

# Ultrafast Studies of Electron Dynamics in Semiconductor and Metal Colloidal Nanoparticles: Effects of Size and Surface

JIN Z. ZHANG

Department of Chemistry, University of California,  
Santa Cruz, California 95064

Received January 16, 1997

## 1. Introduction

Nanoparticles have chemical and physical properties different from those of the bulk and isolated atoms or molecules with the same chemical composition. A typical nanoparticle has length of a few to a few tens of nanometers and contains atoms or molecules numbering from tens to tens of thousands. Nanoparticles exhibit unique electronic, magnetic, and optical properties because of their small size and extremely large surface-to-volume ( $S/V$ ) ratio.<sup>1–8</sup> They offer an intriguing possibility to study a state of matter intermediate between bulk and isolated atoms or molecules as well as the effect of spatial confinement on electron behavior. They also provide an opportunity to investigate problems related to surfaces or interfaces because of their interfacial nature.<sup>9</sup> Nanomaterials have tremendous potential applications in areas including microelectronics, electrooptics, nonlinear optics, catalysis, photography, and electrochemistry.

The past decade has witnessed a huge upsurge in research on nanomaterials, and progress made in the area has been outlined in several excellent review articles<sup>1–5</sup> and books.<sup>6–8</sup> Two key factors in this research are the size and surface characteristics of nanoparticles. These two are interrelated since the  $S/V$  ratio increases as the size decreases. For a spherical particle, the  $S/V$  ratio is inversely proportional to its radius,  $R$ , i.e.,  $S/V = 3/R$ . A fascinating feature of nanoparticles is that their small size results in spatial confinement of the wave function of charge carriers, which is termed quantum size confinement.<sup>10–13</sup> This effect becomes significant especially when the size is smaller than the Bohr exciton radius, which is around 24 Å for CdS.<sup>6</sup> The quantum confinement is manifested as dramatic changes in the material properties.

As illustrated in Figure 1, the density of states (DOS) and energy level spacing change as a function of size.

Jin Z. Zhang was born in Henan, China, in 1962. He received his B.Sc. in chemistry from Fudan University, Shanghai, in 1983 and his Ph.D. in physical chemistry from University of Washington, Seattle, in 1989. He was a postdoctoral research fellow at UC Berkeley from 1989 to 1992. In 1992, he joined the faculty at UC Santa Cruz, where he is currently assistant professor of chemistry. Zhang's research interests include experimental and theoretical studies of molecular reaction dynamics in the gas phase and condensed phases, e.g. interfaces and solutions. In recent years, his research has focused on reaction dynamics at liquid–semiconductor and liquid–metal interfaces with emphasis on interfacial electron dynamics in colloidal metal and semiconductor nanoparticles.

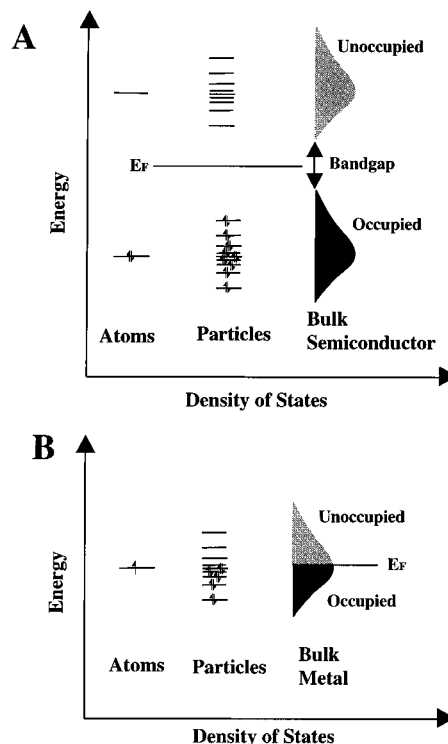


FIGURE 1. Schematic illustration of the energy levels as a function of density of states for different sized systems for semiconductor (top panel, A) and metal (bottom panel, B).

Using a simple particle-in-a-box model, the energy level spacing for a spherical particle is predicted to be inversely proportional to  $R^2$ .<sup>4</sup> Thus, with decreasing size, the effective bandgap increases and the relevant absorption and emission spectra shift to bluer wavelengths.

Recent studies by us and others have found that the surface of particles plays as important a role as particle size in the equilibrium and dynamic properties of both semiconductor and metal particles. In particular, direct measurements of charge carrier dynamics in nanoparticles using time-resolved techniques have allowed us to gain a fundamental understanding of how charge carriers interact with phonons, other carriers, and the surface.<sup>9,14–33</sup> The large percentage of surface atoms, which often have

