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PERSPECTIVE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Linking Surface Chemistry to Optical Properties of Semiconductor Nanocrystals

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The intricate chemistry occurring at the surface of semiconductor nanocrystals is crucial to tailoring their optical properties to a myriad of applications. This perspective aims to re-evaluate long held ideas in semiconductor nanocrystal surface science in the light of a body of new and rich research. We start by reviewing recent developments in ligand chemistry, followed by a discussion of spectroscopic and computational approaches used for advancing the poorly-understood electronic structure of the surface. With the insights gained, we show how the surface impacts emissive behaviour and we summarize strategies to increase fluorescent quantum yield. This discussion is followed by a review of experimental approaches for quantitative analysis of the surface chemistry at concentrations relevant to spectroscopic measurements. We end by highlighting some new directions in ligand chemistry, namely all-inorganically passivated semiconductor nanocrystals and new applications of surface emission.

1. Introduction

Since the publication of the first reproducible, size tuneable nanocrystal (NC) synthesis[10] an increasing amount of research has been dedicated to understanding the chemical nature of ligand binding and the effects of different surface stoichiometries. Though originally ligands were seen as mere capping groups based on the coordinating solvent used in hot-injection synthesis, an ever increasing amount of research has shown that changing from one ligand system to another can affect fundamental NC properties.

The chemical nature of the NC surface dictates far more than its interaction with its environment (e.g. solubility, charge transfer). The chemical nature of the surface also has fundamental effects on intrinsic attributes like electronic structure[11], spectral shapes[2, 12, 13], and photo luminescence (PL) quantum yield (QY)[14, 15]. The primary role of these ligands is as a surfactant during the growth of the NC.[16, 17] They may then be chosen so as to optimize the PL QY. Since organically passivated NCs tend to have low PL QY (~ 10%), inorganic shells of various designs have been implemented which can increase the PL QY (>50 %) as well as decrease other deleterious emissive properties such as blinking.[18-20] However, these inorganic shells may also block desired function of NCs, e.g. charge transport in a film. Such transport processes are of importance in applications spanning lighting[21, 22] and displays[23] to photovoltaics[24, 25] and detectors[26]. In short, there has been considerable investigation into the ways in which ligand choice can dictate both growth as well as optical properties of the NC.

What is missing from prior work on the surface of the NC is a physical understanding of the nature of the surface/ligand system in terms of electronic structure. To illustrate by comparison, the core of the nanocrystal is now well understood in terms of electronic structure.[27] With theories spanning particle in a sphere[28], to multiband effective mass approximation (EMA)[29], to atomistic calculations[30], the community has hierarchies in the level of theory which can be used to describe the optical properties as well as the function of the NC. The elementary excitation of note in the core of the NC is the exciton – the bound electron/hole pair. The structure and dynamics of excitons in the core of the NC has been well explored via spectroscopy.[31-33] In contrast, the understanding of the electronic structure of the surface of the NC remains in its infancy. Moreover the manner in which the surface couples to the core is also in its early stages. Yet the surface is of great importance to a wide variety of properties spanning simple PL, blinking, Auger recombination, optical gain, transport and other phenomena.

The primary approach to understanding the interaction of the surface with the excitonic core of the NC is based upon simple spectroscopy such as PL. The primary observables with which to assign some aspect of surface passivation are: PL QY, PL lifetime, and the relative amount of surface PL. The surface PL is often observed as a broad band that is redshifted from the core excitonic peak. The general strategy is to identify surface passivation schemes which result in NC with high PL QY, single exponential lifetimes, and no surface PL at room temperature. Yet mere optimization of these measures gives somewhat limited insight into the electronic structure of the ligand/surface complex. One ultimately aims for a microscopic understanding of the chemical and physical nature of the surface of the nanocrystal / ligand complex.

We have recently produced the first comprehensive microscopic model of the ligand/surface system which can fully describe all the relevant observables from PL experiments.[1, 9, 34, 35] Based upon measurements of the PL spectra of a variety of NC/ligand systems over a broad temperature range, a simple electron transfer model emerged which can uniquely describe all these surface phenomena. These temperature dependent PL measurements revealed that NCs with no surface PL at 300 K may have appreciable surface PL at some low temperature, e.g. 100 K. The temperature dependence of the PL from the core and the surface can have a complex functional form indicating some thermally activated process that governs the charge equilibria between surface and core. Since the redshift of the surface PL band is much greater than kT, the origin of the broadening and redshift needed clarification as well. Based upon exciton-phonon measurements using both pump/probe spectroscopy and resonance Raman spectroscopy, we showed that the broadening and redshifting of the surface band arises primarily from optical phonon progressions created by the relaxation of charges trapped at the surface of the NC. In this semiclassical electron-transfer approach, all aspects of the surface emission can be described for the first time – from temperature dependence to lineshape, to redshifting – in one unified model.

With this electron transfer model which demonstrates the way in which the surface states are coupled to the core excitonic states, many significant surface dependent emissive phenomena were described. For example, a recent paper from our group compared two commonly used passivations, tetradecylphosphonic acid (TDPA†) and butylamine (BA).[2] Both passivations showed surface PL at 300 K, provided a small NC was used. By simply recording PL spectra at 300 K one could incorrectly conclude that one system was merely better passivated than another, or that one system had a broader energetic distribution of the mysterious surface trap states that are commonly invoked. Such an interpretation based upon the historic view of surface emission would be incomplete. Our work showed that the primary difference between the two ligand systems is in the electronic structure of the surface. Specifically, the amount of surface PL at a given temperature is dictated by the free energy difference between the band edge exciton and the surface electronic state. The lineshape of the surface PL is dictated by the strength of coupling to the optical phonons.

While this semi classical electron transfer model describes the main surface emission observables, it lacks chemical specificity. In contrast, the majority of NC/ligand studies focus upon the chemical specificities of ligand binding to the NC surface. Such chemical interactions are probed by a variety of means discussed in this Review. Based upon a microscopic model which describes the surface electronic structure of the NC and a survey of the chemical interactions which control the structural aspects of the surface, we are poised to advance the basic understanding of this important but elusive aspect of nanocrystal science. The purpose of this perspective is to connect our proposed electronic structure of the surface to recent advances in surface chemistry and point out future avenues of research.

We discuss the nature of the surface on three levels. The first step is to review the chemical structure and synthetic approaches to different surface passivations in a modern context. Second, we monitor the spectroscopic observables that yield deeper insight into the surface. In concert we have supplemented these spectroscopies with a simple analytic theory which suggests the nature of the electronic structure of the surface. Third is an examination of atomistic computational approaches that elucidate the role of specific chemical species of the NC surface in the system's excitonics. These points are followed by a discussion on appropriate quantitative experimental approaches, new ligand systems and applications of surface emission.

