

**OFFICE OF NAVAL RESEARCH**

**TECHNICAL REPORT**

**FOR**

**Grant N00014 91 J 1035**

**R & T Code 413302S - Robert Nowak**

**Technical Report No. 27**

**Electron Transfer from Quantum Confined Semiconductor Materials and Related Molecular  
Clusters to Simple Organic Acceptors: The Role of Surface Localized States for  
Metal-Chalcogenide Systems**

**(Presented in abstract form at the NATO Conference on Nanoparticles  
in Solids and Solution, March, 1996)**

**Donald Selmarten, Hui-Jean Liu, Joseph T. Hupp and Mark A. Ratner**

**Dept. of Chemistry and Materials Research Center  
Northwestern University  
Evanston, IL 60208  
U.S.A.**

**Reproduction in whole, or in part, is permitted for any purpose by the United States Government**

**Abstract:** Nanocrystalline, quantum-confined semiconductors have been extensively investigated from a fundamental physical perspective because of their exotic linear and nonlinear optical properties and their potential for application in submicron electronic and electrooptical devices. Semiconductors are also of considerable interest chemically and electrochemically, however, because of their ability to function as both sources and sinks for redox equivalents in interfacial charge transfer reactions (i.e., electron, hole and ion transfer reactions). These reactions are of potential or existing technological significance principally in five areas: 1) batteries, 2) electrochromics, 3) environmental remediation, 4) sensing, and 5) light to electrical energy conversion. In at least four of the five areas, distinct preparative or functional advantages can accrue from utilization of materials in nanocrystalline form. This, in turn, implies that issues of quantum confinement and semiconductor size may arise in interpreting and understanding interfacial reactivity and, ultimately, device performance.

In this paper we describe studies aimed at elucidating possible confinement and/or nanocrystallinity effects upon interfacial electron transfer reactions. We find that electron transfer from clusters and quantum-confined semiconductor (II-VI) particles to nearby molecular species can be observed optically. Furthermore, vibrational reorganization energies for these reactions can be evaluated in a fully mode-specific fashion via resonance scattering methods. Reaction comparisons as a function of cluster/particle size reveal that electron transfer occurs via surface-localized states, rather than valence bands, when acceptor molecules are covalently tethered. Related experiments involving coulombic association between mixed-chalcogen clusters and a molecular electron acceptor establish that outer-sphere electron transfer also occurs via surface-localized states. The combined results clearly emphasize the importance of surface-localized electronic states in charge transfer reactions. We suggest that they may also have significant implications for electron transfer at bulk semiconductor electrode/solution interfaces.

## I. Introduction

Nanocrystalline, quantum-confined semiconductors have been extensively investigated from a fundamental physical perspective because of their exotic linear and nonlinear optical properties and their potential for application in submicron electronic and electrooptical devices.<sup>1-</sup>

<sup>4</sup> Semiconductors are also of considerable interest chemically and electrochemically, however, because of their ability to function as both sources and sinks for redox equivalents in interfacial charge transfer reactions (i.e., electron, hole and ion transfer reactions). These reactions are of potential or existing technological significance principally in five areas: 1) batteries,<sup>5</sup> 2) electrochromics,<sup>6</sup> 3) environmental remediation,<sup>7</sup> 4) sensing,<sup>8</sup> and 5) light to electrical energy conversion.<sup>9</sup> In at least four of the five areas, distinct preparative or functional advantages can accrue from utilization of materials in nanocrystalline form. This, in turn, implies that issues of quantum confinement and semiconductor size may arise in interpreting and understanding interfacial reactivity and, ultimately, device performance.

