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Surface modification of CdSe nanocrystals with organic ligands

INTRODUCTION

Nanomaterials and nanostructures have organizational features intermediate on a scale between single molecules and about 100 nm. Novel properties occur on this scale, compared with properties of bulk materials (1). As a result of intermolecular Coulomb, Van der Waals and London forces, a particle is always surrounded with other molecules adsorbed on its surface from the environment. However, this simple fact has much more important implications when we consider nanoparticles that have extremely large surface/volume ratio.

First, let us take a look at the results of a simple calculation (Table I). When we compare uniform nanoparticles to a macroscopic object (assuming equal total volume) we find that the surface of these CdSe quantum dots is 2.63 million times larger than of the bulk object. This huge surface results in enormous surface energies, increased physical activity and chemical reactivity which cannot be neglected, unlike in the case of bulk materials. Present technological interest in nanocrystals stems from the prospect of creating novel materials with distinct physical properties. It is clear, that a significant control of particle properties is needed (size, distribution, interactions) to successfully and reproducibly assemble nanostructures with required properties. One of the major inherent problems is a general one, namely that in a closed system, all intensive parameters (pressure, mass, temperature) equalize, while all extensive system parameters (linear characteristic size, volume, surface area, number of particles) sum up. Consequently, manipulation of uniform particles would require a perfect process to preserve the narrow distribution of size related properties.

Surprisingly, there are such processes that are close to ideal (2,3). Recent improvements in the synthesis of CdSe nanoparticles organically passivated with trioctylphosphines, allow one to obtain very low polydispersity nanocrystals with only a 5-10%

<table>
<thead>
<tr>
<th>Table I - Comparison of diameter, volume and surface of two spherical particles: one is a macroscopic object, the other is a Cd$<em>{32}$Se$</em>{527}$ nanoparticle (see later)</th>
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<tbody>
<tr>
<td>Particle Diameter</td>
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<tr>
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<tr>
<td>d = 1 cm</td>
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<td>d = 39 Å</td>
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Every solid particle has adsorbed molecules on its surface under atmospheric conditions. This interface is particularly important when a system is composed of nanoparticles thus change of optical properties can directly be observed.
standard deviation in size and with photoluminescence (PL) quantum yields of 10-15%. We will illustrate the importance of surface conditions from the point of view of the surface chemistry of these inorganic semiconductor nanocrystals. The interest in this field keeps increasing due to various potential applications of QDs, such as in optical applications (4,5) optoelectronic devices (6-8) and multi-color biosensing (9-11) as they are more stable against photobleaching than functionalized organic dyes. Understanding and controlling factors that govern these properties will benefit everyone in society, as these materials and structures open up the way towards smaller, faster, bright, and low-cost devices.

SEMICONDUCTOR NANOCRYSTALS

Luminescent properties of semiconductor nanocrystals have attracted a lot of attention recently because at room temperature nanocrystals can be better photoemitters than bulk semiconductors. Semiconductor nanocrystals possess unique properties that change with the particle size due to size quantization effect on the nanometer scale (12-15). These properties are equally interesting for physicists, material scientists, and chemists. Semiconductor nanocrystals, sometimes called quantum dots, QDs, exhibit these unique optical and electronic properties due to confinement of the electronic excitations. These nanocrystals act like molecules as they interact with light via their electronic transition dipoles (16). The important difference is that the radiationless internal conversion (recombination of an electron-hole pair by unimolecular decay converting electronic energy into heat) is extremely slow in these nanocrystals and excited states decay radiatively in a defect-free, direct gap semiconductor such as CdSe (17). These simple facts have important practical consequences. Semiconductor light-emitting diodes have narrow emission bands and can show near 30% efficiency in converting electrical power into light. Semiconductor lasers and diodes also show excellent long-term stability against photochemical and current-induced degradation, when compared with many organic materials. Their photoluminescence (PL) emission can be tuned across the visible spectrum by simply changing the particle radius for CdSe nanocrystals (18).

Note: The strong size dependence of nanocrystal optical properties, while an asset in their practical use, represents a problem in scientific experiments. Even the best samples may have distributions of size, shape, and surface chemistry, and thus have slightly varying optical properties.

SINGLE NANOCRYSTAL LUMINESCENCE

After a decade of research, recent single nanocrystal luminescence studies still have revealed new processes in nanocrystals, such as spectral diffusion and the random intermittency of the fluorescence (19-21). It was observed that single CdSe nanocrystals embedded in a thin polymer film do individually "blink" (the luminescence turns on/off) on a several second time scale (17). In previous experiments this "blinking" was missed, as it averages to zero when many nanocrystals are observed simultaneously. Fluorescence intensity versus time traces taken at low and at high intensity show that the "on" period duration scales inversely with excitation intensity, while the "off" period appears to be intensity independent. This result suggests that the nonemissive state is created via the nanocrystal excited state. The bright state is however recreated by a spontaneous thermal process from the nonemissive state.