- (1) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- (2) Kamat, P. V. *Prog. Inorg. Chem.* **1997**, *44*, 273.
- (3) Wang, Y. *Acc. Chem. Res.* **1991**, *24*, 133.
- (4) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
- (5) Tolbert, S. H.; Alivisatos, A. P. *Annu. Rev. Phys. Chem.* **1995**, *46*, 595.
- (6) Gratzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC Press: Boca Raton, FL, 1989; p 87.
- (7) Miller, R. J. D.; McLendon, G. L.; Nozik, A. J.; Schmickler, W.; Willig, F. *Surface Electron-Transfer Processes*; VCH: New York, 1995; p 311.
- (8) Schmid, G., Ed. *Clusters and Colloids*; VCH: New York, 1994.
- (9) Zhang, J. Z.; O'Neil, R. H.; Roberti, T. W. *J. Phys. Chem.* **1994**, *98*, 3859.
- (10) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (11) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.
- (12) Heath, J. R. *Science* **1995**, *270*, 1315.
- (13) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.
- (14) Mittleman, D. M.; Schoenlein, R. W.; Shiang, J. J.; Colvin, V. L.; et al. *Phys. Rev. B: Condens. Matter* **1994**, *49*, 14435.
- (15) Heilweil, E. J.; Hochstrasser, R. M. *J. Chem. Phys.* **1985**, *82*, 4762.
- (16) Skinner, D. E.; Colombo, D. P., Jr.; Cavaleri, J. J.; Bowman, R. M. *J. Phys. Chem.* **1995**, *99*, 7853.
- (17) Ernsting, N. P.; Kaschke, M.; Weller, H.; Katsikas, L. *J. Opt. Soc. Am. B* **1990**, *7*, 1630.
- (18) Smith, B. A.; Waters, D. M.; Faulhaber, A. E.; Kreger, M. A.; Roberti, T. W.; Zhang, J. Z. *J. Sol-Gel Sci. Technol.* **1997**, *9*, 125.

dangling bonds, as well as surface defects and adsorbates introduce a high density of "surface states". These states can fall within the bandgap for a semiconductor and function to trap charge carriers (electron or hole). They are often termed trap states and significantly influence the charge carrier behavior. Therefore, surface characteristics, in conjunction with size, critically affect the properties of nanoparticles and they often have competing effects on the charge carrier behavior.<sup>24–26,31</sup>

The purpose of this Account is to examine recent progress made in the study of charge carrier dynamics in both semiconductor and metal nanoparticles with special attention to work in our laboratory. I will focus on one fundamental question: *how do particle size and surface characteristics influence the behavior of charge carriers in confined systems?* Electron lifetime is determined by both radiative and nonradiative decay pathways. To understand the issue of interest, therefore, we must know how these different decay pathways are affected by size and surface. Time-resolved laser techniques have been demonstrated to be most suitable for probing electron dynamics in real time.<sup>9,14–33</sup>

## 2. Preparation and Characterization of Semiconductor and Metal Nanoparticles

Common techniques for preparing semiconductor nanoparticles include arrested precipitation of colloidal particles from homogeneous solution by controlled release of ions or forced hydrolysis in the presence of surfactants. For example, controlled mixing of Cd<sup>2+</sup> with sulfide ions yields colloidal particles of CdS.<sup>34</sup> Surfactants are often used to stabilize the particles.<sup>35–38</sup>

For metal particles, chemical reduction of metal ions is the common approach. For example, Au colloidal

particles can be prepared by reducing HAuCl<sub>4</sub> with sodium citrate.<sup>39</sup> Similarly, Ag and Pt colloids can be prepared by reducing silver or platinum ions with borohydride.<sup>40,41</sup> The size and distribution of particles are sensitive to experimental conditions such as concentration, temperature, surfactant, and dispersion medium.

One challenge in preparing nanoparticles is to control size and surface properties. For many studies it is desirable to prepare particles with a single size and well-defined surface characteristics. However, to date, only a few single-sized semiconductor nanoparticle samples, mainly of CdS, have been synthesized.<sup>42–44</sup> Some particles, e.g. CdSe, can be prepared with a very narrow size distribution and capped with well-defined surface ligands.<sup>45,46</sup> For metals, only small single-sized nanoparticles have been prepared, including Au, Pt, and Pd.<sup>47–49</sup>

Characterization of the size and surface properties of nanoparticles has been mainly by spectroscopy and microscopy techniques, including UV–visible,<sup>9,50</sup> fluorescence,<sup>20,37,43,51</sup> Raman,<sup>46</sup> scanning tunneling, transmission electron, and atomic force microscopy.<sup>1–3,52,53</sup> Other techniques such as X-ray diffraction have sometimes been used.<sup>43,44,47–49,54,55</sup> UV–visible spectroscopy can be used to infer particle size on the basis of the correlation between the exciton band and particle size.<sup>10,11,55</sup> More recent experiments have started to explore the shape of particles<sup>1</sup> and assembly of nanoparticles into ordered arrays.<sup>12,13,56</sup>

Direct measurements of charge carrier dynamics in nanoparticles have been conducted primarily by ultrafast laser techniques. A popular approach is transient absorption spectroscopy. In this approach, a short laser pulse (~100 fs) is used to create excited-state electrons and a second laser pulse is used to probe the excited population. The dynamics are measured from the change in absorbance of the probe pulse due to excited-state absorption, as a function of delay time between the two pulses.<sup>9</sup>