In this paper we describe studies aimed at elucidating possible confinement effects upon interfacial electron transfer reactions, where emphasis - for experimental reasons - is placed upon direct light-induced reactions.<sup>10-13</sup> The target materials are II-VI semiconductors (specifically, cadmium sulfides and selenides) together with covalently or electrostatically attached organic acceptors. The strategy entails a “bottom up” approach: We begin with molecular clusters of sufficiently small size that all chalcogen atoms are necessarily surface atoms. We progress to larger clusters featuring both surface and core chalcogens. Ultimately we examine even larger quantum-confined semiconductor particles containing large numbers of core atoms and featuring real electronic band structure. The advantages of the “bottom up” approach lie in the ability to achieve essentially complete crystallographic<sup>14-18</sup> and electronic<sup>19</sup>

structural characterization of the smallest clusters and in the ability, in principle, to examine the size-based electronic evolution from molecule (cluster) to material.

## 2. Experimental

### 2.1 MATERIALS

$[\text{Cd}_4(\text{S-}\phi)_{10}](\text{N}(\text{CH}_3)_4)_2$  (S- $\phi$  is benzene thiolate),  $[\text{Cd}_4(\text{S-NB})_{10}](\text{N}(\text{CH}_3)_4)_2$  (S-NB is *para*-nitrobenzene thiolate),  $[\text{Cd}_{10}\text{S}_4(\text{S-}\phi)_{16}](\text{N}(\text{CH}_3)_4)_4$  and  $[\text{Cd}_{10}\text{Se}_4(\text{S-}\phi)_{16}](\text{N}(\text{CH}_3)_4)_4$  were prepared by literature methods.<sup>13,14</sup> Satisfactory elemental analyses were obtained.

$[\text{Cd}_4(\text{Se-}\phi)_{10}](\text{N}(\text{CH}_3)_4)_2$  (Se- $\phi$  is benzene selenolate), a synthetic intermediate, was prepared by adding  $\text{Cd}(\text{acetate})_2 \cdot 2\text{H}_2\text{O}$  (5.07 g, 19.0 mmol) in anhydrous methanol (20 ml) to a solution of benzene selenol (5.4 ml, 51 mmol) and triethylamine (7.1 ml, 51 mmol) in anhydrous methanol (20 ml) at room temperature under a nitrogen atmosphere, followed by addition of tetramethyl ammonium chloride (2.36 g, 21.5 mmol) in anhydrous methanol (20 ml). The mixture was stirred, with heating (65°C), until all the product had dissolved. A pale yellow precipitate (product) formed during cooling to room temperature. The product was isolated by filtration, washed with ether and dried in air. Anal. calcd. for  $\text{C}_{68}\text{H}_7\text{N}_2\text{Se}_{10}\text{Cd}_4$ : C, 37.84; H, 3.46; N, 1.30. Found: C, 37.92; H, 3.47; N, 1.28.

$[\text{Cd}_{10}\text{S}_4(\text{Se-}\phi)_{16}](\text{N}(\text{CH}_3)_4)_4$ . Powdered sulfur (0.046 g, 1.45 mmol) was added to a solution of  $[\text{Cd}_4(\text{Se-}\phi)_{10}](\text{N}(\text{CH}_3)_4)_2$  (2.31 g, 1.07 mmol) in acetonitrile (20 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred until all of the elemental sulfur had reacted. Addition of anhydrous ether yielded pale yellow microcrystallites. These were collected by filtration, washed with ether and stored under a nitrogen atmosphere. Anal. calcd. for  $\text{C}_{112}\text{H}_{128}\text{N}_4\text{S}_4\text{Se}_{16}\text{Cd}_{10}$ : C, 33.25; H, 3.19; N, 1.38. Found: C, 33.70; H, 3.18; N, 1.30.

$[\text{Cd}_{10}\text{Se}_4(\text{Se-}\phi)_{16}](\text{N}(\text{CH}_3)_4)_4$ . Powdered selenium (0.099 g, 3.11 mmol) was added to a

