in CdSe is $0.41m_0$, which is larger than that of the electron ($m_e=0.13m_0$).¹⁹ Here, m_0 is the free electron mass. Its mobility is over one order smaller than that of the electron.²⁰ Therefore hole trapping is known to occur on a longer time scale and we ignored it in the modeling.

Considering $\tau_i \ll \tau_s$ and $n_s(0)=0$, we obtain

$$n_i(t) = n_0 e^{-t/\tau_i}, \quad (3)$$

$$n_s(t) = \frac{N_0(1 - e^{-t/\tau_i})e^{-t/\tau_s}}{[1 + cN_0^2\tau_s(1 - e^{-t/\tau_i})^2(1 - e^{-2t/\tau_s})]^{1/2}}, \quad (4)$$

where $N_0 = bn_0$. As to the signal, we have the following equation:

$$T(t) \propto \alpha_i \frac{n_i}{n_0} + \alpha_s \frac{n_s}{n_0} + \beta. \quad (5)$$

For understanding the parameters α_i and α_s we consider the ultrafast initial decay of the transient transmission. In the case of $t \sim \tau_i$,

$$n_s \sim n_0(1 - e^{-t/\tau_i}), \quad (6)$$

$$T(t) \propto (\alpha_i - b\alpha_s)e^{-t/\tau_i} + \text{constant}. \quad (7)$$

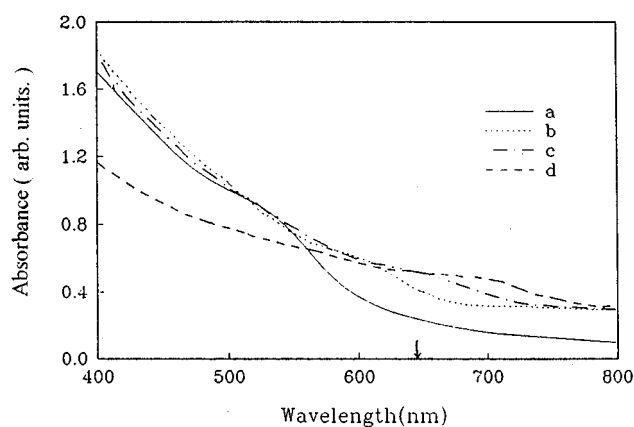


FIG. 1. The linear absorption spectra of CdSe nanocluster films at room temperature. The cluster radii are 3.2 nm (a), 4.1 nm (b), 6.5 nm (c), and 27 nm (d). The laser wavelength used in the pump–probe experiments was 647 nm.

In order to compare the results of the model to the experimental data, we should make the assumption that $\alpha_i > b\alpha_s$. During the trapping process the electrons may dissipate their energy as phonon emission. In our pump–probe experiments the probe beam is in the same wavelength as the pump beam. It is assumed that the shallowly trapped electrons only make a small contribution to the bleaching and the electrons trapped by interstitial defects should have no influence on the bleaching.

The long-lived trapped electron–hole recombination is responsible for the baseline (β) in Equation (5). $\beta/(\alpha_i + \beta)$ is a fraction of the initially generated electrons, they became the long-lived trapped electrons.

IV. RESULTS AND DISCUSSION

In this section, we report the intensity dependence of the carrier relaxation process systematically and extensively analyze the dynamics.

Figure 1 shows the linear absorption spectra of our CdSe films with different particle radius at room temperature. The quantum confinement effect can be observed clearly since the particle radii are comparable to the Bohr radius (~ 5.6 nm) of the exciton in bulk CdSe crystals.^{2,8} Because of radii inhomogeneity and phonon broadening, the exciton absorption peaks show up as the broad shoulders at wavelengths of 530, 600, 650 and 700 nm for the cluster radius of 3.2 nm (a), 4.1 nm (b), 6.5 nm (c) and 27 nm (d), respectively. The absorption peaks correspond to the $1S_e-1S_h$ transition, as the cluster radius decreases the excitonic absorption shifts to higher energies.

