The Possibility and Implications of Dynamic Nanoparticle Surfaces

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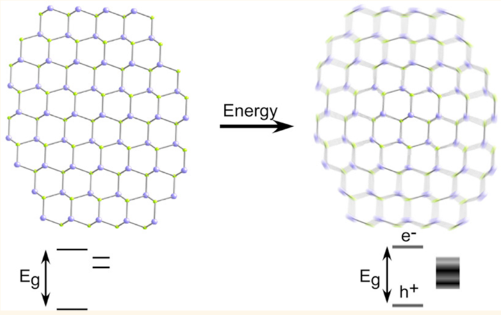
ABSTRACT Understanding the precise nature of a surface or interface is a key component toward optimizing the desired properties and function of a material. For semiconductor nanocrystals, the surface has been shown to modulate fluorescence efficiency, lifetime, and intermittency. The theoretical picture of a nanocrystal surface has included the existence of an undefined mixture of trap states that arise from incomplete passivation. However, our recent scanning transmission electron microscope movies and supporting theoretical evidence suggest that, under excitation, the surface is fluctuating, creating a dynamic population of surface and subsurface states. This possibility challenges our fundamental understanding of the surface and could have far-reaching ramifications for nanoparticle-based technologies. In this Perspective, we discuss the current theories behind the optical properties of nanocrystals in the context of fluxionality.



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For materials scientists, the surface has long been a paradox; it can enable exciting new capabilities in an otherwise mundane material while causing endless frustration in trying to describe how the surface enables these useful phenomena. At the surface, the comforting periodicity of the bulk crystal lattice gives way to faceting, bond contraction, reconstruction, unsaturated/dangling bonds, as well as physisorbed and chemisorbed molecular species. As a result of how dissimilar the surface is from the rest of the material, one is often reduced to describing a material property by separating phenomena as either originating from the bulk or from the surface. Nanoparticles, however, begin to muddle this simple distinction. With dimensions on the order of a few nanometers, the majority of the atoms are located at or near the surface, while atoms that exist in bulk-like configurations are the exception (Figure 1). Therefore, knowledge of the physical and electronic structure of the nanoparticle surface is crucial.

Semiconductor nanocrystals are ideal examples of the challenges the surface poses for nanomaterials. These elegant real world examples of 'the particle in a box' classroom model exhibit size-tunable band gaps as a result of quantum confinement. For example, nanocrystals of CdSe can be synthesized with a band edge absorption ranging from 365−650 nm. Paired with this absorption is a narrow, Stokes-shifted fluorescence that can possess efficiencies approaching unity. From crude origins as micellar colloidal suspensions for photocatalysis, the syntheses of nanocrystals now enable sophisticated control over their size, shape, and composition. Practical applications for current nanocrystals include the following: fluorescent biomarkers for drug discovery, phosphors for solid-state lighting, and light harvesters for photovoltaics.[1−4] However, the fruition and continued improvement of their utility hinges on mastering their surface structure and chemistry.

One of the first clues that the surface and the optical properties of nanocrystals are interdependent was the observation of a broad secondary fluorescence feature strongly red-shifted from the band edge luminescence in CdSe nanocrystals. Measurements of temperature dependence and the decay kinetics of this feature indicated that it was a manifestation of surface-related mid-gap trap states.[5,6] It was proposed that Se surface states localize photogenerated

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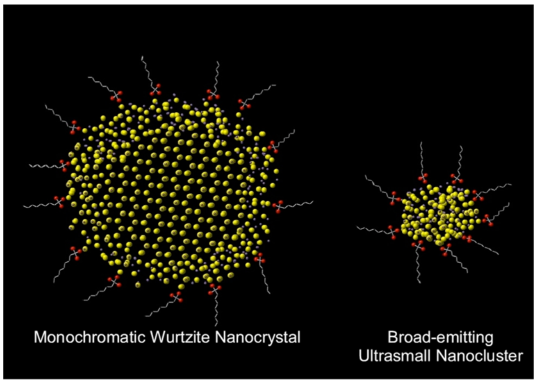

Figure 1. Cross-sectional illustrations of a large monochromatic-emitting nanocrystal and a broad-emitting ultrasmall nanocrystal. In the center of the large nanocrystal, there are atoms that exist in an environment that resembles that of the bulk crystal. Progressing toward the surface, there is an intermediate (selvage) region where atoms are fully coordinated but are in contact with the surface atoms. The surface region is a mixture of fully passivated and unpassivated atoms, ligands bound to the surface, and water and oxygen, if present. In the ultrasmall nanocluster, the crystal core is missing and the entire particle resembles the disordered surface of the large, monochromatic nanocrystal.