solution of  $[\text{Cd}_4(\text{Se}-\phi)_{10}](\text{N}(\text{CH}_3)_4)_2$  (2.10 g, 0.97 mmol) in acetonitrile (10 ml) at room temperature under a nitrogen atmosphere. The mixture was stirred until all of the elemental selenium had reacted. Addition of ether yielded pale yellow microcrystallites. These were collected by filtration, washed with ether and stored under a nitrogen atmosphere. Anal. calcd. for  $\text{C}_{112}\text{H}_{128}\text{N}_4\text{Se}_{20}\text{Cd}_{10}$ : C, 31.77; H, 3.05; N, 1.32; Cd, 26.55; Se, 37.30. Found: C, 29.81; H, 2.77; N, 1.10; Cd, 30.87; Se, 37.63. The analytical data here are less satisfactory than for related compounds. We tentatively ascribe the problem to loss of a selenolate capping group and a charge-compensating counter cation. (See, for example, reports by Herron and co-workers.<sup>17,18</sup>) Under these circumstances, the expected composition is: C, 30.60; H, 2.79; N, 1.05; Cd, 28.08; Se, 37.47.

Nitrobenzene functionalized, quantum-confined cadmium sulfide particles were obtained by a route similar to that used to obtain  $[\text{Cd}_{10}\text{S}_4(\text{Se}-\phi)_{16}](\text{N}(\text{CH}_3)_4)_4$  except that  $[\text{Cd}_4(\text{S}-\text{NB})_{10}](\text{N}(\text{CH}_3)_4)_2$  was used in place of  $[\text{Cd}_4(\text{Se}-\phi)_{10}](\text{N}(\text{CH}_3)_4)_2$ . Transmission electron microscopy studies established that the particles were nanocrystalline and yielded an average particle diameter of  $25 \pm 7$  Å. That quantum-confined particles rather than molecular clusters were obtained is somewhat surprising. This outcome is presumably a reflection of the comparatively poor basicity and, therefore, weak ligation and limited cluster “capping” ability, of *para*-nitrobenzene thiolate. In any case, the preceding protocol reproducibly yielded quantum confined particles. We acknowledge the efforts of Dr. Dong I. Yoon in preparing this compound and in pursuing additional characterization studies to be described elsewhere.

## 2.2 MEASUREMENTS

Electronic absorption spectra were obtained with a Hewlett-Packard model 8452A diode array spectrophotometer. Raman spectra were obtained by using instrumentation previously

described. Transmission electron microscopy data were obtained with a Hitachi model HF-2000 instrument.

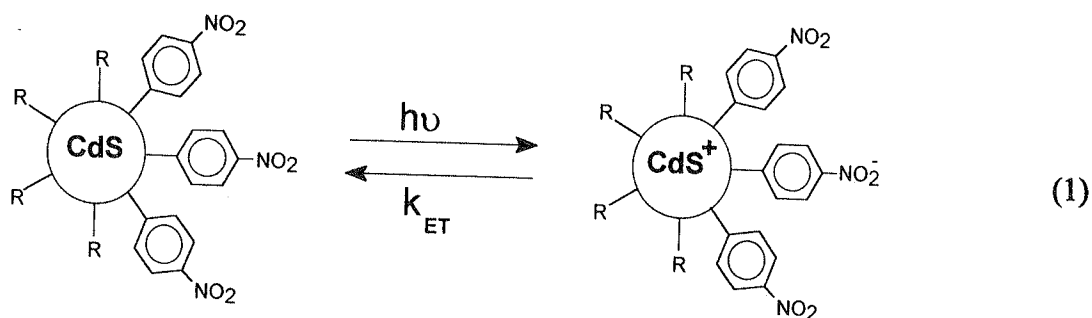
### 3. Results and Discussion

#### 3.1 GENERAL STRATEGY

Our general strategy is to use a semiconductor particle or cluster as an electron donor and an external molecule as an electron acceptor, or vice versa. When the donor and acceptor are in physical contact, a charge transfer absorption band can appear. Photolysis of this band then directly induces interfacial electron transfer (i.e. neither bandgap excitation nor intramolecular excitation is involved). By using this approach one can assess reaction energetics (by monitoring and fitting absorption lineshapes and maxima),<sup>13</sup> quantitatively evaluate reaction kinetics (by employing transient absorbance or luminescence spectroscopy)<sup>11,13</sup> and determine reaction barrier composition (by observing and processing resonance Raman scattering spectra).<sup>10,13</sup>