- (19) Brelle, M.; Zhang, J. Z. *J. Chem. Phys.* **1997**, submitted for publication.  
 (20) Roberti, T. W.; Cherepy, N. J.; Zhang, J. Z. *J. Phys. Chem.* **1997**, submitted for publication.  
 (21) Ahmadi, T. S.; Logunov, S. L.; El-Sayed, M. A. *J. Phys. Chem.* **1996**, *100*, 8053.  
 (22) Perner, M.; Bost, P.; Pauck, T.; von Plessen, G.; Feldmann, J.; Becker, U.; Mennig, M.; Porstendorfer, J.; Schmitt, M.; Schmidt, H. *Springer Ser. Chem. Phys.* **1996**, *62*, 437.  
 (23) Stella, A.; Nisoli, M.; De Silvestri, S.; Svelto, O.; Lanzani, G.; Cheyssac, P.; Kofman, R. *Springer Ser. Chem. Phys.* **1996**, *62*, 439.  
 (24) Roberti, T. W.; Smith, B. A.; Zhang, J. Z. *J. Chem. Phys.* **1995**, *102*, 3860.  
 (25) Faulhaber, A. E.; Smith, B. A.; Andersen, J. K.; Zhang, J. Z. *Mol. Cryst. Liq. Cryst.* **1996**, *283*, 25.  
 (26) Zhang, J. Z.; Smith, B. A.; Faulhaber, A. E.; Andersen, J. K.; Rosales, T. J. *Ultrafast Processes Spectrosc.* **1996**, *9*, 561.  
 (27) Groeneveld, R. H. M.; Sprik, R.; Lagendijk, A. *Phys. Rev. Lett.* **1990**, *64*, 784.  
 (28) Brorson, S. D.; Fujimoto, J. G.; Ippen, E. P. *Phys. Rev. Lett.* **1987**, *59*, 1962.  
 (29) Belotskii, E. D.; Tomchuk, P. M. *Int. J. Electronics* **1992**, *73*, 955.  
 (30) Gorban, S. A.; Nepijko, N. P.; Tomchuk, P. M. *Int. J. Electronics* **1991**, *70*, 485.  
 (31) Smith, B. A.; Zhang, J. Z.; Giebel, U.; Schmid, G. *Chem. Phys. Lett.* **1997**, *270*, 139.  
 (32) Skinner, D. E.; Colombo, D. P.; Cavaleri, J. J.; Bowman, R. M. *J. Phys. Chem.* **1995**, *99*, 7853.  
 (33) Kamat, P. V.; Ebbesen, T. W.; Dimitrijevic, N. M.; Nozik, A. J. *J. Phys. Chem.* **1989**, *93*, 4259.  
 (34) Duonghong, D.; Ramsden, J. J.; Gratzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977.  
 (35) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.  
 (36) Gallardo, S.; Gutierrez, M.; Henglein, A.; Janata, E. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 1080.  
 (37) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221.  
 (38) O'Neil, M.; Marohn, J.; McLendon, G. *J. Phys. Chem.* **1990**, *94*, 4356.

- (39) Frens, G. *Nature: Phys. Sci.* **1973**, *241*, 20.  
 (40) Suh, J. S.; DiLella, D. P.; Moskovots, M. *J. Phys. Chem.* **1983**, *87*, 1540.  
 (41) Wilenzick, R. M.; Russell, D. C.; Morriss, R. H.; Marshall, S. W. *J. Chem. Phys.* **1967**, *47*, 533.  
 (42) Vossmeier, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Weller, H. *Science* **1995**, *267*, 1476.  
 (43) Herron, N. Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426.  
 (44) Lee, G. S. H.; Craig, D. C.; Ma, I.; Scudder, M. L.; Bailey, T. D.; Dance, I. G. *J. Am. Chem. Soc.* **1988**, *110*, 4863.  
 (45) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.  
 (46) Bowen Katari, J. E.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1994**, *98*, 4109.  
 (47) Fauth, K.; Kreigib, U.; Schmid, G. *Z. Phys. D* **1991**, *20*, 297.  
 (48) Benfield, R. E.; Creighton, J. A.; Eadon, D. G.; Schmid, G. *Z. Phys. D* **1989**, *12*, 533.  
 (49) Schmid, G. *Mater. Chem. Phys.* **1991**, *29*, 133.  
 (50) Weller, H.; Schmidt, H. M.; Koch, U.; Fojtik, A.; Baral, S.; Henglein, A.; Kunath, W.; Weiss, K.; Dieman, E. *Chem. Phys. Lett.* **1986**, *124*, 557.  
 (51) Chestnoy, N.; Harris, T. D.; Hull, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 3393.  
 (52) Evans, J. E.; Springer, K. W.; Zhang, J. Z. *J. Chem. Phys.* **1994**, *101*, 6222.  
 (53) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 267.  
 (54) Tolbert, S. H.; Alivisatos, A. P. *Science* **1994**, *265*, 373.  
 (55) Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmuller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7673.  
 (56) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690.

A related approach based on transient bleaching measurement, in which the probe pulse monitors the ground-state recovery, has also been used to study charge carrier dynamics and nonlinear optical properties of nanoparticles.<sup>57–61</sup> The large bleach at the first exciton energy may arise from a decrease in oscillator strength of the excitonic transitions due to trapped electrons and holes<sup>62</sup> or band filling due to excess conduction band electrons.<sup>58</sup>

Time-resolved fluorescence measurements have also been applied to characterize excited charge carriers in semiconductor nanoparticles. Charge carriers may radiatively recombine, emitting near band-edge and sub-bandgap light. The near band-edge emission is attributed to band-edge excitons, shallow trapped charge carriers,<sup>38</sup> and “dark” excitons.<sup>63</sup> The sub-bandgap emission is proposed to arise from recombination of surface trapped carriers.<sup>6,35,38</sup> Thus, the rise and decay of the time-resolved fluorescence yield information on the formation and depletion of band-edge and trap states.