2. The chemistry of ligand binding and exchange

In order to understand and ultimately control the surface of the NC one begins with a modern approach to the synthesis and ligand chemistry. In this section we will show how recent synthetic work has drastically improved our understanding of the chemical nature of the surface and how this new language forms the basis of a rational discussion. A very common synthetic approach is to synthesize NC with long chain aliphatic amine/carboxylate/phosphonate ligands and to post-synthetically functionalize the surface with task-specific ligands. These can range from ligands that allow particle stabilization in water like biotin[36] for biological applications,

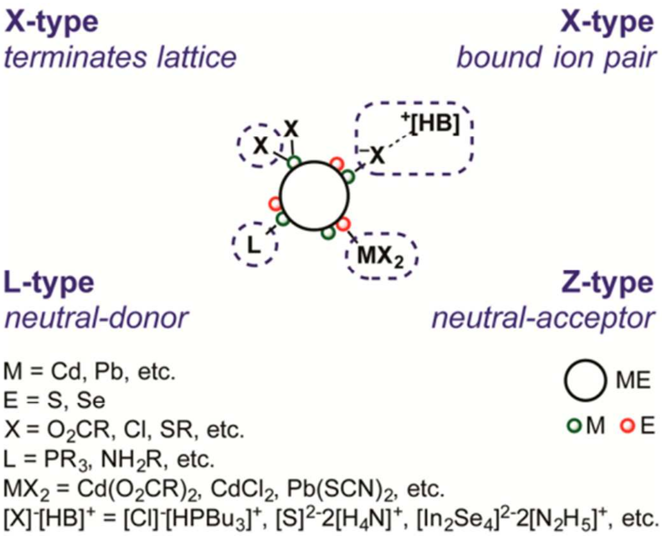

Figure 1. Ligand Binding According to Covalent Bond Classification Method Reprinted with permission from Reference 5. Copyright (2013) American Chemical Society.

primary amines for high PL QYs[19], to short thiol ligands for photovoltaic applications[37].

Popular and simple synthesis methods based on hot injection of metal and chalcogenide precursor into a solution of tri-n-octylphosphine oxide (TOPO) and tri-n-octylphosphine (TOP) perpetuated the idea these solvents become the ligand passivation shell.[10] This TOPO based model assumes that TOPO binds to surface metal (i.e. cadmium) sites and TOP binds to surface chalcogenide (i.e. selenium, sulphur) sites of a charge neutral and stoichiometric NC core, and idea support by an early 31P NMR study by Becerra et al.[38]

More recent studies have convincingly challenged the accuracy of the TOPO based model. There have been several reports of metal enrichment occurring at the NC surface.[39-41] This excess metal is in its cationic form and needs to be balance by an anion other than the core chalcogenide.[42] Since the neutral TOPO and TOP passivation does not allow for a charge balanced NC, the model is inadequate. A more recent study[43] on cleaving the ligand shell of NCs synthesized in a TOPO-type approach shows that the actual, charge balancing passivating groups are phosphonate anions rather than datively bound TOP/TOPO. The study also reproduces the 31P NMR spectra by Becerra et al. and shows that they were inaccurately assigned to TOP/TOPO.

The source of these phosphonate anions originate from phosphonic acid impurities in commercially available TOPO and a TOPO synthesis using recrystallized and pure TOPO does not yield any NCs.[44]. In the hot injection method the phosphonic acid impurity species are deprotonated and react to form the active metal precursor.[45] This is the reason for the common ancient lore among physical chemists that certain batches of commercially available TOPO produced “better” NCs than others, which lent NC synthesis a near voodoo-esque quality.

In later versions of the hot injection method dimethyl cadmium was replaced by Cadmium oxide (CdO), as it represents a far less toxic alternative.[46] This method allowed for a rapid growth of the NC research field, as this synthesis is much safer than previous methodologies. In these methods CdO is dissolved with phosphonic acids in hot TOPO and selenium dissolved in TOP is injected. In this synthetic approach the resulting ligands are phosphonate anions formed from the added phosphonic acid and the impurities from the TOPO, and TOP. The resulting NCs also haven been incorrectly referred to (including by the authors of this perspective) as TOPO-capped.

Recently the Owen group has proposed a model for ligand passivation that accounts for the need to charge balance metal rich surfaces and can explain ligand exchange chemistry.[5] This model uses standard covalent bond classification method (Fig. 1), and divides ligands into L-type (two electron donors, neutral Lewis basis), X-Type (one electron donors, anions), and Z-type (two electron accepting, neutral Lewis acids). In this model the NC core is stoichiometric and the metal richness of the surface is caused by charge balanced MX_2-complexes bound to core chalcogenides.

As NCs’ versatility relies heavily on the ability to switch between passivations it is important to understand the chemistry of exchanging ligands. There are two different approaches to ligand exchange. Firstly, one can “simply” exchange ligands of the same class, by for example dissolving NCs capped with one Lewis base in a different, more reactive Lewis base, which represents an L-type ligand exchange (X-type and Z-type ligand exchange are analogous). Secondly a so called L-promoted Z-type ligand displacement can be performed. In this type of reaction a MX_2 ligand is displaced by an L-type ligand, resulting in a surface metal L type bond and an $L\text{-}MX_2$ leaving group. This displacement results in a decrease of surface metal richness.[5] An excellent account of the surface chemistry of metal-chalcogenide NCs can be found in this dissertation.[47]

A proper understanding of what ligand actually binds to the surface of the NC (e.g. TOPO vs phosphonate) and what chemical mechanism allows for ligand exchange is essential to tailoring NC surface chemistry for applications.

3. Spectroscopy and Electronic Structure of the Surface

The objective of controlling the surface chemistry of NCs is to control the excitonics of the NC. Typically the excitonics of the NC are discussed in terms of the core excitons. The electronic structure of the surface and its coupling to the core has been ignored historically.[27, 48, 49] By performing temperature-dependent PL we have gleaned significant insight into the electronic structure of the surface.[9, 35]

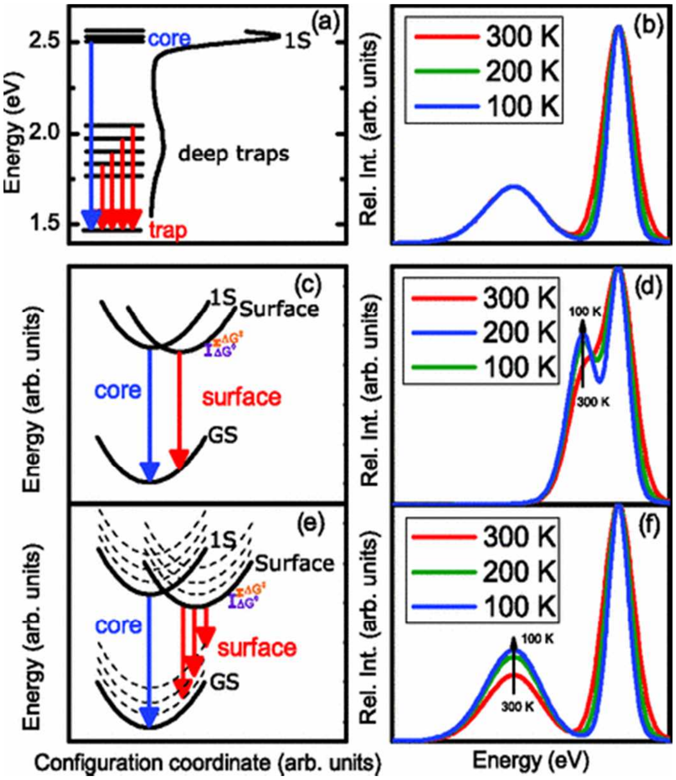

Figure 2. Three different models to explain temperature dependent PL and their generic temperature dependent PL spectra. a) The classical deep trap model does not account for the different functional form of temperature dependent core and surface intensity changes. c) The classical Marcus model does not explain breadth nor position of the surface emission. e) Semi-Classical Marcus-Jortner ET model fully explains temperature dependent PL changes and spectral features of NCs. Reprinted with permission from Reference 9. Copyright 2013 by the American Physical Society.

