

## REVIEW

# THE BAND EDGE LUMINESCENCE OF SURFACE MODIFIED CdSe NANOCRYSTALLITES AND THEIR APPLICATIONS

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**Abstract** – In this paper, a brief overview of nanocrystallites of metal and semi-conductor materials will be presented, and then the novel synthetic method of high quality CdSe nanocrystallites developed by Bawendi group at MIT will be introduced. It will be shown that results of optical properties of surface modified nanocrystallites give the evidence that the luminescence of CdSe nanocrystallites is not originated from surface related trap states, but from intrinsic spin forbidden core states. Some of the interesting applications of CdSe nano-crystallites will also be discussed at the end.

## INTRODUCTION

The fundamental feature of nanocrystallites (or nanoclusters) is their diminutive size; they have diameters of only tens or hundreds of Angstroms. Nanoclusters are so small because they contain a relatively small number of atoms, and they have properties that are characteristic of neither the corresponding molecules nor the bulk materials. Therefore, nanocluster properties bridge the gap between molecular and bulk properties. With so few atoms, the molecular orbital band structure is not completely developed as it is in bulk material. The incomplete band structure causes a variety of quantum size effects such as new electric, electronic, optical and magnetic properties.<sup>1,2</sup> Due to these quantum size effects, nanoclusters are often called as quantum dots (QDs). Various nanoclusters such as metals, metal oxides, and semiconductor materials have been prepared and studied not only to study their fundamental quantum size properties, but also to use their novel properties for many interesting applications.<sup>1-3</sup>

## PREPARATION METHODS

There are a variety of methods to prepare nanoclusters. One of the most common and oldest ways to synthesize metal nanocluster is the reduction of metallic acid or salt in a colloidal solution. A typical example to make gold nanocluster starts with a solution of chloroauric acid. The gold is reduced with reducing agents such as sodium citrate, and collected within the colloid to form nanocluster. Then

the surface of nanocluster is passivated with protecting agents to hinder further aggregation. The size of nanocluster obtained depends upon the pH of the initial solution, the concentration of the reducing agent, temperature. Monodisperse 3-5 nm particles of gold, palladium, platinum, rhodium, and iridium have been synthesized with this technique. The colloidal technique has been used to synthesize metal alloy nanoclusters of gold and platinum<sup>4</sup> or of palladium and platinum<sup>5</sup>. In both cases, salts of the two metals were simultaneously reduced.

Another common nanocluster synthesis technique is the evaporation of metals in a vacuum. A large number of articles have been published to account for the observed early stages of evaporation and to discuss the various mechanisms leading to cluster growth including island coalescence and single-atom processes often referred to as Ostwald ripening. The metal atoms condense on a cold substrate, and aggregate to form clusters. The evaporation / condensation process provides little control over the location of the clusters on the substrate. This technique also suffers from the drawback of not providing large quantities of materials. In order to avoid difficulties of coalescence and growth limiting the production of very small particles, new improved technique employs vacuum evaporation onto a running oil substrate (VEROS). Evaporated metal atoms could be collected into a suitable matrix such as cryogenic CO<sub>2</sub> or Xe matrices, inorganic SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> matrices, and organic polymer matrix.<sup>3</sup>

Semiconductor nanoclusters such as CdS and CdSe have been synthesized by modified colloidal technique, so called inverse micelle preparation.<sup>6</sup> This inverse micelle preparation has the advantage that the surface of the nanoclusters can be passivated or capped in a secondary reaction. Zeolites and Nafion( have also been loaded with metal salt and chalcogenide reagents to produce a variety of

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† Presented in part at the Annual Meeting of the Korean Society of Photoscience, Taejon, Korea, June 12, 1998.