### 3. Electron Dynamics in Semiconductor Nanoparticles: Effects of Size and Surface

The effect of size on equilibrium properties of semiconductor nanoparticles have been extensively studied. It has been shown that, as a consequence of quantum confinement, the effective bandgap and redox potential increase with decreasing size. The exciton absorption band and emission maximum shift to the blue with decreasing size.<sup>2,10,11</sup> The oscillator strength of the first excitonic transition increases proportional to  $1/R^3$ .<sup>55</sup> The electron–phonon coupling, in some systems such as CdSe, has been found to decrease with size due to stronger electron–hole interaction.<sup>64</sup>

The effect of size on dynamic properties of charge carriers is less understood. To understand the effect of size on electron dynamics, one must recognize how factors that determine the electron lifetime are affected by size. The behavior of an electron in a bulk solid reflects its interaction with the lattice, other carriers, and, if present, defects and impurities. In nanoparticles the lattice structure, charge carrier coupling, and electronic structure may change with size, thereby causing changes in the electron lifetime. Moreover, the surface is expected to affect the charge carrier behavior.

Compared to bulk, two changes may be expected for semiconductor nanoparticles that have effects on the electron lifetime. First, the density-of-state (DOS) for both the electron and phonons will decrease with size, which is likely to result in weaker electron–phonon interaction and less nonradiative decays. The electron lifetime is then expected to increase with decreasing size. On the other

hand, spatial confinement can lead to stronger electron–hole interaction,<sup>64</sup> possibly increasing electron–hole recombination. These two factors may compete with each other and result in an overall weak size dependence of electron dynamics.

In an early study of CdS colloids, it was concluded that the rate of electron transfer across the interface increases with decreasing size, with the assumption of electron–hole recombination rate independent of size.<sup>65</sup> In our study of CdS, we did not observe any noticeable size dependence of the electron dynamics between 2 and 4 nm.<sup>9</sup> The decay was attributed primarily to electron–hole recombination.<sup>9</sup> This assignment was supported by transient bleach experiment<sup>66</sup> performed on a similar system,  $Zn_xCd_{1-x}S$ .<sup>17</sup> Similar findings were made independently on  $TiO_2$  colloids.<sup>16</sup> A weak size dependence of the electron lifetime was found in CdSe nanoparticles which show a slightly shorter lifetime for smaller sizes,<sup>14</sup> indicating that the effect of stronger electron–hole interaction may be dominant. However, these results need to be interpreted with caution since the dynamics observed were probably influenced by surface properties.

The influence of surface on electron dynamics is mainly due to the exceedingly large  $S/V$  ratio of nanoparticles and often a high density of trap states on the surface resulted from extrinsic defects and dangling bonds. For CdS colloids, electron trapping was found to be dominant in the early dynamics, which occurs in  $<100$  fs,<sup>9</sup> consistent with earlier suggestions<sup>33,62</sup> and more recent studies.<sup>32</sup> A longer trapping time (500 fs to 8 ps) was deduced for CdSe from photon echo experiments.<sup>14</sup> A 30 ps risetime of trap state emission has also been measured.<sup>68</sup> Evidence of fast (1 ps) hole trapping has been reported on the basis of time-resolved photoluminescence experiments.<sup>69</sup> The difference in trapping time could be due to either difference in the quality of samples studied or the operation of different decay mechanisms. There is little doubt that trapping plays an important role in charge carrier dynamics. However, the time scale for trapping and chemical nature of trap states in most colloids are yet to be unequivocally identified. That electron dynamics are dependent on surface characteristics is supported by the observation that they are sensitive to environmental factors, including adsorbates, surfactants, solvent, pH, electron or hole scavengers,<sup>9,18</sup> and coupling to other colloidal particles.<sup>53</sup> Recent studies of core–shell nanoparticles such as CdSe/ZnS<sup>70</sup> and CdS/HgS<sup>71</sup> also demonstrate that charge carrier behavior is affected by the shell present on the core surface.

Important evidence supporting the assignment of the dominant decay features to recombination is the excitation power dependence of the dynamics. For both CdS and  $TiO_2$ , a strong power dependence has been observed;

(57) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1987**, *91*, 2096.

(58) Kamat, P. V.; Dimitrijevic, N. M.; Nozik, A. J. *J. Phys. Chem.* **1989**, *93*, 2873.

(59) Haase, M.; Weller, H.; Henglein, A. *J. Phys. Chem.* **1988**, *92*, 4706.

(60) Wang, Y.; Herron, N.; Mahler, W.; Suna, A. *J. Opt. Soc. Am. B* **1989**, *6*, 808.

(61) Eychmueller, A.; Vobmeyer, T.; Mews, A.; Weller, H. *J. Lumin.* **1994**, *58*, 223.

(62) Hilinski, E. F.; Lucas, P. A.; Wang, Y. *J. Chem. Phys.* **1988**, *89*, 3435.

(63) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, A. L.; Rosen, M. *Phys. Rev. Lett.* **1995**, *75*, 3728.

(64) Shiang, J. J.; Risbud, S. H.; Alivisatos, P. A. *J. Chem. Phys.* **1993**, *98*, 8432.

(65) Nosaka, Y.; Ohta, N.; Miyama, H. *J. Phys. Chem.* **1990**, *94*, 3752.

(66) de Heer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 611.

(67) Bawendi, M. G.; Wilson, W. L.; Rothberg, L. J.; Carroll, P. J.; Jedju, T. M.; Steigerwald, M. L.; Brus, L. E. *Phys. Rev. Lett.* **1990**, *65*, 1623.