Semiconductor nanocrystals primarily gain their optical properties from excitonic quantum confinement, which leads to particle-in-spherical-box like energy levels.[50] However, unlike in this idealized model, the surface forms a finite potential barrier of the stoichiometric semiconductor lattice core, which results in wave function leakage.[51] One of the main motifs in NC research is to obtain particles with high PL QY. In order to achieve this goal it is pertinent to have control over chemical environment of the surface, and thus to manipulate the potential barrier and leakage.

A major obstacle to highly fluorescent NCs are charge carrier mid-bandgap trap states that are known to lie on the NC surface.[52-54] If a leaked charge carrier is trapped on such a surface site, it can either relax radiatively or non-radiativly.[55] The atomistic nature of these traps is not fully understood, but recent computational approaches[3, 56] have drastically advanced our understanding. These will be discussed in detail in the next section. This review focuses on the radiative surface trap states, since their emission has been one of the main observables used in the investigation of the surface state.[9, 57, 58]

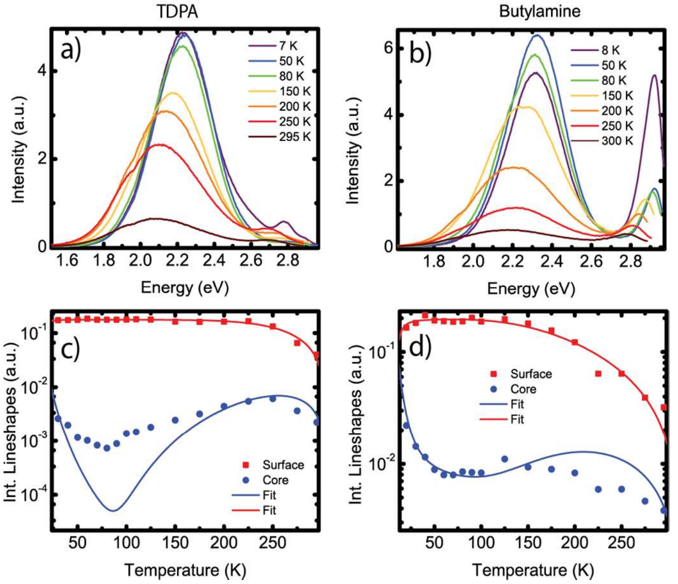

Figure 3: Temperature dependent PL emissive behaviour for ultr-small NCs PL spectra for a) TDPA and b) butylamine passivated NCs with their corresponding integrated lineshapes and fits to a semi-classical Marcus-Jortner type ET model. Figure adapted with permission from Reference [2]. Copyright (2013) American Chemical Society.

A well-studied approach to avoid these traps is to coat the NC surface with a higher bandgap semiconductor layer (e.g. Type I CdSe/ZnS), which limits non-radiative traps to core defects and the semiconductor/semiconductor boundary.[59] Since the capping layer can inhibit charge transfer to external charge acceptors, such NCs are less suited for photovoltaic or photodetector applications[60],

The primary observation relevant to radiative surface traps is the existence of an extremely broad emission band to the red of the core excitonic PL. Historically this spectral feature has been thought to arise from surface trap states that have a large energy distribution within the band gap.[52, 61] This broadening and redshifting of the surface PL with respect to the core PL was rationalized by the energetic distribution of trap states (Fig. 2a-b). This theory however fails to explain emissive behaviour at different temperatures. The intensity of core and surface radiation changes with distinct and complementary functional forms.[2, 9, 57] This is an indicator for population exchange between core and surface. Since the surface emission is redshifted from the core peak by >10 k_BT, there would not be enough thermal energy under normal experimental conditions to allow for this exchange. Further if there were a random distribution of trap states, one would observe the surface emission red shift with decreasing temperatures, which is not the case. Jones et al.[62] explained surface trapping using a

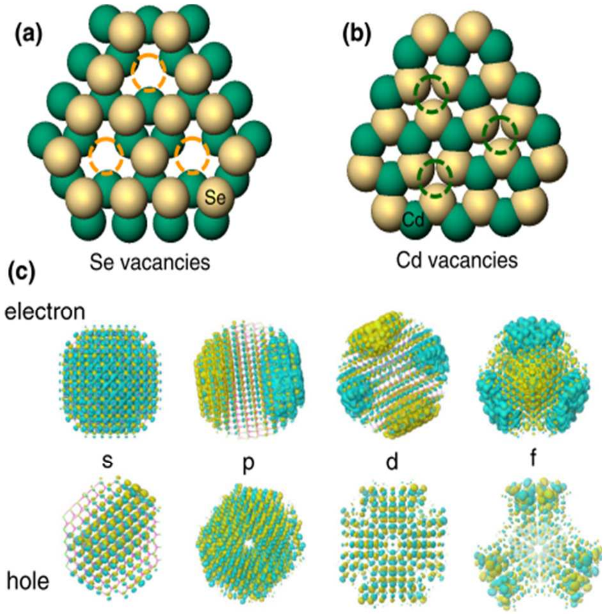

Figure 4: NC (111) facets with selenium a) and cadmium b) vacancies. These vacancies eliminate surface states and result in quantum confined levels with s, p, d, f envelope functions. Reprinted with permission from Reference 3, Copyright 2014 by the American Physical Society.

classical Marcus electron transfer (ET) model, in which there is an energetic barrier for a carrier (ΔG‡) transition from the delocalized core excitonic to the localized surface state (Fig. 2c-d).

In order to account for the temperature dependent PL changes the surface state has to lie within k_BT below the core state (ΔG°) and the energy barrier has to be less than ΔG°. Since for these conditions to apply the surface can only be displaced minutely on the classical polarisation coordinate, the model does not account for the breadth and redshift of the surface peak (Fig. 2). In addition, once $k_BT <$ ΔG‡, no surface emission would be observed which is contrary to experimental evidence.[2, 35, 57]

A Semi-Classical Marcus-Jortner ET type model that accounts for all emissive attributes was recently developed by our group.[9] In this model the surface state is coupled via the classical polarisation coordinate and a quantum coordinate to the core state (Fig. 2e-f). This means that a carrier in the core state can either relax to the surface by thermally overcoming ΔG‡, or by tunnelling through the barrier, which accounts for surface PL at very low temperatures. Once in the surface state the carrier can relax radiatively into different vibronic levels of the ground state. These Franck-Condon phonon progressions are the cause for the spectral width of the surface PL, and have been theorized previously.[57, 63]

We have recently shown that this model also holds for the extreme case of NCs with diameters < 2 nm, for which most atoms lie at the surface.[2] In these systems the emission is mainly surface dominated over a large range of temperatures (Fig. 3). We have further shown that the ligand chemistry of these systems controls the thermodynamics of the excitons population and thus changes temperature-dependent emissive behaviour. We observed that for TDPA† passivated NCs the core peak disappears in an intermediate temperature range (between ~80K- and 40K) and reappears at temperatures below this range. As for butylamine passivated NCs both core and surface emission bands were observed over the entire experimental temperature range. We explain this difference by the distinct chemical environments created by the ligands. Different functional groups appear to change the energy difference between the core excitonic state and the surface state, as well as the reorganization energy of the ligand bath.[2] Correspondingly, in the "particle-in-a-spherical-box" picture ligands are part of the finite potential barrier[64], and thus also regulate wave function leakage.[65]

Our simple analytic Marcus-Jortner type model rationalizes all the spectroscopic observations in light of carrier transfer between the core and the surface of the NC. Yet the surface in our model remains an invoked quantum state in which the chemical details are parameterized. The model thus lacks chemical specificity. In order to incorporate this important detail one must ultimately rely on high level atomistic theory.