The transient transmission signals of the sample a at different light intensities are shown in Fig. 2. The pump and probe intensities varied from I_0 , $0.8I_0$, $0.6I_0$ to $0.4I_0$, where $I_0 \sim 0.56$ GW/cm² for pump beam. As shown in Fig. 2, the fast decay component is nonexponential and becomes slower and slower with the decrease of intensity while the long decay component is almost unchanged. We found that the fast decay component could not be fitted to a second- or third-

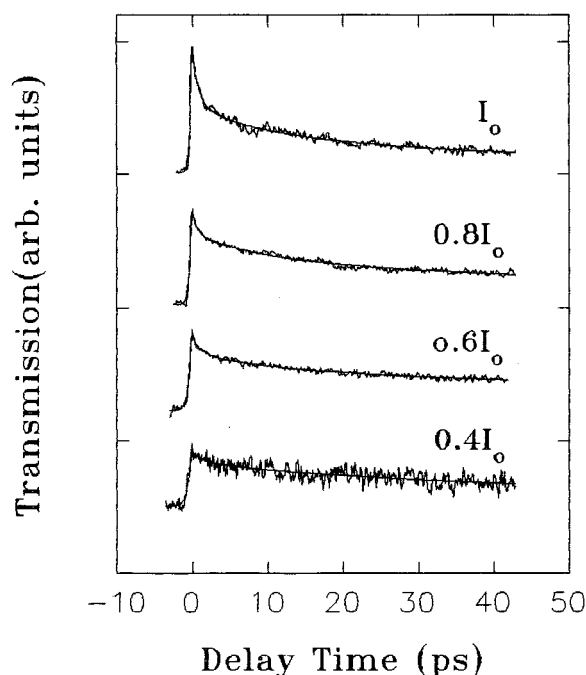


FIG. 2. The transient transmission signals of sample a at different light intensities. I_0 is about 0.56 GW/cm^2 . The smooth lines are fits using the equations discussed in the text. The fitting parameters are given in Table I.

order process alone, whereas a fast initial decay plus a third-order (Auger) process can reproduce the whole experimental data very well. We have used Equations (3)–(5) to fit the signal decay. The experimental data are well represented by a fit to a fast initial decay with a third-order process followed by a constant slow decay ($\sim 46 \text{ ps}$). The smooth solid lines in Fig. 2 are the fitting results and the fitting parameters are listed in Table I.

The initial fast decay caused by the electron trapping is quite rapid and intensity independent, the electron trapping time τ_i is about 560 fs . It is much longer than the time predicted by the quantum mechanical picture or the classical diffusional model.^{11,14} In the quantum mechanical picture the electronic wave function overlaps with the entire nanocluster and the electrons excited by the pump beam would be trapped by the surface state immediately. On the other hand, according to the classical diffusional model, the electron trapping time is estimated to be the average transit time of a conduction band electron from the center of the nanocluster to the surface. It should be equal to $r^2/\pi^2 D$.²¹ Here r is the radius of the nanocluster and D is the diffusion coefficient. Using a value of $5.2 \text{ cm}^2/\text{s}$ for the CdSe bulk diffusion coefficient, the average transit time is calculated to be 2 fs for sample a. The long trapping time was also obtained by others in different semiconductor nanoclusters.^{2,5,7,9–11,22,23}

More recently Cavaleri *et al.*²⁴ reported the study of the charge carrier dynamics in ZnO nanocluster solutions. They found the electron trapping rate increased with large cluster radius and introduced a mechanism for electron trapping involving trap-to-trap hopping to explain the observations.

At high intensity, the third-order kinetics (Auger pro-

TABLE I. Parameters for the transient transmission signals in Fig. 2.