(68) O’Neil, M.; Marohn, J.; McLendon, G. *Chem. Phys. Lett.* **1990**, *168*, 208.

(69) Klimov, V.; Bolivar, P. H.; Kurz, H. *Phys. Rev. B* **1996**, *53*, 1463.

(70) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802.

(71) Kamalov, V. F.; Little, R.; Logunov, S. L.; El-sayed, M. A. *J. Phys. Chem.* **1996**, *100*, 6381.

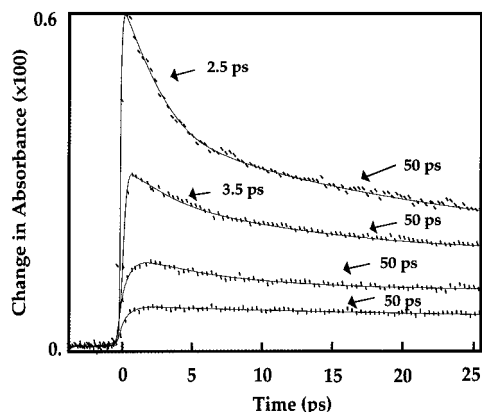


FIGURE 2. Power dependence of electron dynamics in CdS colloidal particles. The measurement was carried out at probe wavelength of 780 following excitation at 390 nm with four excitation intensities (signal size increasing with intensity): 0.12, 0.20, 0.59, and 1.18 photons/Å<sup>2</sup>. The numbers are time constants obtained from a double exponential fit (solid lines) of the experimental data (dotted). Adapted from ref 9.

the decay is faster and more dominant at a higher excitation intensity. Figure 2 shows the data for CdS at different excitation intensities. At low intensities, relaxation is dominated by a 50 ps decay followed by a small amplitude slow decay (>1 ns).<sup>9</sup> At higher intensities, a fast (2–3 ps) decay component appears. The appearance of the fast decay at high excitation intensities suggests that it is due to exciton–exciton interaction as a result of multiple excitons created per particle. Several explanations for the fast decay have been offered, including nongeminate recombination,<sup>9</sup> second-order recombination,<sup>16</sup> enhanced tunneling for secondary recombination,<sup>17,72</sup> and Auger processes.<sup>70,72,73</sup> The power-dependent dynamics in CdS,<sup>9</sup> in conjunction with power dependent fluorescence of CdS<sub>x</sub>Se<sub>1-x</sub> in glass<sup>74</sup> and time-resolved fluorescence of aqueous CdS,<sup>20</sup> suggest a strong dependence of decay pathways on the number of photogenerated carriers per particle. New decay mechanisms become important as the number of carriers per particle increases.<sup>74</sup> The fast decay appears to be mainly associated with band-edge states with blue emission, while the slower decays (50 ps and greater than nanoseconds) are due to deep traps with red emission.<sup>20,74</sup>

Studies of the surface effect on electron dynamics provided further insight into the electronic relaxation mechanism. One way to change the surface characteristics is to chemically modify the surface, which often results in removal of certain trap states and enhanced fluorescence.<sup>20,62,68</sup> For CdS, we have found that the early electron dynamics are relatively insensitive to surface modification even though fluorescence is substantially enhanced.<sup>20</sup> As shown in Figure 3, the dynamics remained essentially unchanged while fluorescence increased 200-fold upon modifying the surface with excess Cd<sup>2+</sup>.<sup>38,68</sup> It would be difficult to understand these results on the basis of the simple relation  $\tau_{\text{obs}} = \Phi_{\text{fl}} \tau_{\text{R}}$ , where  $\tau_{\text{obs}}$  is the

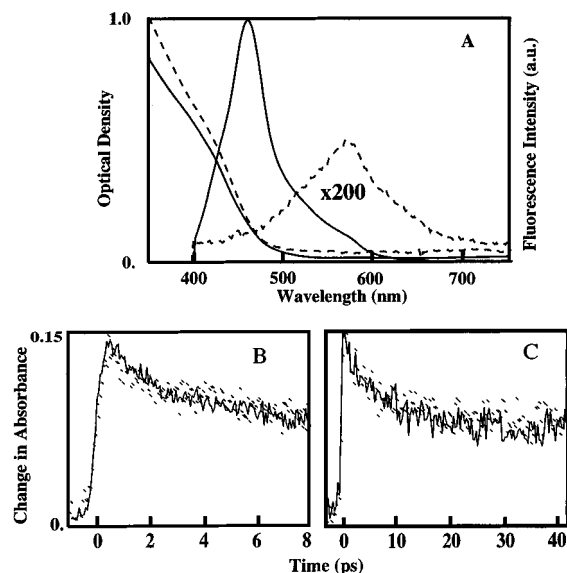


FIGURE 3. Effect of surface modification in CdS colloids. Panel A shows the electronic absorption (left) and fluorescence (right) spectra for modified (solid) and unmodified (dashed) samples. The bottom panel shows the dynamics measured for the modified (solid) and unmodified (dotted) samples on a short (B) and longer (C) time scales.