4. Computational Approaches

Our analytic model can describe the experimental observables, but undoubtedly there remains considerable work to be done. In order to fill the gaps left in our current model it is paramount to study the NC surface from an atomistic approach. The computational work described here forms a connection between the chemical composition of the surface and its resulting electronic structure as suggested by the electron transfer model.

New computational work has begun to yield insight into the atomic nature of surface traps. Traditionally hole trapping has been associated with surface selenium[66, 67] and electron trapping with surface cadmium[68], but this picture has been refined by recent density functional theory (DFT) studies.

In a surface DFT study Voznyy employs a spherical NC cut from a zinc blende lattice terminated by three distinct surface facets.[56] There are cadmium-terminated and selenium-terminated (111) facets, whose terminating atoms are triply bound to the layer below and mixed cadmium and selenium facets (100) with doubly bound cadmium atoms. The study demonstrates that in NCs that are charged-balanced by an appropriate number of ligands (the number depending on the NC size and surface composition), there will inevitably be unpassivated surface atoms, i.e., unpassivated Se atoms will have dangling bonds filled with two electrons whereas Cd atoms will have completely empty bonds.

In the case of this small DFT model[56] the surface sites do not contribute to mid-gap states, as the filled Se 4p states make up the valence band and the empty Cd 5s states make up part of the conduction band. In comparison, in larger models of more realistic systems, the unpassivated (111) sites display trap states.[3] Cd-terminated facets are associated with traps on the conduction band side and Se-terminated facets are associated with traps on the valence band side. Apart from these intrinsic trap states caused by the terminating facets, deviation from an ideal stoichiometry and thus electronic balance will result in partially filled dangling surface orbitals that are situated in the bandgap. The resulting readjustment of the number of bonds, so-called NC self-healing, can created local strains that in return can push states into the bandgap and increase the amount of traps.[56] Such trap inducing deviation from an electroneutral NC can occur if an extra ligand is added to the surface.

If an extra ligand is placed on the Cd (111) facet the electronegative functional group of the ligand creates mid gap traps near the top of the valence band. Even though the ligand is bonded to a Cd atom the trap is delocalized over the neighbouring Se atoms. The optical transition from these trap states is allowed and its magnitude depends on their vibrational coupling to the core state. Surface PL has been linked to dangling bonds of surface selenium atoms[67, 69, 70], but it appears that trap states can have different sources and are localized over several atoms, rather than a single bond.

Furthermore the DFT study shows that these traps are not locally fixed entities, but rather are mobile occurrences that can not only be filled or emptied, but created and annihilated. X-type ligands like carboxylic acids that can either bond as bridges between two Cd-atoms or chelate one, have the ability to diffuse (or “walk”) over the (001) crystal face (rather than just de-and adsorb) on a subpicosecond timescale.

There are some limitations to the modelled NC in this study. The lattice is rather small ($Cd_{56}Se_{50}$) and the only ligands considered are acetate molecules, an X-type ligand representative of long chain carboxylic acids, bonded to surface cadmium. This means that MX_2-type ligands are not modelled, leaving the selenium (111) facet unpassivated. Nevertheless this paper gives interesting insight into the atomistic nature of surface traps. Even though these simulations were done on an idealized zinc blende lattice, the insights gained are valuable for other geometries and lattice structures. Wurtzite lattices for example have similar terminating facets and thus similar ligand/lattice interactions are to be expected.[71]

DFT studies like this help to explain spectroscopic observation in the context of actual atomistic changes on the NC surface. Rapidly advancing computational methods allow for more realistic NC models and let us re-evaluate long held theories about surface chemistry.

In a more recent DFT study on a larger and more realistic NC (~1200 atoms) it has been shown that surface vacancies can decrease the number of traps.[3] NCs are most stable in stoichiometric form with a closed electron shell, a condition that is highly dependent on NC geometry. In real NCs this condition is not necessarily fulfilled, and the removal of certain surface Cd or Se atoms can function as a form of surface reconstruction. By removing several of these atoms one can construct a trap-less NC with clearly resolved (s,p,d,f) wave functions (Fig. 4). Like the X-type ligands mentioned above, these vacancies are mobile, and similarly their rearrangement can cause non-emitting configurations on different time scales (i.e. “fluorescent blinking”).[3] Surface vacancies are generally only thought of as trap states themselves[13, 72, 73], but the idea that vacancies can in some cases preserve the core excitonic state is another example of how surface stoichiometry (in concert with ligands) influence the excitonic NC core.

Complementarily to these specific DFT models, a more general approach describes Auger-mediated trapping as a universal trapping mechanism in NCs.[74] A hole from a core-delocalized state relaxes into a localized trap state by transferring the energy of the trapping transition to a conduction band edge electron. This electron is excited from an s-like state to a p-like state. This mechanism is not limited to surface traps, but can be applied to core impurity states.

The atomistic theories are now beginning to offer insight into surface structure. Mobile traps, localized over several surface atoms, can be caused by additional ligands on an otherwise electrically balanced NC and stop an NC from emitting, which can explain our group’s observation on temperature dependent PL of NCs.[1] Similarly, mobile atomic vacancies can be arranged to cause emitting and non-emitting configurations.[3] These results show that the connection between ligands, atomic vacancies, and trap states are far more intricate than previously thought and they support the idea that the surface has considerable impact on NC trap emission. Any comprehensive model aiming at explaining surface excitonics has to take surface stoichiometry into account. We anticipate that there will be more work needed in order to fully connect the general analytic ET theories of kinetics and thermodynamics to the atomistic structure of the NC surface.