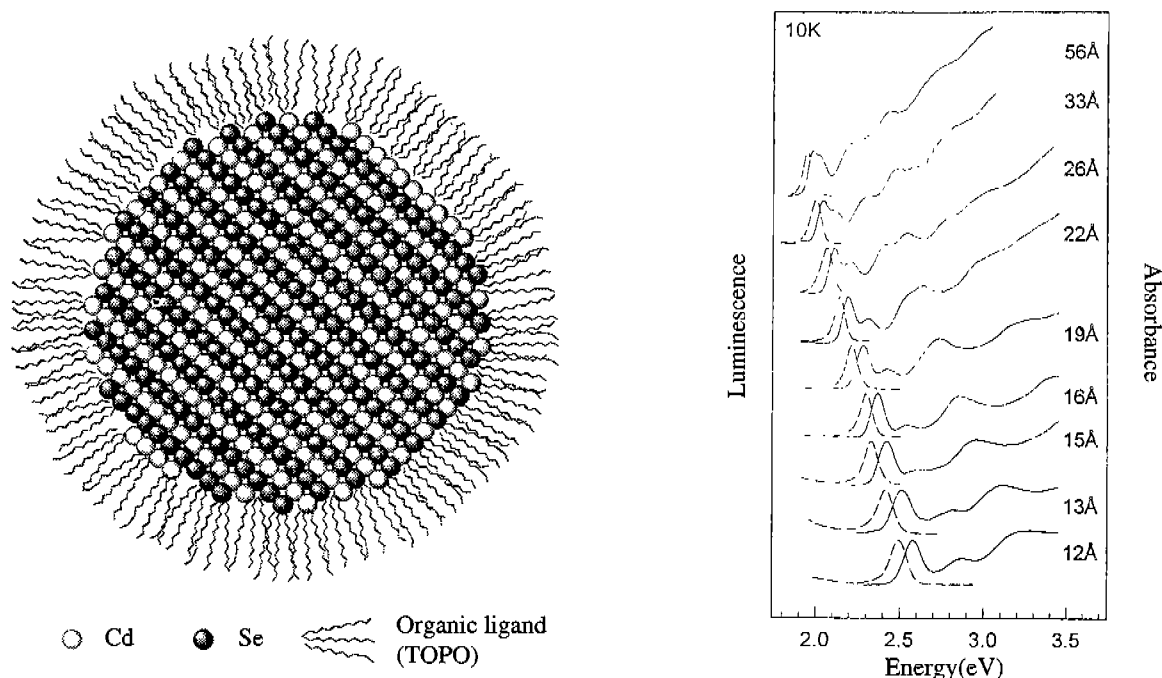


Figure 1. Schematic structure of CdSe nanocluster stabilized with TOPO and its absorption and emission spectra.

different semiconductor nanoclusters.<sup>7</sup> In contrast to the inverse micelle preparation, however, the pore size of the materials does not act to physically limit the size of nanoclusters and nanoclusters formed in zeolites and nanoporous resins is permanently imbedded in the host.

#### NEW PYROLYSIS TECHNIQUE OF ORGANOMETALLIC PRECURSORS

One of the most significant progresses in preparing semiconductor nanoclusters is the pyrolysis of organometallic precursors in the presence of excess organic ligands, developed by Bawendi group at MIT.<sup>8</sup> This synthesis derives from classical colloidal chemistry where a rapid nucleation event is followed by slow growth of the nuclei.<sup>9</sup> The organometallic precursor, dimethyl cadmium ( $\text{CdMe}_2$ ) and trioctylphosphine selenide (TOPSe), are injected into a coordinating solvent (trioctylphosphine oxide, TOPO) at high temperature ( $340 \sim 360^\circ\text{C}$ ). Pyrolysis of the precursors leads to a supersaturation of reactants followed by the formation of small CdSe nuclei almost instantaneously. The nuclei grow via Ostwald ripening (the growth of large particles at the expense of smaller ones due to the difference in surface free energies between the different sizes) at moderately high temperatures ( $250 \sim 300^\circ\text{C}$ ). When a desired size is reached the samples are cooled to  $80^\circ\text{C}$  and mixed with butanol to prevent solidification of the TOPO during storage at room temperature. The size distribution of the samples is improved further by using size selective precipitation.<sup>3</sup> In this technique, a poor-solvent (methanol)

is slowly added to the CdSe solution until the largest nanoclusters begin to flocculate leaving smaller nanoclusters in solution. From this technique, nearly monodisperse ( $\sigma \leq 5\%$ ) CdSe nanoclusters ranging in size from  $1.5 \sim 10$  nm can be prepared. (Figure 1) The nanocluster is slightly prolate (aspect ratio between  $1.1 \sim 1.3$ ), and has a crystalline Wurtzite core with the lattice parameter of bulk CdSe and a surface passivating layer of TOPO making the nanoclusters hydrophobic and soluble in non-polar or slightly polar organic solvents.