In the absence of defects, internal or surface, a nanocrystal should exhibit near unity fluorescence quantum yield, and partial protection from quenching. This represents a significant advantage over organic chromophores.

STABILIZATION OF CdSe QDs BY INORGANIC OVERCOATING: SHELL NANOCRYSTALS

While the "band edge" emission is intrinsic in origin, the surface still provides sites for nonradiative recombination. As synthesized, the TOPO/TOPSe passivated CdSe nanocrystals exhibit room-temperature quantum yields between 5 and 10%. Substitution of the TOPO/TOPSe surface capping groups results in variations in the luminescence yield and a suppression/increase in the "deep trap" emission (22,23).

To increase the quantum yield the elimination of midgap surface states is necessary with appropriate surface passivation. This is usually done either by inorganic overcoating or by absorbing protective organic molecules onto the surface.

The beneficial effect of inorganic overcoating was understood in terms of a higher band gap material (ZnS) passivating a lower band gap material (CdS) (24). Near epitaxial monolayer of ZnS on CdSe nanocrystals (25,26) exhibit quantum yields of up to 50% at room temperature. However, the 12% difference in bond lengths between CdSe and ZnS results in significant lattice mismatch and increasing strain with ZnS thickness. Recently CdS-overcoated CdSe nanocrystals with only 3.9% of lattice mismatch have also been synthesized (27).

Encapsulated nanocrystals exhibit improved photostability. However, a strong decrease in the photoluminescence (PL) intensities was observed with time even for highly luminescent (CdSe)ZnS core-shell nanocrystals in quantum dot composites, due to degradation. Experiments carried out at high laser fluences show that the PL intensity decay with time depends both on the size of the nanocrystals and the nature of the surrounding matrix (28).

Based on theoretical considerations, the influence of
external charges on the photoluminescence of a CdSe/TOPO have recently been calculated for Cd_{34}Se_{17}, and for Cd_{35}Se_{23} nanocrystallites (29). It has been concluded that when a negative trapped charge is on the surface near a top Cd atom, it is enough to cause a significant seventy-fold reduction on the radiative decay rate by pulling the electron and hole apart.

In short, nanocrystals have the potential to serve as ideal chromophores if their surface chemistry can be understood and controlled.

ORGANIC SURFACE LAYERS ON THE CdSe SURFACE

Now it is generally accepted that the origin of the narrow, band-edge photoluminescence of QD band edge emission is intrinsic (30-32), while the surface provides nonradiative recombination sites that influences quantum yield (17). Organic ligands were mainly used only to provide QDs with solubility and stability. Recently, several studies have reported results emphasizing the importance of organic surface layers (33). For example, enhanced photoluminescence was observed using simple amine (e.g. triethylamine) caps for CdS or Cd_{3}As_{2} (34) thioglycolic acid for CdTe (35), and hexadecylamine for CdSe (36).

The PL enhancements in the above cases were explained by binding at the defect Cd site to decrease nonradiative recombination, formation of cadmium thioglycolic acid complexes, and a redistribution of surface electronic density, respectively. The adsorbed molecules not only determine the stability of the nanoparticles, but also influence their optical properties and control their compatibility with the actual physical environment.

Apparent, organic surface ligands play a very important role in changing the PL properties of QD systems, however, this issue is not completely understood so far.

Mechanism of “capping” nanoparticles with organic molecules appear to be similar to metal ion complexation, i.e., a donor-acceptor type interaction between the NP surface and the ligand site of the organic molecule. If surface caps were bound covalently, dry nanoparticles may remain soluble when solvent is added. However, in case of a dynamic equilibrium between the absorbed and the “free caps”, an excess of organic molecules must be present in the solution and dilution of a sample may lead to precipitation.

In an effort to elucidate the influence of the different functional groups, we studied the optical behavior and stability capped with organic molecules as a function of their binding functionalities. In our approach, we have used constant amount of nanoparticles and preset an identical amount of air present in each vial. We also used chloroform as a solvent, which does not favor the absorption of moisture. Therefore, we assume that short-term changes are dominated by the exchange of ligands and their donacity, but later data are informative of the protection of nanoparticles by the various dendrimer caps. We followed the optical properties of the CdSe/PAMAM systems for over two months.

Systematically varying the binding moieties we found that different binding functionalities led to dramatically different PL properties for the CdSe QDs (Figure 1).

We started with CdSe nanocrystals capped with TOP/TOPO (triocylphosphine and trioctylphosphine oxide). Based on NMR (37) and XPS (38) analysis of CdSe nanoparticle surface, it is believed that TOPO coordinates with the Cd sites on the surface. (Notice that although Cd atoms are usually passivated by the TOPO molecules, for the unpassivated Cd dangling bonds, they are the trapping sites for electrons.)