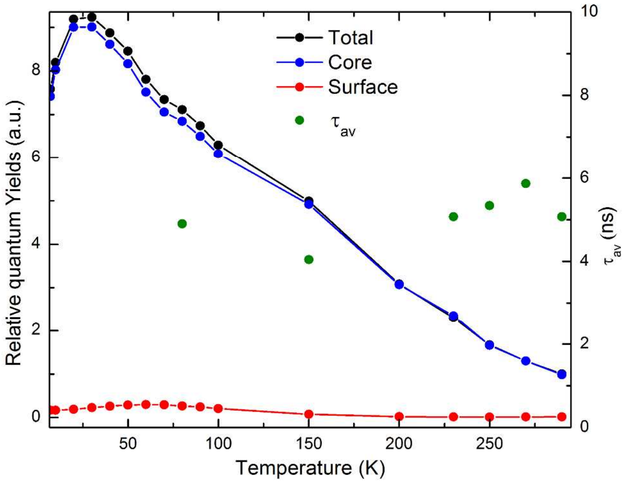

Figure 5: Taken spectral blue shift into account, the fluorescent lifetimes of the NC emission stay constant with temperature. Figure adapted with permission from Reference [1]. Copyright (2014) American Chemical Society.

5. Surface Effects on PL Quantum Yield

As one of the main goals of NC ligand chemistry is to obtain NCs with high PL QY, it is paramount to understand how specific chemical species can influence the amount of radiative and non-radiative traps at the surface.

As discussed in section 2, temperature dependent PL spectroscopy can give specific insight into competing excitonic relaxation pathways. Fig. 5 shows the relationship between PL, PL QY, and PL average lifetime. The total PL monotonically increases as temperature is lowered. In contrast, the PL average lifetime shows little change over this regime. As we recently discussed, these observations have implications on the surface processes which yield PL.[1] The main point from these measurements is that the PL QY is not related to any temperature dependence of the radiative or non-radiative decay rates. Instead, the PL QY appears to be dictated by the fraction of particles that can emit, n(T). Our group has suggested that the decrease in PL QY with increasing temperature is caused by mobile surface modifications on this subset of NCs[1, 35], which is somewhat analogous to the mobile nature of traps described in section 4. Research into what specific structural differences set single NCs apart in terms emissive properties is currently limited to core/shell systems.[75-77] Nevertheless there exist some general strategies to increase ensemble PL QY of "uncapped" NCs, of which two common approaches are discussed in the section.

There is experimental evidence that suggests that PL QY increases with the ratio of cadmium to chalcogenide at the surface.[5, 6, 68, 78] Using a SILAR (successive ionic layer adsorption and reaction) approach it has been shown that by adding chalcogenide layers to an NC the PL can be totally quenched[68] and completely recovered by the addition of Cd layers (Fig. 6).[6] Cd rich surfaces cause the emission to be core dominated, whereas chalcogenide rich surfaces tend to display more surface dominated spectra (Fig. 6). DFT calculations of Cd and S rich clusters suggest that chalcogenide rich clusters display a myriad of highly localized midgap trap states.[6] In order to obtain highly emissive NCs one can choose synthetic measures that produce a metal rich surface, or post synthetically add CdX_2-type ligands.

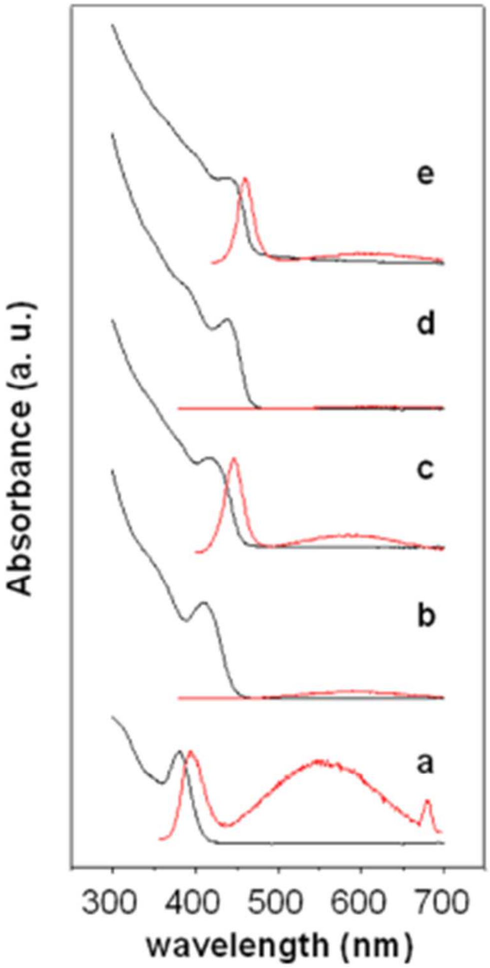

Figure 6: SILAR type surface modification of CdS NCs**.** As prepared NCs a) were coated with a monolayer of DDP-S b). A mono layer of Cd stearate was added c), followed by an additional monolayer of S d). A last layer of Cd was added e) and the PL QY was restored. Reprinted with permission from Reference 6. Copyright (2012) American Chemical Society.

The other common method to obtain high PL QY is an important exception to the rule of thumb that PL QY scales with the amount of Cd at the NC surface. Increases in PL QY of up to 50% in L-promoted Z-type ligand displacement using primary amines have been reported.[14, 19, 79] In these reactions L-MX_2 ligands become the leaving group and there is a net decrease in surface cadmium. Even with very efficient ligand exchange procedure that leave the vast majority of surface Cd passivated the relative amount of selenium atoms with dangling bonds is higher than before. If PL QY was proportional to surface metal coverage, one would assume that this kind of ligand exchange would decrease the PL QY, but in the case of primary amine exchange the opposite is observed.

The exact reason for the increase in quantum yield is not fully understood, but there are several different factors that are thought to contribute to this observation. It is known that primary amines allow for much higher capping densities than ligands that are more sterically hindered.[80] High ligand coverage has been linked to an increase in PL QY.[81] These capping agents are less sterically hindered then for example native cadmium carboxylate (MX_2-type) ligands. In addition, X-type ligands can form bridges and tilted bridges between two metal sites and with this decrease the overall surface coverage.[56] Primary alkylamide capping allows for significantly higher ligand passivation and PL QY than the use of secondary amines (which in turn passivate NCs somewhat better than tertiary amines).[14]

In addition to higher capping densities, it has also been suggested that amine-binding raises the energy of surface traps out of the mid-bandgap and thus increases PL QY by eliminating these traps.[14] In contrast, in a Marcus type electron transfer model primary amine passivations (as compared to TDPA) changes the relative energy difference of the surface to core and thus creates a higher energy barrier for charge carriers to relax from the core excitonic state to the surface.[2]

Conversely to the aforementioned accounts there have been reports that the addition of n-alkylamines decreases PL QY.[82, 83] It has been shown that their effect on PL QY depends on dilution and that there is a peak concentration after which PL QY is decreased.[81] One explanation could be that since most ligands are reversibly bound to the surface there is an equilibrium of bound and unbound alkylamines in solution. Since amines are known as universal PL quenchers, a high concentration of unbound alkylamines might decrease the PL QY.[84] This explanation however contradicts experimental observations by our group that show that after a ligand exchange from phosponate anion to amine ligands, without removal of excess amine, the total PL QY remains relatively unchanged.[2] More research will have to be performed in order to explain apparent contradictory experimental observations pertaining to the relationship of primary amide addition to NC solutions and PL QY.

These strategies to obtain highly luminescent NCs show that in order to understand the effects the surface has on the emissive properties of NCs, both ligands and surface stoichiometry have to be taken into account. As well as the NC synthesis itself, post-synthetic procedures have to be equally understood in order to avoid surface detrition.