#### 3.2 COVALENTLY-LINKED INTERFACIAL DONOR/ACCEPTOR ASSEMBLIES

Our initial studies utilized cadmium sulfide species as electron donors and nitrobenzene molecules as acceptors:



As suggested by the drawings in eq. 1, the nitrobenzene molecules are covalently linked (via carbon-sulfur bonds) to the semiconductor particle or cluster. We recently described studies in

the extreme molecular limit where all sulfur atoms within a cadmium sulfide cluster ( $\text{Cd}_4(\text{S-NB})_{10}^{2-}$ , **1**) were also surface atoms.<sup>13</sup> Figure 1 shows electronic absorption spectra for **1** and for an analogue ( $\text{Cd}_4(\text{S-}\phi)_{10}^{2-}$ , **2**) featuring redox inactive capping groups. Based on resonance Raman scattering studies, the intense absorption band observed at 376 nm for **1** (but not for **2**) is associated with light-induced cluster-to-nitrobenzene charge transfer (eq. 1). A time-dependent analysis of resonance Raman enhancement effects induced by transition 1 yields a quantitative, mode-specific description of the vibrational reorganizational effects (Franck-Condon barrier effects) associated with the process. These effects, which are described in detail elsewhere,<sup>13</sup> are summarized graphically in Figure 2. Among the most significant observations in the Raman experiment is that charge transfer entails both inorganic cluster ( $\nu_{\text{Cd-S}}$ ) and organic acceptor (e.g.  $\nu_{\text{C-N}}$ ) mode displacement.

Despite the description of the excitation of **1** as a cluster-to-molecule charge transfer process, the possibility exists that it is a highly localized excitation. To test this possibility, we examined charge transfer in a larger system: a 25 Å diameter, quantum confined particle (**3**) capped with nitrobenzene. The expectation was that if the entire particle (i.e. the spatially delocalized valence band, in the semiconductor particle limit) served as the electron donor, the donor energy level would move higher, the nitrobenzene-localized acceptor energy level would remain fixed and the interfacial charge-transfer transition would move to lower energy with increasing cluster or particle size. Figure 3 shows the electronic absorption spectrum of **3**. A sharp feature exists at 376 nm and is assigned as an excitonic absorption. Observation of this feature provides evidence for: a) the existence of real electronic band structure, b) quantum confinement, and c) reasonable monodispersity (see experimental section). To expand briefly, in light of the known particle size dependence of excitonic absorption band energies in metal-

chalcogenide particles,<sup>1-4</sup> a well-resolved band would be expected only if a substantial population of particles of similar size were present. The second significant feature in Figure 3 is a broad absorption centered at 360 nm and assigned as the interfacial charge-transfer transition (eq. 1). In contrast to our expectations, charge transfer from the large particle to attached nitrobenzene occurs at nearly the same energy as charge transfer from the molecular cluster to nitrobenzene (Figure 1). The energy equivalence implies electron transfer in both cases from surface localized states – specifically, surface sulfur *p*-orbital localized states, where the driving force for localization presumably is surface sulfur-carbon bond formation (i.e. acceptor attachment). Supporting evidence for the localized donor state comes from comparative resonance Raman experiments. Resonant scattering from the putative charge transfer band yields data similar to that shown in Figure 2. Resonant scattering from the excitonic transition, on the other hand, yields enhancement – as expected – only in a CDs lattice or phonon mode. Importantly, however, the phonon mode, which describes collective *interior* cadmium-sulfur stretching motions, occurs at a different frequency (370 cm<sup>-1</sup>) than the charge-transfer coupled  $\nu_{\text{Cd-S}}$  mode (325 cm<sup>-1</sup>).