The TOP/TOPO were first exchanged with pyridine, which was then exchanged with the new caps bearing amine, acid and thiol functionalities - lauric acid, dodecanethiol, and octadecylamine (Scheme 1). The quantitative cap exchange was always checked by NMR.

Equal aliquots of the stock solutions were stored in CHCl_3 in separate positive sealing glass vials with

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Figure 1 - Differences in photoluminescence between chloroform solutions of otherwise identical CdSe quantum dots with different organic surfaces as observed in front of a UV lamp (365 nm)

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Scheme 1 - Cap exchange procedure
Teflon-lined screw caps. Each vial contained 0.50 mL solution and 1.5 mL air. The vials were also sealed with parafilm and kept in a refrigerator in the dark. Only one set of samples was removed each time, when the solutions were transferred into closed quartz cuvettes for PL and UV-vis absorption measurements. Optical measurements were conducted on Day 1, 4, 12, 26, 33, 42 and 70. (Details are reported in a separate publication (39).)

What we have learned from the CdSe surface exchange procedures
We have found that CdSe/pyridine is an essential intermediate in this process because a direct cap exchange from TOP/TOPO to the new caps is impossible. Pyridine capped and vacuum-dried CdSe/pyridine particles were insoluble in any solvents including chloroform and toluene, and they were only soluble in pyridine and piridazine (40). However, surface bound pyridine in the solution of CdSe/pyridine system, can be replaced readily by new functional caps and the resultant QDs were soluble in common organic solvents.

It must be noted that even after seven cycles of pyridine exchange there are still some residual and presently unknown phosphorous compounds remaining, the amount of which can not be reduced any further (41,32).

We performed a quantitative surface derivatization of CdSe/TOPO/TOP using P(OMe)3 as an internal standard in 1H- and 31P-NMR analysis, we were able to quantify the remaining phosphorous compounds (expressed as TOPO). These compounds were reproducibly 10-20% of the weight of CdSe for different batches of CdSe/TOPO/TOP. However, with the new caps introduced, the phosphorus residue only accounted for ~1 mol% of the total amount of caps in our experiments, so the change of optical properties can be safely attributed to the new caps.

Note: in most of the previous work on surface derivatization of CdSe/TOPO/TOP, limited efforts were made to remove the TOPO/TOP and/or quantify the amount of residual phosphorus caps. As a result, what have been studied are usually a mixture of new caps and TOPO/TOP of unknown amounts and proportions.

Absorption spectra of CdSe with different caps
We have attempted the reconstruction of the original starting material from the CdSe/pyridine and we found that it took about 10 times of the "removed" TOPO to bring the CdSe back to solution. An insufficient amount of TOPO simply led to insoluble CdSe aggregates.

Shown in Figure 2 are the UV-vis spectra of the lauric acid, dodecanethiol and octadecylamine capped identical CdSe right after the new caps have been introduced and the pyridine completely removed. Compared with the original CdSe/TOPO/TOP, CdSe/pyridine intermediate shows a blue shift of ~20nm in its absorption edge. However, when it was replaced with dodecanethiol, the original position was fully restored (with lauric acid or octadecylamine, it was only partially restored). The immediate changes either in PL or in absorption wavelength and intensity cannot be related to size change of the CdSe particles. Apparently, the above-observed shifts were caused by the interactions between the CdSe surface and ligands, similar to the redistribution of electronic density in the semiconductor under the influence of passivating groups.

Photoluminescence
While the UV-vis absorption of the acid, amine and thiol capped CdSe showed blue shift and decrease in intensity, the PL of these systems also showed blue shifts, but the intensity increased over time. Shown in Figure 2 are the PL spectra of amine, thiol and acid capped CdSe on Day 1, in comparison with those on Day 70. In the case of lauric acid capped CdSe, the PL intensity exhibited an order of magnitude increase during the two months, and the final PL intensity was about three times of the original CdSe/TOPO/TOP (Figure 3). The observation that placement of carboxyl groups that carry negative charge over the CdSe nanocrystals binding sites leads to increase in PL intensity, seems to support nicely the theoretical calculations above.

Different surface ligands also led to different decay patterns over time. Among the three functional ligands studied, lauric acid greatly enhanced the photoluminescence, and led to a three-fold increase in intensity compared to the original CdSe/TOPO/TOP nanoparticles. Other ligands resulted in lower activity and faster decay.

Gradual blue shifts of the absorption and emission maxima were observed over time, probably due to slow oxidation of the nanocrystal surface. PL intensity of the resultant CdSe nanoparticles showed an initial increase, and then decreased over time. This "aging" effects can be attributed to a
Physical properties of dendrimers, such as solubility, and interactions with the surrounding environment, can be altered by changing the characteristics of terminal groups (42-44).