Unintentional surface Modifications

In addition to these intended manipulations, there are inadvertent changes to the surface that have adverse effects on PL QY. Changes in solvent system of NC samples can affect the surface passivation and thus the PL QY. The primary reason for this phenomenon is that different solvents show different equilibria for bound and free ligands.[14] For example, it has been shown that the addition of chloroform to phosphonate passivated (in the report originally described as TOPO passivated) NCs in toluene decreases the PL QY due to a net decrease of bound ligands.[14] Similar changes in PL are observed upon NC dilution, as this also pushes the equilibrium toward the unbound ligand.[12]

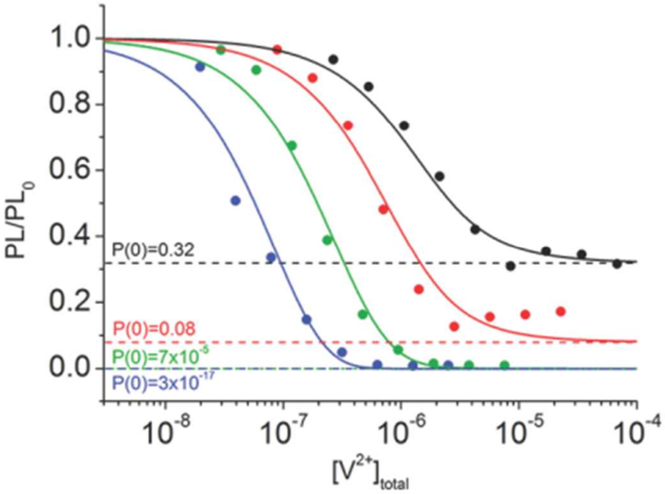

Figure 7: Probability of finding a QD with zero adsorbed V^{2+} ligands (PL/PL_0) as a function of the total V^{2+} concentration for NC samples of different concentrations**.** Black: 1.4×10^{-6} M CdS, Red: 4.6×10^{-7} M CdS QDs, Green: 1.5×10^{-7} M CdS QDs, Blue: 5.1×10^{-8} M CdS QDs. The dashed lines indicate the fraction of NCs that are not quenched and do not appear to have accessible surface sites for V^{2+}. Reprinted with permission from Reference 7. Copyright (2011) American Chemical Society.

Another often underestimated factor in the attempt to obtain high PL QY NCs is the choice of post-synthetic purification procedure. In NC synthesis it is a common practice to precipitate the particles from the reaction mixture by adding a non-solvent and centrifuging the resulting suspension. A prevalent non-solvent used in the past was methanol. The problem using a short chain primary alcohol is that they facilitate the stripping of X-type ligands from the NC surface.[85] In the case of oleic acid capping, the alcoholic proton in methanol is acidic enough to release some bound oleate ligands and exchange them by a methoxy moiety. The overall replacement of ligands results in a net loss of passivated binding sites on the NC, likely by surface oxidation, and losses in PL QY of up to 20% have been reported.[85] To avoid this kind of post-synthetic degradation the use of aprotic polar non-solvents (e.g. acetonitrile, methyl acetate) is advised.[85] In order to make synthetic procedures more reproducible (especially when aiming at NCs with high surface to core emission ratios) it is paramount to employ PL QY preserving purification methods.

PL QY can give a general idea about the quality of surface passivation and the motivation of a lot of research is to increase it. However, in order to obtain a more quantitative picture of the NC surface, other experimental methods with observables other than the absolute PL QY are needed.

6. Quantification and study of ligand binding sites

In addition to new computational methods to elucidate the atomistic nature of the surface, there has been recent development in quantitative experimental ligand binding studies. In order to form a complete picture of the NC surface, one relies on experimental approaches that probe the system in question under realistic conditions.

Traditionally NMR is used to study NC ligand binding.[86, 87] The main issue with NMR studies is that they require very high NC concentrations in order to obtain usable signal to noise.[88] As discussed earlier, the surface coverage by bound ligands depends on NC concentration.[12] Thus the results obtained from these NMR studies might not be valid at the (much lower) NC concentrations used for spectroscopic measurements. An alternative approach to quantify different chemical species on the NC surface is to adsorb a charge and/or energy acceptor to the NC and monitor changes in PL QY, fluorescent lifetimes, and transient absorption spectra. Apart from gaining deeper insights into binding sites[88, 89] and surface composition effects[90], this approach has been used to study photo induced charge transfer[91, 92] and energy transfer[93].

The basic design of many of these studies is to introduce a new ligand that binds via the same functional group as the native ligands of the NCs studied.[88, 89, 94] The number of new ligands per NC is commonly calculated using a Poisson distribution. It has been pointed out that in cases were the number of new ligands adsorbed approaches saturation, a Poisson distribution predicts a non-zero probability of finding NCs with more ligands than available surface sites. Since this is a non-physical solution, distributions for systems close to saturation should be calculated by binomial distribution, if possible.[7]

A very common ligand for these quantitative binding studies are functionalized viologens (V^{2+}), which have been used to study interfacial NC charge transfer phenomena.[92, 95, 96] V^{2+} are electron acceptors, and their presence on the NC surface affects exciton dynamics and PL properties. As the rate of ground state bleach recovery increases upon viologen addition, it has been used to calculate the V^{2+}/NC binding constant.[92] An analysis of NC PL quenching by V^{2+} has shown that ensemble emission cannot be quenched completely (Fig. 7).[7] There appears to be a subset of NCs that has no available surface sites and remains fluorescent even at high V^{2+} concentrations. The existence of such subset of NCs might be analogous to our observation that only a fraction of an NC ensemble remains emissive with increasing temperature (Fig 5). So far there is no microscopic picture explaining this observation, but fully understanding the chemical nature of this subset of NCs would give great insights for how to synthesize highly fluorescent and resilient ensembles.

With the recent refinements of the understanding of the NC surface, more attention has been given to how different NC stoichiometries affect the adsorption of molecules. A study of

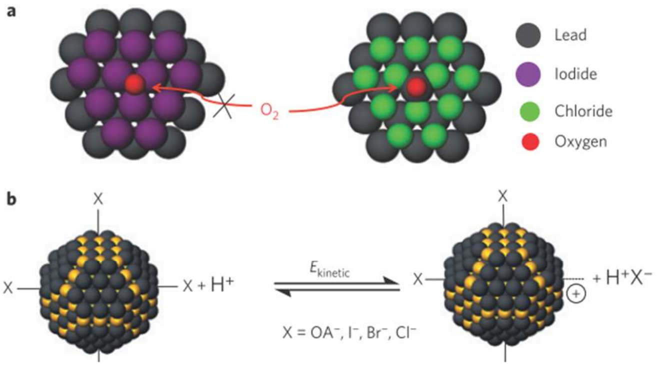

Figure 8: a) A more complete ligand passivation protects the NC from oxidation. b) Compared to other halide ligands and to oleic acid, as widely used organic ligand, the removal of iodide with hydrogen protons is energetically less favourable. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials (Reference 8), copyright (2014).

methyl viologen (MV^{2+}) adsorption to CdS NCs with either Cd or S enriched surfaces has shown different site-specific binding affinities.[90] MV^{2+}either adsorbs by displacing native Z-type ligands (in this case Cd-OA complexes) and adsorbing to the underlying core, or by directly adsorbing to the exposed NC core. This means that either surface termination allows for MV^{2+} adsorption. However, *ab initio* calculations from the same paper suggest that MV^{2+} adsorbs more readily to sulphur terminated surfaces. It appears that electron poor nitrogens of the MV^{2+} bipyridyl core interact with the chalcogenide ions and that the complex formed is interlinked by van der Waals interactions rather than a well-defined bond. This approach to surface adsorption appreciates differences in surface stoichiometry and allows for a more nuanced evaluation of a surface's resilience to quenching adsorbates. Quantitative research on how ligands bind to the NC surface is not limited to these charge transfer studies, and significant work on how NCs interact with energy acceptors has been published.