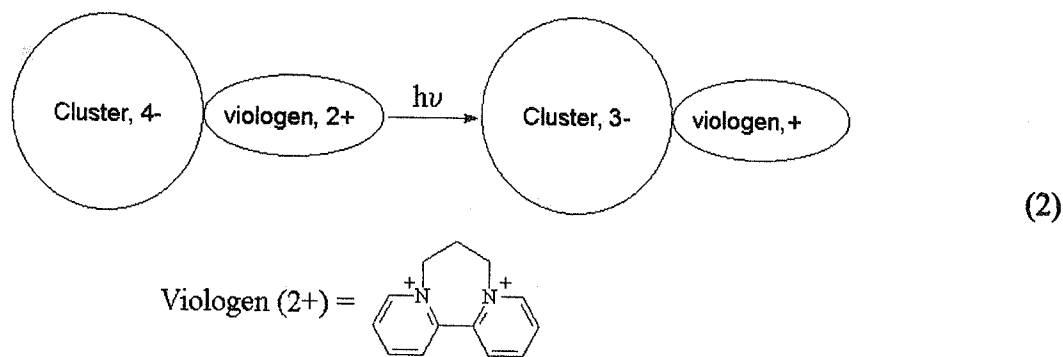
### 3.3 ELECTROSTATICALLY LINKED DONOR/ACCEPTOR ASSEMBLIES

To gain further insight into the role played by surface electronic states, we additionally prepared a series of systems in which we arbitrarily changed the chemical identity of core versus surface chalcogen atoms. Each system featured 4 core chalcogen atoms, 16 surface chalcogen atoms and 10 cadmium atoms.<sup>14</sup> Thus, the systems are best described as large molecular clusters, rather than quantum-confined particles. Electronic absorption spectra for the four clusters (Cd<sub>10</sub>S<sub>4</sub>(S- $\phi$ )<sub>16</sub><sup>4+</sup>, 4; Cd<sub>10</sub>Se<sub>4</sub>(S- $\phi$ )<sub>16</sub><sup>4+</sup>, 5; Cd<sub>10</sub>S<sub>4</sub>(Se- $\phi$ )<sub>16</sub><sup>4+</sup>, 6; Cd<sub>10</sub>Se<sub>4</sub>(Se- $\phi$ )<sub>16</sub><sup>4+</sup>, 7) are shown in Figure 4. The spectra are remarkably similar. Significant differences exist, however, for



wavelengths greater than ~310 nm: Distinct shoulders exist in the spectra of 5 and 7, a red tail is observed for 6, but absorption is absent for cluster 4. The spectrally unique cluster (4) is also compositionally unique in the sense that it is the only cluster that lacks selenium. In each system, the lowest energy transitions almost certainly involve chalcogenide charge transfer – either to cadmium(II) or possibly to a benzene-based  $\pi^*$  orbital. Selenium, with its diminished electronegativity, should be superior to sulfur as an electron donor. This, in turn, will cause selenium based charge-transfer transitions to appear at lower energy (longer wavelength) than sulfur based transitions.

We have taken advantage of the electronegativity differences in a series of experiments in which clusters serve as electron donors and electrostatically bound viologen molecules (see eq. 2) serve as electron acceptors. The objective of the experiments was to determine whether electrons



were transferred from the cluster core or instead from the cluster surface. Figure 5 summarizes the findings: Weak donor-acceptor charge transfer bands appear as shoulders in the blue and green portions of the electronic spectrum when clusters coulombically associate with viologens. Clusters 4 and 5, which feature sulfur atoms in surface coordination sites, yield charge transfer transitions at similar wavelengths (ca. 450 nm). Cluster 6, on the other hand, features selenium atoms in surface coordination sites and yields a charge transfer transition at considerably lower

energy (longer wavelength; ~520 nm). (Cluster 7 proved to be insufficiently soluble in the presence of the viologen to yield a satisfactory spectrum.) Thus, charge transfer energies for reaction 2 are correlated with the ease of reduction of chalcogenides on the surface of the cluster. A corresponding correlation with core chalcogenide properties, however, is absent. We conclude that outer-sphere optical charge transfer from small clusters containing both surface and core chalcogen atoms occurs from orbitals that are largely surface localized.