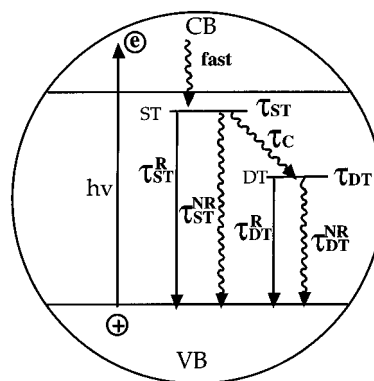


FIGURE 4. Two-state trapping model for explaining the effect of surface modification and the relation between lifetime and fluorescence yield of trap states. Notations are defined in the text.

observed lifetime,  $\Phi_{\text{fl}}$  is the fluorescence yield, and  $\tau_{\text{R}}$  is the intrinsic radiative lifetime. The results can be partly rationalized using a model involving at least two trap states, as shown schematically in Figure 4 and suggested by others before.<sup>75</sup> The lifetime of the deep trap (DT) is given by

$$\tau_{\text{DT}} = \Phi_{\text{DT}}^{\text{R}} \tau_{\text{DT}}^{\text{R}} (1 + \tau_{\text{C}} / \tau_{\text{ST}}^{\text{R}} + \tau_{\text{C}} / \tau_{\text{ST}}^{\text{NR}}) \quad (1)$$

where  $\tau_{\text{DT}}$ ,  $\tau_{\text{DT}}^{\text{R}}$ , and  $\Phi_{\text{DT}}^{\text{R}}$  are the observed lifetime, radiative lifetime, and fluorescence quantum yield, respectively;  $\tau_{\text{C}}$  is the crossing time constant from shallow to deep traps; and  $\tau_{\text{ST}}^{\text{R}}$  and  $\tau_{\text{ST}}^{\text{NR}}$  are the radiative and nonradiative decay time constants for the shallow traps (ST). If surface modification leads to a longer  $\tau_{\text{ST}}^{\text{NR}}$  and simultaneously a higher  $\Phi_{\text{DT}}^{\text{R}}$ , the observed  $\tau_{\text{DT}}$  may not change appreciably. This model is certainly not unique but does suggest that it is possible to observe little or no change in the dynamics while fluorescence is enhanced, if the deep trap is being observed. Perhaps, more

(72) Rothenberger, G.; Moser, J.; Gratzel, M.; Serpone, N.; Sharmar, D. K. *J. Am. Chem. Soc.* **1985**, *107*, 8054.

(73) Ghanassi, M.; Schanne-Klein, M. C.; Hache, F.; Ekimov, A. I.; Ricard, D.; Flytzanis, C. *Appl. Phys. Lett.* **1992**, *62*, 78.

(74) Zheng, J. P.; Shi, L.; Choa, F. S.; Liu, P. L.; Kwok, H. S. *Appl. Phys. Lett.* **1988**, *53*, 643.

(75) Weller, H.; Eychmuller, A.; Vogel, R.; Katsikas, L.; Hasselbarth, A.; Giersig, M. *Israel J. Chem.* **1993**, *33*, 107.

importantly, it points out the complex interrelation between the lifetimes and fluorescence yields of different traps. This model would also predict enhanced fluorescence for the shallow trap, which is consistent with experimental observations.

An alternative way of rationalizing the above observation is that surface modification affects mainly the lifetime of deep traps, which is relatively long<sup>74</sup> and thus does not show appreciable change in the early dynamics.<sup>20</sup> The early dynamics are dominated by the lifetime of shallow traps, which is shorter<sup>74</sup> and essentially not affected by surface modification.<sup>20</sup> At low excitation intensity, only one photogenerated exciton exists per particle and the carriers are trapped in surface states and recombine slowly via deep traps. This recombination pathway will be strongly surface dependent. At high intensities, multiple excitons are created per particle and strong charge carrier interactions is possible, allowing new, faster routes for carrier relaxation, e.g. exciton–exciton annihilation and Auger recombination. Fluorescence data<sup>20,74</sup> clearly show that at high power recombination from band-edge states is favored, consistent with trap state saturation and band filling. Thus, the fast decay is less sensitive to the surface since these band-edge states are more strongly associated with the nanocrystal than with the surface.

This phenomenon may be special to semiconductors in the quantum confinement regime, where charge carrier interaction is significantly enhanced due to spatial confinement. The recombination dynamics in particles with radii larger than the Bohr exciton radii either exhibit a simple second-order power-dependent decay<sup>16</sup> or show no power dependence,<sup>19</sup> which occurs when the multiple carriers per particle are not strongly coupled. These results will have direct implications on applications of quantum-confined semiconductor nanoparticles, where the surface is important for low-power uses such as photocatalysis while less important for high-power, nonlinear optics applications such as saturable absorbers and nanoparticle lasers.

Similar observations were made in our study of AgI colloid, an important photographic material;<sup>76</sup> again, the fluorescence yield can be enhanced with different surfactants while the dynamics remains essentially unchanged.<sup>19</sup> Figure 5 shows the electronic absorption and fluorescence spectra and electron dynamics of AgI. In contrast to CdS<sup>9</sup> and TiO<sub>2</sub>,<sup>16</sup> the AgI dynamics are found to be independent of pump power. The amplitude ratio between the fast (2 ps) and slow (> 1 ns) components in AgI remains the same for different powers. Apparently, the recombination mechanism in AgI is different from that in CdS or TiO<sub>2</sub>. One possible explanation is that the two decays are from two completely uncoupled trap states, in contrast to the two coupled trap states for CdS.<sup>9</sup> Only the shallow trap has weak near-bandgap emission. This study shows that electronic relaxation processes are dependent on the nature of the colloids.