Some studies have used fluorescent dyes, in which adsorption of FRET accepting molecules is probed by measuring dye emission.[88, 97, 98] A study performing ligand exchange between native oleic acid ligands and carboxylate acid functionalized boron-dipyrromethene dye found that NCs have multiple, identical binding sites.[88] These sites have identical affinity for the new ligand and binding at these sites does not change the ligand affinity of other sites. Assuming a Poisson distribution, the authors fit a modified Langmuir isotherm to experimental PL data and found that only an isotherm allowing for multiple identical (as supposed to a single, or multiple different) binding sites fits the data. In the specific system studied they find that an average of 3 dye molecules can bind identically to the NC.[88]

There are some limitations to this approach. Single molecular experiments will have to be performed to assess whether this is an ensemble or an NC intrinsic property. Currently it is not possible to distinguish whether a subset of NCs exists that has high affinity for new ligands and other subsets that do not exchange ligands. In addition, it is currently not known if the functionalized dye molecules replace existing oleic acid ligands or bind to previously unpassivated surface sites.[88] As in all quantitative NC studies, the numerical result is somewhat system dependent, but nevertheless this approach allows for a deeper understanding of specific surface sites at NC concentrations relevant for spectroscopic analyses

The quantitative ligand binding studies discussed in this section give some deeper insight on how specific chemical species interact with the NC surface. These are helpful complemental analyses to temperature dependent PL and computational studies that allow a more complete picture on how the surface effects optical properties of NCs.

7. New directions in NC surface chemistry

Recent developments have drastically enriched the field of NC surface science. In this section we will discuss ligand orbital mixing, new all-inorganic NC passivations, and applications of NC surface emission.

Ligand Orbital Mixing

Apart from stabilizing the NC in solution and passivating trap states ligands can influence the electron and hole wave functions. In order to obtain an exhaustive picture of the surface these ligand/lattice interactions have to be taken into account. Thiols for example have been known to extract holes from the surface of CdSe NCs and thus drastically decrease PL QY.[99] In CdTe NCs on the other hand thiols are used to obtain highly fluorescent and water soluble NCs.[100] The reason for this drastic dissimilarity is the relative potential difference of the valence band (the difference over the size range of NCs is about 0.5 eV[101]). Since many thiols have oxidation potentials between these two values, only holes from the CdSe valence band can relax into the thiol highest occupied molecular orbital (HOMO). There are thiol molecules that have higher redox energies than the CdTe valence band edge hence decrease PL QY via ligand hole trapping. 4-Mercaptophenol is an example of a thiol that fall into this category.[99]

Phenyldithiocarbamate (PTC) is a ligand known for causing significant bathochromic red shifts in CdSe NC absorption spectra.[11, 102] The HOMO of PTC has the correct energy and spatial alignment to strongly mix with the valence band of commonly used semiconductors. This allows for a relaxation of the core excitonic confinement via delocalization of the hole into the organic ligand shell. This approach allows a fundamental shift in energy of spectroscopic features without manipulating the NC core, and red shifts of up to 1 eV for CdS and 220 meV for CdSe have been reported. In a more recent study this exciton delocalization has been linked to increases in the rate constant for radiative decay and thus the PL QY. [103]

The reason for this increase is non-trivial. The radiative rate is proportional to the molar extinction coefficient, which in turn depends (amongst other factors) on the sum of the transition dipole matrix elements for transitions involving all angular momentum sublevels of the first excitonic state. This quantity increases with the number of states participating in the transition and adsorbed PTC ligands donate near valence band resonant states. In addition, the magnitude of the matrix elements for transitions between specific sublevels increases due to symmetry breaking caused by anisotropic ligand adsorption.[103]

These examples show that ligands are more than mere passivation groups and can be chosen specifically to interact with the NC core wave function and exciton relaxation. Comprehensive review papers have been published focusing on this aspect of NC surface science.[11, 104]

All-Inorganic ligand passivation

With the rapid advancement of NC devices that are based on inter-particle CT new synthetic approaches that allow more control over trap states are needed. Devices that are based on injection or extraction of charge carriers to/from NCs require systems in which these charges can travel as far as possible without being trapped at defect sites, or encountering ligand based tunnelling barriers. Although many passivation schemes employing long chain organic ligands have been developed to generate relatively trap free surfaces, the insolating nature of the aliphatic moiety of these ligands inhibit interfacial charge transfer.[65] In order to tailor surfaces specifically for device applications all-inorganic passivations have been developed. These small ligands are far less sterically hindered than traditional organic ligands, and high ligand densities are achieved. There are several different groups of inorganic ligands that can be used to passivate the NC surface. Amongst the most common schemes are metal chalcogenide complexes ($SN_2S_6^{4-}$, AsS^{3-}, …), chalcogenides (S^{2-}, S^2, …), and halides (Cl^-, I^-, ...).

Metal chalcogenide complexes (MCCs) were the first modern inorganic NC ligands.[105] In a generic method that allows the preparation of a large variety of MCCs, bulk metal chalcogenide is dissolved in hydrazine with excess chalcogenide.[106] In this case the stabilizing counter ion is hydrazinium. Although these passivation schemes allow for high electron mobility in NC films[107], the fluorescent properties are somewhat lacklustre, thus their usage is mostly limited to electronic applications.[108] Fluorescence blinking studies show that MCC capped NCs display long off times. This appears to be caused by the free electrons on the MCC which form stable surface hole traps.[109] In addition to these ligand intrinsic trap states, the ligand metal ions can function as redox partners which can add a new level of complexity to the system.[110]

An effective approach for chalcogenide passivated NCs is to exchange native organic ligands by the respective chalcogenide ions. NCs suspended in a non-polar solvent (i.e. toluene) are mixed with an immiscible polar solvent containing the ions (i.e. K_2S) in formamide.[110] The ligand exchange is easily monitored as the (coloured) S^{2-} passivated NCs phase transfer into the polar solvent. The negatively charged surfaces form an electrical double layer around each NC which prevents colloidal aggregation. Unlike sulphur containing thiols, these chalcogenide ion ligands are not intrinsic hole traps. In InP NCs it has been shown that S^{2-} ligands allow for higher retention of PL QYs at high temperatures and show better PL recovery in cyclic heating experiments.[111] The major disadvantage of chalcogenide capped NCs however is their propensity to oxidation.[105]

Many NC based devices contain rectifying P-N junction which rely on stable electron-rich (n-type) NCs in addition to better investigated hole-rich (p-type) NC. As an alternative to unsuitable chalcogenide passivations, air stable halide and pseudohalide ligand exchange reactions have been developed.
A phase transfer reaction approach employs a solution of organic ligand capped NCs in a non-polar solvent and a polar solution containing the halide and pseudohalide ligands.[112] In a different approach that yields partially iodine and organic ligands, oleic acid capped NCs are heated with tetrabutylammonium iodide in oleylamine.[8] This surface modification is reported to increase PL QY by 1.7 times. Compared to bromide and chloride ligands, iodide passivation is the most robust to oxidation (Fig. 8). It appears that iodide ligands allow for a more complete surface passivation than other ligands as they are less likely to desorb from the NC.[113]

In order to obtain a complete picture of the NC surface, these new all-inorganic systems will have to be studied with the tools developed for classical organic-capped NCs.