Intensity	I_0	$0.8I_0$	$0.6I_0$	$0.4I_0$
$\tau_i(\text{ps})$	0.56	0.53	0.56	0.56
$CN_0^2(\text{ps}^{-1})$	0.078	0.051	0.029	0.013
$\tau_s(\text{ps})$	47	46	46	46
$b\alpha_s$	0.56	0.70	0.65	0.78
$\frac{\alpha_i}{\beta}$				
$\frac{\alpha_i + \beta}{\beta}$	0.036	0.16	0.22	0.23

cess) becomes an important item in accurately describing electron–hole recombination processes in CdSe nanoclusters. After initial surface trapping of the carriers, the concentration of electron–holes increases dramatically on the surface of clusters and the third order kinetics shows its importance in the relaxation. The Auger process offers a nonexponential decay and the initial instantaneous Auger decay rate is proportional to the square of pump intensity. The initial Auger decay rates (CN_0^2) for different intensities are shown in Table I. The initial excited carrier density is equal to the number of absorbed photons. For a pump beam intensity of 0.56 GW/cm^2 the initial carrier density is estimated to be 10^{20} cm^{-3} . We find that the Auger constant C is about $8 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$. It is consistent with the reported values.^{13,25–27} The possible discrepancy may result from the uncertainty in the estimated value of the pump beam intensity and of the volume fraction.

As the pump intensity decreases, Auger decay becomes slower and slower because of the lower density of electron–hole pairs built up on the surface. This is consistent with our observation of intensity dependent carrier dynamics shown in Fig. 2.

The constant decay ($\sim 46 \text{ ps}$) represents the recovery of electrons (holes) staying in shallow surface traps to the ground states which is intensity independent. The baseline which can last to nanoseconds or more implies that there must be some long-lived trapping states on the surface or inside the nanocluster. Without the electrons ejected into the solution in our dry nanocluster films, the signal can no longer be attributed to solvated electrons resulting from the electron ejection.^{10,14} The only source of baseline is the electrons staying in long-lived trapping states, such as the deeply trapping states with high barriers and the interstitial defects. There are two pathways to populate the deeply trapping states: one comes from the shallowly trapped or internally excited electrons which diffuse to the deep trapping states;⁷ the other comes from the electrons ejected by the Auger process as proposed by Colombo.¹⁴ We conclude that the surface trapped electrons can either decay to the ground state rapidly ($\sim 46 \text{ ps}$) or be trapped by other long-lived states. They then return back to the ground state slowly and make a contribute to the baseline. The value of $\beta/(\alpha_i + \beta)$ expresses the relative numbers of electrons in the long-lived trapping states, from Fig. 2 and Table I. It was decreased continuously when the Auger recombination became stronger.

Our studies of the trap-to-trap recombination can be compared to the reports by Brus' lab.^{2,3} and Peyghambarian'

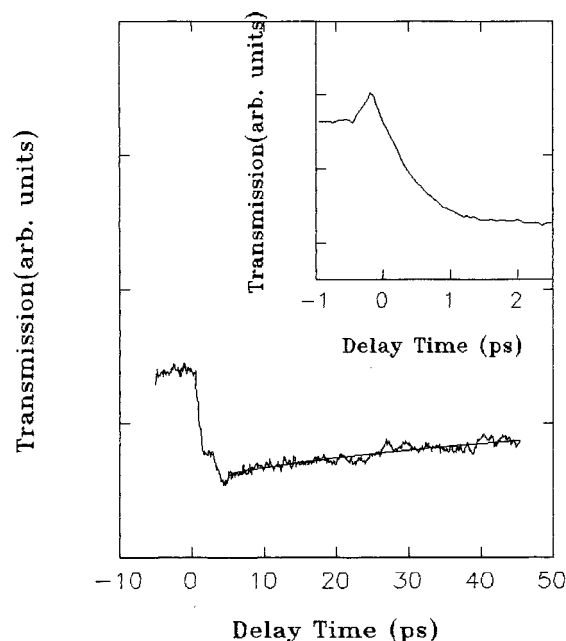


FIG. 3. The transient induced absorption of sample d. The inset shows the signal on a low scan speed.

lab.,⁸ where a two-component decay was observed in an organic solution of CdSe nanoclusters or in CdSe nanoclusters doped in silicate glasses. The fast decay (50 ps) in CdSe nanoclusters doped in silicate glasses⁸ was attributed to the recombination through surface states. In the studies of the organic solution of CdSe nanoclusters by time-resolved emission experiments a short temperature insensitive component on the 100 ps scale has been observed.³ According to these data our measurement (~ 46 ps) is responsible. In our experiments we have not measured the long-lived trapped electron-hole recombination time due to the limited length of the optical delay stage. According to the reports by Peyghambarian's lab. and Brus' lab. it is about 500 ps in CdSe nanoclusters doped in silicate glasses⁸ and 10–100 ns in the organic solution of CdSe nanoclusters.²