#### 4. Conclusions

Electron transfer from clusters and quantum-confined semiconductor (II-VI) particles to nearby molecular species can be observed optically. Furthermore, vibrational reorganization energies for these reactions can be evaluated in a fully mode-specific fashion via resonance scattering methods. Reaction comparisons as a function of cluster/particle size reveal that electron transfer occurs via surface-localized states, rather than valence bands, when acceptor molecules are covalently tethered. Related experiments involving coulombic association between mixed-chalcogen clusters and a molecular electron acceptor establish that outer-sphere electron transfer also occurs via surface-localized states. The combined results clearly emphasize the importance of surface-localized electronic states in charge transfer reactions. We suggest that they may also have significant implications for electron transfer at bulk semiconductor electrode/solution interfaces.

#### 5. References

1. Bawendi, M. G., Steigerwald, M. L., Brus, L. E., (1990) *Ann. Rev. Phys. Chem.* **41**, 477.
2. Brus, L. E., (1990) *Acc. Chem. Res.* **23**, 183.
3. Wang, Y.; Herron, N., (1991) *J. Phys. Chem.* **95**, 525.
4. Alivisatos, A. P., (1996) *Science* **271**, 933.

5. Megahed, S., Scrosoti, B., (1995) *Interface* **4** (no. 4), 34.
6. Zhang, J-G., Benson, D. K., Tracy, C. E., Deb, S. K. Czanderna, A. W., Crandall, R. S., (1994) *J. Electrochem. Soc.* **141**, 2795.
7. Gerischer, H., Heller, A., (1992) *J. Electrochem. Soc.* **139**, 3136.
8. Neu, D. R., Olson, J. A., and Ellis, A. B., (1993) *J. Phys. Chem.* **97**, 5713.
9. O'Regan, B., Grätzel, M., (1991) *Nature* **353**, 737.
10. Blackbourn, R. L., Johnson, C. S., and Hupp, J. T., (1991) *J. Am. Chem. Soc.* **113**, 1060-1062.
11. Lu, H., Preiskorn, J. N., Hupp, J. T., (1993) *J. Am. Chem. Soc.* **115**, 6428.
12. Tuerk, T., Resch, U., Fox, M. A., and Vogler, A., (1992) *Inorg. Chem.* **31**, 1854.
13. Yoon, D. I., Selmarten, D. C., Lu, H., Liu, H.-J., Mottley, C. A., Ratner, M. A., and Hupp, J. T., (1996) *Chem. Phys. Lett.*, in press.
14. Dance, I. G., Choy, A., and Scudder, M. L., (1984) *J. Am. Chem. Soc.* **106**, 6285.
15. Dance, I. G., (1986) *Polyhedron* **5**, 1037.
16. Lee, S. H., Fisher, K. J., Vassallo, A. M., Hanna, J. V., and Dance, I. G., (1993) *Inorg. Chem.* **32**, 66.
17. Herron, N., Suna, A., and Wang, Y. (1992) *J. Chem. Soc., Dalton Trans.* 2329.
18. Herron, N., Calabrese, J. C., Farneth, W. E., and Wang, Y. (1993) *Science* **259**, 1426.
19. Liu, H.-J., Hupp, J. T. and Ratner, M. A., *J. Phys. Chem.*, submitted.

## FIGURE CAPTIONS

1. Electronic absorption spectra for clusters 1 (solid line) and 2 (dotted line) in methanol as solvent.
2. Mode-specific contributions to the vibrational reorganization energy for cluster to nitrobenzene charge transfer in assembly 1.
3. Electronic absorption spectrum for a nitrobenzene decorated cadmium sulfide nanoparticle in acetonitrile as solvent.
4. Electronic absorption spectra for clusters 4 ( $\epsilon_{\max}(256 \text{ nm}) = 160,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 5 ( $\epsilon_{\max}(256 \text{ nm}) = 140,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 6 ( $\epsilon_{\max}(246 \text{ nm}) = 170,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 7 ( $\epsilon_{\max}(250 \text{ nm}) = 190,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) in acetonitrile as solvent.
5. Charge transfer absorption spectra for 4/viologen, 5/viologen and 6/viologen donor-acceptor pairs in acetonitrile as solvent.