#### PHOTOLUMINESCENCE FROM THE CdSe NANOCLUSTERS

Since the emergence of relatively new techniques for the preparation of nanoclusters, considerable progress has been made in the analysis and assignment of most of the features in the optical absorption spectra.<sup>10</sup> These various models have been proposed which quantitatively explain the observed trends and for the most part the linear absorption is thought to be well understood. The emission of these nanoclusters, however, has been fairly controversial and difficult to interpret. This is due to the fact that the luminescence of many nanoclusters is dominated by a broad featureless emission (known as "deep trap" emission) strongly red-shifted from the band edge. Recent results obtained from high quality CdSe nanoclusters have shown strong luminescence near the band edge and in doing so have raised a number of questions regarding the nature of the emitting state.<sup>11</sup> For example, the luminescence has a

long lifetime at 10K ( $\sim \mu\text{s}$  vs. ns in the bulk CdSe) and has size-dependent redshift from the peak of the band edge absorption. Earlier papers in this field attributed the emission to shallow surface trap states.<sup>12</sup> In the surface model it was believed that one carrier, presumably the hole, would become localized onto a shallow surface trap site while the other carrier remained delocalized over the entire volume of the nanocluster. The localization of the hole would lead to reduced overlap of the electron and hole wavefunctions and hence increased radiative lifetimes.

A recently developed theory by Efros attributes the luminescence in CdSe nanoclusters to intrinsic spin forbidden core states.<sup>13</sup> This theory takes into account the electron-hole exchange interaction, the nonspherical shape of individual crystallites, and the hexagonal symmetry of the lattice. These effects lift the 8 fold degeneracy of the exciton states yielding five new fine structure states with total angular momentum projections  $\pm 2$ ,  $\pm 1$ ,  $0$ ,  $\pm 1$ ,  $0$ . Most importantly this model predicts that the lowest excited state in CdSe nanoclusters is an optically inactive fine structure state or "dark" exciton with angular momentum projection  $\pm 2$ . The presence of the dark exciton explains both the long lifetimes and the redshift of the luminescence as linear optical transitions into and out of the state are formally spin forbidden.

### SURFACE MODIFICATION OF CdSe NANOCLUSTERS

In order to address the issue of whether the luminescence from CdSe nanoclusters is surface related or arises from the radiative recombination of core states as discussed above, the surface of CdSe nanoclusters were systematically changed with a variety of organic and inorganic ligands.<sup>14</sup> Then the effect of the surface ligands on the luminescence is monitored through two experiments; a photoluminescence (PL) and a fluorescence line narrowing (FLN) experiment.<sup>15</sup> In these experiments, non-resonant and resonant Stokes shift for a series of surface modified CdSe nanoclusters passivated by trioctylphosphine oxide (TOPO), ZnS, 4-picoline, 4-(trifluoromethyl)thiophenol, and tris(2-ethylhexyl)phosphate are in good agreement with each other and with the predictions of the intrinsic exciton ("dark" exciton) model.

There is couple of more important reasons for modifying the CdSe nanoclusters. First of all, the processible (soluble in common solvent) CdSe nanoclusters have attracted much attention to use them as an "artificial" atom, and to explore further chemical reactions on the surface ligands. The optical, electrical, and electronic properties are expected to be very sensitive to the properties of surface ligands either in solution or in solid film states. Modifying the surface ligands to make them soluble in water can open new areas of the nanocluster application. The water-soluble CdSe nanoclusters make it possible to use lots of well developed

processing techniques in water, and when they are attached into biomaterials they can provide a new powerful analysis method such as a multi-site diagnostic sensor.