The overall kinetics can be summarized as follows: (i) the excited electrons are trapped rapidly in 560 fs to the surface states, (ii) the surface trapped carriers undergo the Auger process with one electron-hole pair recombination and one electron excited to a long-lived state, (iii) the surface trapped electrons can either relax back to the ground state or be trapped by some long-lived deep traps and then return to the ground state, (iv) the electrons in the long-lived states return to the ground state very slowly, which forms the baseline in the transient transmission signals.

As the cluster radius was up to 27 nm (sample d), an induced absorption shown in Fig. 3 was observed. From Fig. 1, we find the laser wavelength is on the blue side of the exciton peak of sample d. The induced absorption can be attributed to the biexciton effect^{8,28} or the trapped-carrier-induced Stark effect.^{29,30} The relatively slow decay component (~ 46 ps) is almost unchanged in this sample. As mentioned before, this decay is a recovery of the electrons in

shallowly trapping surface states to the ground state and is insensitive to the cluster size and pump light intensity. Our results of the experiments in low light intensity are consistent with the measurement of CdSe nanoclusters in silicate glasses.⁸

If the time scan speed is too fast, the ultrafast response may be averaged by the lock-in amplifier. To more carefully observe the relaxation process of sample d, we made another transient measurement on a short time scale as shown in the inset of Fig. 3. We find a sharp rise to a positive peak near zero time delay, then it falls to a negative maximum in the time of ~ 1 ps. We attribute the sharp positive peak to the bleaching of the $1S_e-1S_h$ transition. The ~ 1 ps rapid recovery of the bleaching can be attributed to the fast surface trapping. We can see that only after surface trapping can the induced absorption be observed. It seems that we cannot attribute the induced absorption solely to the biexciton effect. The origin of the induced absorption can be assigned to the generation of two-pair states in the nanocluster. The two pairs are created by the sequential absorption of one pump and one probe photons. The electric field produced by the separation of the first electron-hole pair causes a Stark effect on the absorption of a second pair. Both the shallow surface trapped as well as long-lived trapped carriers made contributions to the Stark effect.

V. CONCLUSION

In summary, we have performed femtosecond measurements of the dynamics of photoinduced electrons of CdSe nanocluster films. The observed transient absorption revealed that there are at least four processes involved in the electronic kinetics: surface trapping, most likely at or near the surface, which subsequently undergoes very rapid third order (Auger) recombination followed by a fast constant decay (~ 46 ps), the baseline of our transient signals arises from the relaxation of the long-lived trapped electrons. The long-lived deep traps which give the baseline may be populated in a way from the shallow trapped or internal excited electrons with excess energies. The induced transient absorption for sample d is due to the formation of the biexcitons or the trapped-carrier-induced Stark effect.

ACKNOWLEDGMENTS

The authors wish to thank Professor Zongju Xia for assistance in performing the experiments. This work was supported in part by the China Postdoctoral Science Foundation and by the Natural Science Foundations of China.

¹ *Optics of Semiconductor Nanostructures*, edited by F. Henneberger, S. Schmitt-Rink, and E. O. Göbel (Akademie, Berlin, 1993).

² M. G. Bawendi, W. L. Wilson, L. Rothberg, P. J. Carl, T. M. Jedju, M. L. Stegerwald, and L. E. Brus, *Phys. Rev. Lett.* **65**, 1623 (1990).

³ M. G. Bawendi, P. J. Carrol, W. L. Wilson, and L. E. Brus, *J. Chem. Phys.* **96**, 946 (1992).

⁴ Y. R. Wang and C. B. Duke, *Phys. Rev. B* **37**, 6417 (1988).

⁵ J. Z. Zhang, R. H. O'Neil, and T. W. Roberti, *J. Phys. Chem.* **98**, 3859 (1994).

⁶ J. Z. Zhang, R. H. O'Neil, T. W. Robert, J. L. McGowen, and J. E. Evans, *Chem. Phys. Lett.* **218**, 479 (1994).