We have selected hydrophobically modified poly(amideamine) PAMAM dendrimers to carry multiple electron donating amine ligands (45, 46).

Using dendrimers as surface ligands, we wish to develop a universal method for adjusting the nanoparticle surface in a controlled manner. Dendritic molecules, with exact number of functional groups, should provide excellent model compounds to study surface passivation of NPs. These multifunctional dendrimer caps possess “heads” that are able to bind to the NP surface, while other parts of the molecule may increase the solubility and may provide stability against aggregation and crystal growth. In our case the binding is provided through the fourteen lone electron pairs per molecule located on the tertiary nitrogens that serve as branching sites in the dendrimer structure.

The size of the above CdSe nanoparticles was studied under TEM, but no significant change in size was observed. Based on the absorption and emission changes observed in the CdSe systems, we think that the effective size of the CdSe particles may get smaller over time due to surface oxidation. This explanation is also supported by the PL characteristics, as indicated by the blue shift of the PL emission maxima.

**AMPHIPHILIC DENDRIMERS AS CAPS**

Based on analogy with metal ion chelation, we assume that multi-ligand polymers should form more stable surface caps than molecules with a single ligand if bound by non-covalent interactions.

Thus, in addition to single molecular agents, we also placed dendrimer caps on preformed CdSe nanocrystals. These molecules have pre-determined size with narrow molecular weight distributions and reproducibly from generation to generation.

When generation 2.0 PAMAM with primary amine terminal groups was added directly to the CdSe/TOPO system or to the CdSe/pyridine solution, (d=5.5 nm CdSe was used in these experiments) a solid precipitate formed instantaneously, which proved to be insoluble in any solvents. This precipitation is most likely induced by the strong interactions between the primary amino groups on the multifunctional dendrimer surface and the CdSe surface. To decrease the inter-particle interaction through terminal amine groups and avoid physical cross-linking, we have modified the surface properties of the full generation ethylenediamine (EDA) core PAMAM dendrimers by reacting it with 1,2-epoxyhexane (47). In order to tailor the amphiphilic properties of PAMAMs we varied the 1,2-epoxyhexane/dendrimer ratio. Starting with 8, 16, 24, and 32 equivalents of 1,2-epoxyhexane, we obtained PAMAMs with 8, 16, 24, and 28 respective side arms attached on average, designated as PAMAM_E2R_8, PAMAM_E2R_16, PAMAM_E2R_24, and PAMAM_E2R_28. The previously described standard cap-exchange procedure was used (Scheme 2).

The flexible network of the PAMAM_E2.Rn molecules undergo a conformational change upon...
the slight differences in chemical structure, e.g. the number and nature of amine groups of the modified PAMAMs involved in the capping.

Our observations suggest that primary amines (just like ethylenediamine) probably slowly react with the surface of the CdSe nanoparticles gradually making them physically smaller. Following the absorption and PL change over a two months period (Figure 5), we have found that the PAMAM_E2.R28 provided the most effective protection of the NPs against oxidation (about 50% reduction in PL intensity in dilute CHCl3 solution under air in 65 days).

These simultaneous actions of passivation, stabilization, and compatibilization are due to the adsorption of the amphiphilic dendrimers on the surface of the nanoparticles.

In summary, there seems to be two simultaneous mechanisms for the changes in the photoluminescence of the CdSe/organic cap systems. One is a reversible process, which is probably related to the direct physicochemical interaction between the CdSe and the surface ligands, and an irreversible one, likely related to the shrinkage of effective particle size and other chemical reaction, such as oxidation of surface layers without losing the atoms of the surface layers themselves to the solvent. The reversible shift occurs when new caps are introduced, and the irreversible one occurs during storage in ambient atmosphere for a longer time. A plausible explanation for the irreversible changes, is the slow surface oxidation of the particles, similar to the CdSe/ZnS system (23).

FUTURE RESEARCH

In our present research we focus on the better understanding of nanoscale phenomenon using a variety of particles and organic molecules. To gain a better insight into the mechanism of the change of the CdSe/PAMAMs, a more detailed study under strictly
controlled conditions is in order. We are presently investigating the optical properties of CdSe nanoparticles modified by various surface ligands that are bound to linear and dendritic molecules. These results will be reported in a forthcoming paper. In another similar study, higher generation and hence more rigid PAMAM dendrimers are to be used to provide further insight into the utilization of amphiphilic dendritic ligands as nanoparticle surface modification agents. In the long run, nanoparticles that are stable in air will be essential for many different applications. To achieve this stabilization is an existing challenge for both chemists and material scientists.

The key to the success of our future research lies certainly in better understanding of the underlying science in these structures. Better understanding of these nanomaterials will lead ultimately to better materials and construction of novel structures. Patterned placement of uniform nanomaterials can generate new nanostructures with useful, and consequently many innovative applications will open up in the near future.

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