

## Surface Effects on the Chemical and Optical Properties of Semiconductor Nanocrystals

Jess P. Wilcoxon<sup>1</sup>, James M. Kraus<sup>2</sup>, and Billie L. Abrams<sup>1</sup>,

<sup>1</sup>Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-1421

<sup>2</sup>Dept. of Chemistry, U. of Washington, Seattle, WA

We discuss the effect of cluster surface chemistry on the chemical and optical properties of 1-3nm nanocrystals. In this size regime, 90 to 50% of the atoms reside on the surface. Dispersed solutions of such nanocrystals rely on chemical ligation with surfactants. These surfactants affect both the cluster surface structure and the cluster optical properties.

We give examples of the effect of cluster surface structure in two material classes of nanocrystals. The first, CdS with surface deposited Mn(II) and ZnS exhibits major changes in solution photoluminescence (PL) and photoluminescence excitation (PLE) spectra. These changes are dependent upon the Cd:Zn ratio on the surface. Figure 1 demonstrates that for a fixed Mn ion concentration, both the PL and PLE depend strongly on the amount of ZnS deposited on the surface of the 1.9 nm CdS clusters. The effect of deposition of ZnS is to alter the allowed energies of the interface states that efficiently transfer the energy absorbed by the CdS to the emitting Mn ions. Unlike the parent CdS clusters which have a much broader excitation spectrum, these surface modified clusters have a very narrow range of energy which results in PL. The surface deposits of ZnS and Mn have a negligible effect on the cluster absorbance spectra, whose energy onset is determined primarily by the core states of the CdS nanocrystals.

In the second materials class, the effects of the cluster interface of small clusters (1.4-2 nm) of Si and Ge which are initially terminated with hydrogen were investigated [1,2]. Ab initio modeling of the surface chemistry of such clusters has recently identified surfactants as critical to their electronic properties [3]. For example, figure 2, shows the effect of addition of an alkyl amine to a 1.8 nm hydrogen terminated Si cluster. The absorption onset and features remain invariant but the PL red shifts and broadens. We have observed similar effects in the PL of CdS clusters following addition of alkyl thiols. The addition of these surfactants appears to weaken the bonds of the Si atoms in the interface, increasing their mobility and thus the rate of surface reconstruction. This change in the cluster surface affects both the PLE and PL spectra.

Finally, we discuss the effects of addition of luminescent ions like Sb and Mn onto the surface of 1-2 nm Si and Ge clusters. Our purpose is to separate the absorbing states of the core cluster from the emitting states on the cluster surface. We use high performance liquid chromatography to evaluate the changes in cluster surface chemistry and optical properties as a function of surfactant and cluster age.

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### References

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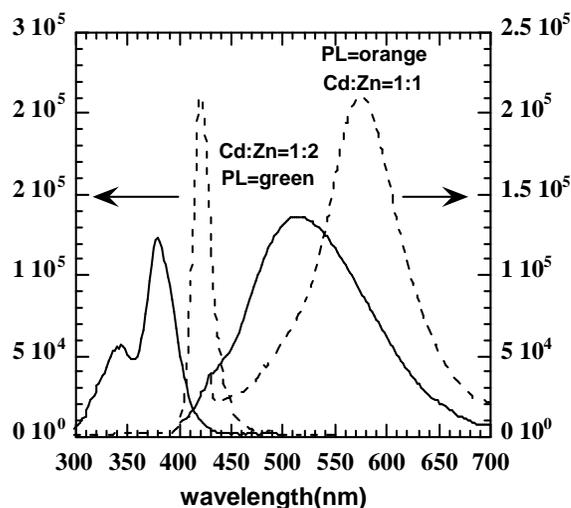


Figure 1. Coplot of Photoluminescence (PL) and Photoluminescence excitation (PLE) spectra of 1.9 nm CdS nanocrystals with Mn(II) on the surface and the indicated Cd:Zn ratio = 1:2 (solid line).

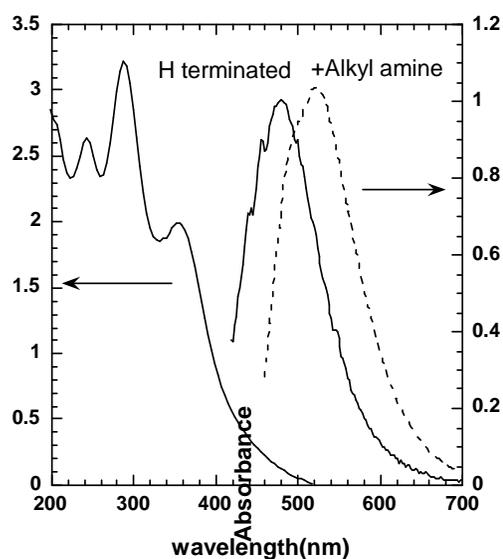


Figure 2. Effect of the addition of an alkyl amine surfactant followed by ambient T aging under inert atmosphere for 1.8 nm hydrogen terminated Si clusters in toluene on the absorbance and photoluminescence (PL).