- ⁷M. O'Neil, J. Marohn, and G. McLendou, *Chem. Phys. Lett.* **168**, 208 (1990).
- ⁸N. Peyghambarian, B. Fluey, D. Hulin, A. Migus, M. Joffe, A. Antonetti, S. W. Koch, and M. Lindberg, *IEEE J. Quantum Electron.* **25**, 2516 (1989).
- ⁹N. P. Ernsting, M. Kaschke, H. Weller, and L. Katsikas, *J. Opt. Soc. Am. B* **7**, 1630 (1990).
- ¹⁰G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, and D. K. Sharma, *J. Am. Chem. Soc.* **107**, 8054 (1985).
- ¹¹D. E. Skinner, D. P. Colombo, J. J. Cavalieri, and K. M. Bowman, *J. Phys. Chem.* **99**, 7853 (1995).
- ¹²R. W. Schoenlein, D. M. Mittelman, J. J. Shiang, A. P. Alivisatos, and C. V. Shank, *Phys. Rev. Lett.* **70**, 1014 (1993).
- ¹³M. Ghanassi, M. C. Schanne-Klein, F. Hache, A. L. Ekimov, D. Ricard, and C. Flytzanis, *Appl. Phys. Lett.* **62**, 78 (1993).
- ¹⁴D. P. Colombo, Jr., K. A. Roussel, J. Saeh, D. E. Skinner, J. J. Cavalieri, and R. M. Bowman, *Chem. Phys. Lett.* **232**, 207 (1995).
- ¹⁵F. Long, H. Lu, X. Shi, and K. B. Eisenthal, *Chem. Phys. Lett.* **185**, 47 (1991).
- ¹⁶X. W. Zhou, X. R. Xiao, and X. P. Li, *Chinese. Chem. Lett.* **7**, 391 (1996).
- ¹⁷S. Gorer and G. Hodes, *J. Phys. Chem.* **98**, 5338 (1994).
- ¹⁸C. Arbour, D. K. Sharma, and C. H. Langford, *J. Phys. Chem.* **94**, 31 (1990).
- ¹⁹P. E. Lippens and M. Lannoo, *Phys. Rev. B* **41**, 6079 (1990).
- ²⁰*Numerical Data and Functional Relationships in Science and Technology*, edited by K.-H. Hellwege, M. Schulz, and H. Weiss (Springer, Berlin, 1982), Vol. 17, Subvol. A, Chap. 3.
- ²¹M. D. Hatlee, J. J. Kozak, G. Rothenberger, P. P. Infelta, and M. Grätzel, *J. Phys. Chem.* **84**, 1508 (1980).
- ²²I. Bedja, S. Hotchandani, and P. V. Kamat, *J. Phys. Chem.* **97**, 11064 (1993).
- ²³Y. Wang, A. Suna, J. McHugh, E. F. Hilinski, P. A. Lucas, and R. D. Johnson, *J. Chem. Phys.* **92**, 6927 (1990).
- ²⁴J. J. Gavalieri, D. E. Skinner, D. P. Colombo, and R. M. Bowman, *J. Chem. Phys.* **103**, 5387 (1995).
- ²⁵K. Nattermann, B. Danielzik, and D. Von der Linde, *Appl. Phys. A* **44**, 111 (1987).
- ²⁶P. Roussignol, M. Kull, D. Ricard, F. de Rougemont, R. Frey, and C. Flytzanis, *Appl. Phys. Lett.* **51**, 1882 (1987).
- ²⁷J. P. Zheng and H. S. Kwok, *Appl. Phys. Lett.* **54**, 1 (1989).
- ²⁸V. Klimov, S. Hunsche, and H. Kurz, *Phys. Rev. B* **50**, 8110 (1994).
- ²⁹E. F. Hilinski, P. A. Lucas, and Y. Wang, *J. Chem. Phys.* **89**, 3435 (1988).
- ³⁰D. J. Norris, A. Sacra, C. B. Murray, and M. G. Bawendi, *Phys. Rev. Lett.* **72**, 2612 (1994).