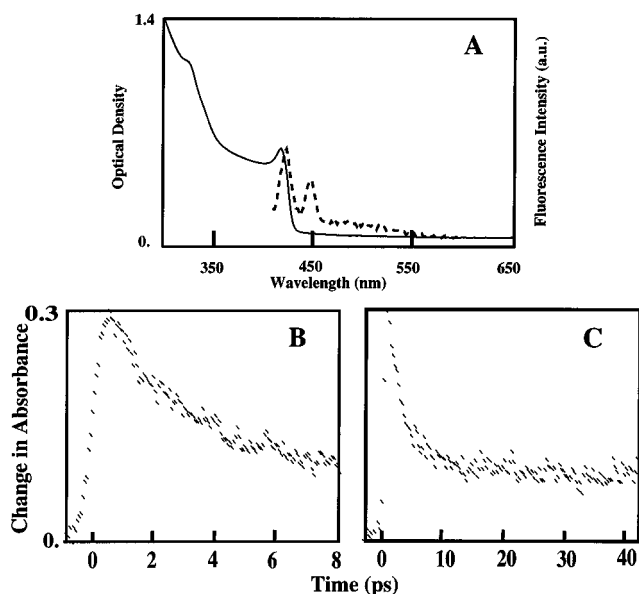


FIGURE 5. Panel A shows the electronic absorption (solid) and fluorescence (dashed) spectrum of a AgI colloid (peak at 450 nm is a water Raman signal). Panels B and C show the electron dynamics on two different time scales, probed at 780 nm following excitation at 390 nm (excitation intensity 0.20 photons/Å<sup>2</sup>).

#### 4. Electronic Relaxation Dynamics in Metal Nanoparticles: Effects of Size and Surface

Metal nanoparticles resemble and differ from semiconductor nanoparticles. A major difference is in their electronic band structure. The bandgap that plays a deterministic role in semiconductors does not exist in metals, since electrons are free to move even at fairly low temperature in their half-filled conduction band. As the particle size increases, the center of the band develops first and the edge last.<sup>1</sup> In metals with Fermi levels lying in the band center, the relevant energy level spacing is very small even in relatively small particles, whose properties resemble those of the bulk.<sup>66</sup> In semiconductors, in contrast, the Fermi level lies between two bands and the edges of the bands dominate the low-energy optical and electronic properties. Bandgap optical excitation depends strongly on particle size. As a consequence, the quantum confinement effect is expected to occur at much smaller sizes for metal than for semiconductor nanoparticles. This difference has fundamental consequences for electronic relaxation processes.

As for semiconductor nanoparticles, most early studies on metal nanoparticles focused on equilibrium properties such as optical absorption and structural properties.<sup>77–81</sup> Study of electron dynamics in metal particles is relatively new. An early picosecond study reported an electronic relaxation time of > 2 ps in Au nanoparticles.<sup>15</sup> The first femtosecond study of metal particles was carried out in our lab on Ag in water;<sup>24</sup> it was followed by studies on Au<sup>25</sup> and Pt<sup>26</sup> in aqueous and organic solvents. For both

(76) Henglein, A.; Gutierrez, M.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 593.

(77) Vijayakrishnan, V.; Chainani, A.; Sarma, D. D.; Rao, C. N. R. *J. Phys. Chem.* **1992**, *96*, 8679.

(78) Leff, D. V.; Brandt, L.; Heath, J. R. *Langmuir* **1996**, *12*, 4723.

(79) Genzel, L.; Martin, T. P.; Kreibig, U. *Z. Phys. B* **1975**, *21*, 339.

(80) Halperin, W. P. *Rev. Mod. Phys.* **1986**, *58*, 533.

(81) Henglein, A. *Israel J. Chem.* **1993**, *33*, 77.

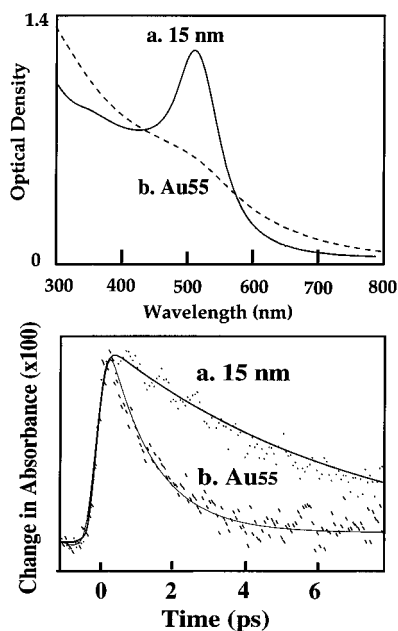


FIGURE 6. (top) Electronic absorption spectra for the two different sized Au particles, solid for 15 nm and dashed for 2 nm. (bottom) Comparison of electron relaxation dynamics in different sized Au particles (*a* for 15 nm and *b* for 2 nm). Dotted lines are experimental data, and solid lines are fits using a single exponential with time constants of 7 ps (*a*) and 1 ps (*b*), respectively.