### INTERESTING APPLICATIONS OF SURFACE MODIFIED CdSe NANOCLUSTERS

Previous studies have aimed at understanding the structural, electronic, and optical properties characteristic of individual CdSe nanoclusters. Most studies have proved dilute sample of nanoclusters where the distance between the clusters is large and random and the clusters behave as individual entities. However, recent advances in the fabrication of two- and three-dimensional nanocluster solids from soluble CdSe nanoclusters make the study of interdot coupling possible.<sup>16</sup> Deposition of nanoclusters, controlled by tailoring the composition of the solvents, can produce either glassy or ordered close packed nanocluster solids. Electronic energy transfer arising from dipole-dipole interactions between proximal nanoclusters in close packed nanocluster solids has been studied.<sup>16c, 17</sup>

Photoconductivity is another well-known phenomenon in semiconductors and organic solids, and as expected close packed CdSe nanoclusters show photoconductivity. However, the physics of electronic transport in these systems is not well understood yet. Preliminary experiments of photoconductivity of close packed CdSe nanoclusters show the dependence of the photocurrent on applied voltage, excitation energy, excitation intensity, and temperature to elucidate the mechanism of charge generation, separation and transport. Most importantly, the spectral response of the photocurrent follows the absorption spectra for the nanocluster solids, demonstrating carrier generation in the nanoclusters. The weak intensity of the photocurrent can be explained due to the high energy barrier of organic ligands (TOPO) between nanoclusters. Since TOPO contains long saturated alkyl chains, it has lower HOMO and higher LUMO states than those of CdSe nanoclusters do. In order to enhance the transportation of photogenerated holes and electrons through close packed nanocluster solids, new organic spacer molecules that have better energy match with CdSe nanocluster have been introduced into the organic space (TOPO region) between nanoclusters in close packed solids. However, the position of both HOMO and LUMO levels of new conjugated ligands compared to CdSe nanocluster is very important, otherwise they actually trap holes and electrons. The solubility of the new spacer molecules in the solvent system from which nanocluster close packed solids are produced, is also another important factor to produce homogeneous solid film. Diphenoquinone type compound is one of the promising candidates, and the preliminary result shows increased photocurrent with this new conjugated spacer molecule.

Other interesting application of nanoclusters is using them

as a sensor for bioanalysis. A conventional technique to monitor the specific site within the biomaterial is called staining technique. In this technique, the affinity-purified antibody is selectively attached to the monitoring site, and organic chromophore molecule is connected either directly onto antibody itself or through a strong biotin-avidin linkage. The chromophore molecule can be attached onto avidin or biotin in the latter case. Organic chromophore molecules using for this staining purpose, however, have relatively broad absorption and emission band width (150 ~ 200 nm). Therefore, the multi-site monitoring by introducing different chromophores in different sites is impossible due to the significant overlap of spectra. Recently surface modified water-soluble Au and Ag nanoclusters were used to monitor the specific site in the biomaterials.<sup>18</sup> Since these metal nanoclusters do not have luminescence property, however, only absorption spectroscopy or electron microscopy (EM) technique was used to monitor their positions. A broadness of metal nanocluster absorption and the complicated preparation for EM technique, however, is a still major drawback of conventional staining technique. As described in the preparation section, nearly monodisperse ( $\sigma \leq 5\%$ ) CdSe nanoclusters ranging in size from 1.5 ~ 10 nm can be easily prepared. Their photoluminescence quantum yield is ranging from 10 ~ 50% at room temperature with narrow absorption and emission band width of 50 ~ 60 nm. In order to use these unique luminescence properties of CdSe nanoclusters for bioanalysis, the surface of nanoclusters is modified with  $\alpha, \omega$ -thioalkylcarboxylic acid followed by titration with base to generate water-soluble salt forms. CdSe nanoclusters still shows a reasonably good photoluminescence quantum yield (~16%) in water solution. These water-soluble CdSe nanoclusters are connected into biotin through amide linkage, and the final biotin-avidin coupling step is under investigation. When these narrow size-distributed CdSe nanoclusters are being used for bio-diagnostics, it will be possible to monitor multi-site at a time with simple absorption or emission technique, and the more precise monitoring is also possible by combining with electron microscopy technique.

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