Applications

There have been recent attempts to utilize the dual NC PL from the core and the surface. The fact that both emissive bands can spread over the entire visible spectrum make small NCs potential phosphors for white light LEDs.[114] While the surface PL has already seen some early application, its suitability has remained controversial. The central problem in applying the surface PL for some application lie in its allegedly undetermined nature arising from ill understood defects. If the surface PL were ill-understood, poorly controlled, and of little stability, it would have no practical use in applications. We address these issues below in some initial applications for lighting and temperature sensing.

Our group has shown that in order obtain an eye pleasing and warm white light there has to be a balance between the core and surface peak. We show that by varying temperature the colour perceived by the human eye can be varied substantially.[2]

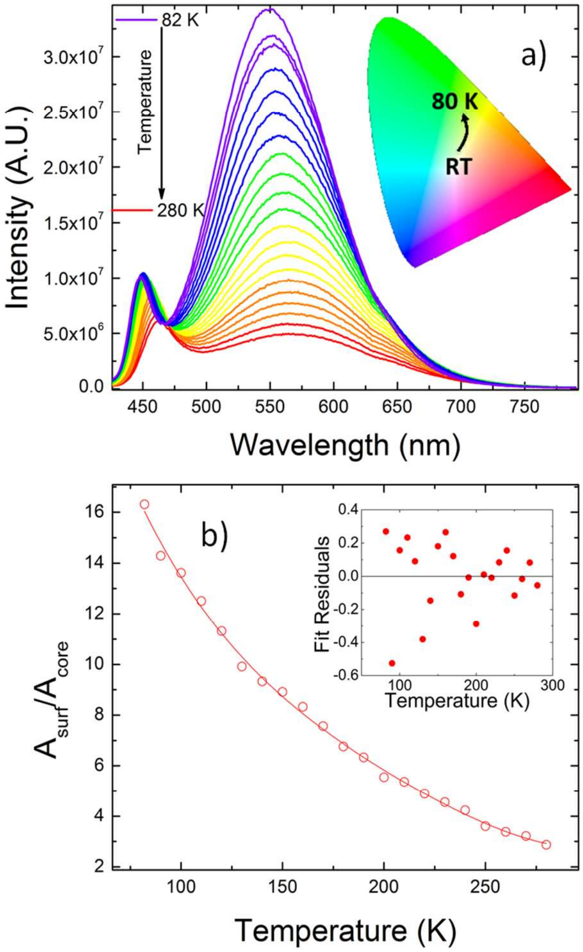

Figure 9: Using intrinsic dual emission as ratiometric temperature sensor. a) Temperature dependent PL of ultra-small TDPA capped NCs. The inset shows the perceived colour b) Ratio of integrated surface to core peak fitted to a fourth order polynomial. Adapted with permission from Reference 4. Copyright (2015) American Chemical Society.

For example, a sample that emits white at room temperature can appear green at low temperatures (Fig. 9). The benefit of creating a broad spectrum using a single NC, rather than a mixture of differently sized particles with narrow emissions, is that there is no self-absorption by the phosphor.[115] Layered nanostructures with different core emission peaks have been proposed as an alternative[116], but these structures also self-absorb their blue and green emission bands and are much more complicated to synthesize.

While there are concerns about the quantum yield and synthetic reproducibility in these NCs, there has been an ever increasing effort to optimize these systems. In order to improve upon the reproducibility of ultra-small NC synthesis every step of the synthetic procedure has to be evaluated. Post synthetic treatment of ultra-small NCs with formic acid increases the PL QY to up to 45% without inducing major spectral shifts.[117] It is thought that the small sterically unhindered carboxylic acids passivate non-radiative trap sites in-between the native ligands. In addition, we have shown that different cooling techniques used to terminate NC growth can influence the spectral peak resolution.[2] Post synthetic procedures can hugely influence the surface composition[85, 118], and can contribute to the apparent non-reproducibility of ultra-small NC synthesis. With increasing knowledge about the atomistic nature of surface trap states, more precise synthetic procedures will emerge.

While the broad bandwidth of surface PL may be controlled for lighting and display applications, the temperature dependence may be used to serve as a ratiometric temperature sensor. In this example of nanothermometry we use core and surface PL, as their ratio is temperature dependent as discussed here. In order to render this phenomenon suitable for thermometry, this ratio of PL areas should follow a simple monotonic functional form.

Most systems we have studied do not show a simple monotonic dependence of the ratio upon temperature. Nevertheless our group has shown that for certain temperature regimes the different temperature responses of the core and surface band can be used to create a ratiometric temperature sensor.[4] Good calibration curves between 290 K and 100 K have been generated with sensitivities ranging from ~0.69–0.32% K^{-1} (Fig. 9), which is comparable to other nanometric ratio based temperature sensors.[119] As in the case of any application, the device needs to be reproducible and robust. Under the assumption that the surface PL arises from ill controlled defects, these objectives will not be met. Consistent with our emergent picture of surface electronic structure of NC, we find that the surface of the NC maybe indeed sufficiently controllable, reproducible, and robust to serve in a variety of applications including temperature sensing.

8. Conclusion

In conclusion it can be said that there have been tremendous advances in the study of the NC surface, but that so far no single theory can exhaustively link spectroscopic observation to the chemical reality of the surface. While our semi-classical ET approach to date is the only model that correctly explains temperature dependent changes in PL and lifetimes, it is only a minimal model. Differences in surface stoichiometries, density of trap states, and ligand-core wave function mixing are aspects not taken into account, but will have to be incorporated in future iterations of our model. In addition single NC PL measurements will have to be performed to further our understanding of the surface. The ever advancing knowledge of ligand chemistry, more powerful DFT simulations, single NC studies, and the advent of all inorganic NCs will progress the scientific conversation about the surface. A holistic model to explain surface excitonics is now more pertinent than ever.

Acknowledgements

The authors would like to thank Oleksandr Voznyy for stimulating discussions. MMK would further like to thank Jonathan Mooney, Samuel L. Sewall and the members of the Kambhampati Group for a very helpful editing process.

Notes and references

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† In the original article we claimed that the NC used were TOPO passivated, which in light of recent advances in ligand chemistry does not appear to be true. The ligands were in fact cadmium phonponates and TOP.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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