Ag and Au the early relaxation was found to be dominated by electron–phonon interaction, with relaxation times of 2.5 and 7 ps, respectively. Both relaxation times were slower than those observed for the corresponding bulk metal films (670 fs for Ag and 1 ps for Au).<sup>27,28</sup> The slower relaxation in nanoparticles was attributed to weakened electron–phonon interaction,<sup>25</sup> which is qualitatively consistent with theoretical predictions<sup>29</sup> and electron–phonon coupling constants measured for Au “islands”.<sup>30</sup>

More recently, similar femtosecond studies have been conducted on Au<sup>21,22</sup> and Sn<sup>23</sup> particles. The study on Au in water, much as in our investigation, monitored the bleach recovery following photoexcitation and revealed an electronic relaxation time of 2.5 ps.<sup>21</sup> A study of Au particles in a glass matrix showed a decay time of 4 ps.<sup>22</sup> The somewhat different time constants found for Au particles in different labs might be due to different surface properties of the samples prepared, as suggested by the observed dependence of relaxation on the surface (solvent) environment. The relaxation time changes from 7 ps in water to 3.5 ps in cyclohexane for particles of the same size (18 nm).<sup>26</sup>

A significant result reported on Sn was that the relaxation time decreases with size in the range 2–6 nm (*R*), which was attributed to enhanced surface collision.<sup>23</sup> This result stimulated us to study size dependence in small Au particles. We have recently examined two single-sized clusters of Au, Au<sub>55</sub> and Au<sub>13</sub>, with well-defined surface properties.<sup>47,48</sup> We have found the electronic relaxation time to be 1 ps for Au<sub>55</sub> and 300 ps for Au<sub>13</sub>. The relaxation in Au<sub>55</sub> (*2R* = 2 nm) is much faster than in large particles, 14–40 nm, which show a 7 ps lifetime, as shown in Figure 6. This faster relaxation in smaller particles is consistent with the observation on Sn clusters. In consideration of these results, we proposed the following phenomenologi-

cal equation to describe electronic relaxation in metal nanoparticles:<sup>31</sup>

$$\frac{1}{\tau_{\text{obs}}} = \frac{aR^\alpha}{\tau_{\text{bulk}}} + \frac{bv_F}{R} \quad (2)$$

where  $\tau_{\text{obs}}$  and  $\tau_{\text{bulk}}$  are the observed and bulk electronic relaxation times, respectively,  $v_F$  is the Fermi velocity of the electron, *a* and *b* are constants characteristic of the metal,  $\alpha$  is a positive integer that can be derived from theoretical models,<sup>29</sup> and *R* is the radius of the particle.  $1/b$  is a measure of the average number of surface collisions.<sup>23</sup> According to this equation, reducing the particle size first increases the relaxation time relative to bulk, since the first term on the right-hand side (derived from reduced electron–phonon interaction) is dominant. As the size decreases further, the second term, which relates to surface collisions, becomes predominant and causes a decrease in relaxation time with size. From eq 2, one would expect the relaxation time in Au<sub>55</sub> clusters, because of their small size, to be faster than the 7 ps observed for 15 nm particles. This is in agreement with our experimental observations. Therefore, we conclude that Au<sub>55</sub> is in the regime of small clusters in which surface collision predominates. Similar observations have been made on Pt nanoparticles which also show a faster decay at smaller size.<sup>31</sup>

An exception is that this equation apparently does not apply to Au<sub>13</sub>, which has a much longer relaxation time. If eq 2 were to apply, the relaxation time in Au<sub>13</sub> would be predicted to be much faster than that of Au<sub>55</sub>, i.e., <1 ps, while a lifetime of about 300 ps has been observed for Au<sub>13</sub>. This suggests that Au<sub>13</sub> behaves completely differently from Au<sub>55</sub> or larger particles. We propose that Au<sub>13</sub> is more molecule-like.<sup>31</sup> This is consistent with the molecular behavior indicated by the multiple bands in its electronic absorption spectrum.<sup>47,48</sup> The results imply that the bulk-to-molecule transition occurs in the narrow regime of 55 to 13 atoms for Au, a range much smaller than for semiconductors.<sup>31</sup>

## 5. Conclusions and Outlook

Both particle size and surface characteristics affect electron dynamics in semiconductor and metal nanoparticles. In semiconductor nanoparticles, the fast charge carrier relaxation processes have been shown to be dependent on power, especially for quantum-confined systems, and dependent on the surface and size under lower power excitation conditions. For metal nanoparticles, the particle size and surface have competing effects on hot electron relaxation. The relaxation is slower than in bulk at large particle sizes due to dominance of weakened electron–phonon interaction. At smaller sizes, surface collision becomes predominant and makes the relaxation faster.

As to the future, it is expected that the research on nanomaterials will receive increasing attention. The two key issues are the influences of particle size and of surface characteristics on optical and electronic properties as well as performance in applications. Future research will

require development of new synthetic techniques to prepare particles with narrow size distributions, well-defined surface properties, and controllable shapes. Also, new experimental techniques are needed for better characterization of particle size, shape, and surface properties. Techniques that can combine the high spatial resolution from microscopy and high time resolution from ultrafast lasers may be able to provide a real time “nanoscopic” view of charge carrier dynamics in nanoparticles.

*I am indebted to my students and postdoctoral associates T. W. Roberti, B. A. Smith, R. H. O’Neil, J. E. Evans, K. W. Springer, M. A. Kreger, D. M. Waters, M. C. Brelle, L. Howe, and Dr. N. J. Cherepy, who participated in the research described here. I thank Drs. Y. Wang and P. V. Kamat for helpful discussions and Prof. J. F. Bunnett for critically reading the manuscript. Financial support from PRF/ACS, UCSC, and UC Energy Institute is gratefully acknowledged.*

AR960178J