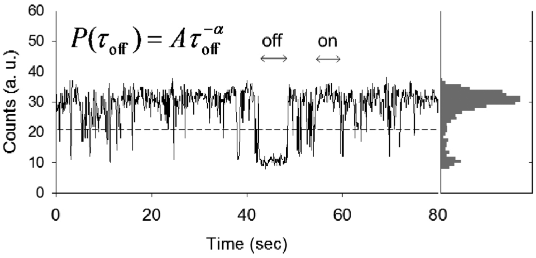

Figure 2. Standard blinking statistics for a commercial quantum dot (QD655) with the inset showing the power-law equation for the OFF time probabilities, where $\alpha \sim 1.5$.

holes, leading toward a predominantly radiationless decay pathway, limiting fluorescence quantum yields to around 10% or less. Supporting this description, Lifshitz *et al.* utilized optically detected magnetic resonance (ODMR) measurements that showed that holes localize at a site with low symmetry, presumably the surface.[7] This low symmetry site is likely an under-coordinated surface atom: either a Se atom for holes or a Cd atom for electrons. Hole trapping at surface Se atoms is expected to be more common relative to electron trapping at Cd atoms due to the fact that the surfactants used to synthesize nanocrystals preferentially bind to the cation more strongly than the anion. The anion is believed to remain unpassivated or partially passivated with the weakly binding phosphine ligands or oxygen. Underwood *et al.* would later corroborate hole trapping on Se surface sites by measuring the trapping rate of the photogenerated holes using ultrafast spectroscopy.[8] Further spectroscopic investigations paint a picture of the charge carrier relaxation pathways coupled to the nature of the surface passivation, surface, and intrinsic defect states.[9]

Semiconductor nanocrystals are ideal examples of the challenges the surface poses for nanomaterials.

There are two routes available for chemists to eliminate surface trap states. One is to utilize the right mixture of surfactants to yield a well-passivated surface.[10] However, organic ligands are easily dislodged during purification and are susceptible to photo-oxidation. Further, little is known about the mechanism behind ligand brightening or quenching of the nanocrystal fluorescence. There are several experimental reports that demonstrate the impact of different ligand structures, but little detailed theoretical work involving realistic surface structures and ligand dynamics under photoexcitation.[11−16] Alternatively, a more robust method to achieve surface passivation is to encapsulate the nanocrystal with an inorganic shell of a wider bandgap material.[17,18] Ideally, the shell eliminates the surface states and confines the electrons and holes to the nanocrystal core. Core/shell nanocrystals, or quantum dots, have been synthesized with a variety of compositions, near unity fluorescence quantum yields, and high photostability. However, despite these gains, complete decoupling of the core (bulk-like) processes with the surface has not been achieved. CdSe/CdS core/shell nanocrystals with shells as thick as 19 monolayers still have middling quantum yields and exhibit fluorescence intermittency, or blinking.[19] This blinking behavior and its peculiar power-law kinetics highlight how little is still known about the nanocrystal surface.

Blinking and Spectral Diffusion. Nanocrystal blinking is readily seen under a conventional fluorescence microscope.[20] Like a starfield, nanocrystals flash on and off at seemingly random intervals. Blinking has been best shown to fit power-law kinetics with blinking intervals from microseconds to tens of seconds (Figure 2). Generally, blinking is useful in fluorescence microscopy as an indicator that one is observing single particles rather than an aggregate. However, blinking can complicate tracking an individual nanocrystal over time and/or distance and is undesirable for lighting applications. Ideally, one could engineer the quantum dot to exhibit a defined blinking rate or eliminate blinking depending on the desired application. To achieve this, a mechanistic understanding is needed to approach this problem intelligently.

The simplest and most common explanation of the origin of quantum-dot blinking is that of the charge-trapping model. If either a photogenerated hole or electron becomes trapped, the nanocrystal becomes charged. During this state, the quantum dot cannot emit until the charge is eliminated by some diffusion-limited process.[20] Improvements in single nanocrystal spectroscopy have illustrated, however, that the processes behind blinking are far more complicated than a simple binary 'On' or 'Off' mechanism.[21−24] Frantsuzov *et al.* neatly summarized five different models that have evolved as new experimental insights were gained.[25]

A recurring theme for the majority of these models is the involvement of a dynamic surface-related diffusion or fluctuation mechanism that modulates trapping probabilities and lifetimes. In particular, the multiple recombination center (MRC) model invokes 'light-induced jumps' of surface atoms as a possible mechanism behind dynamically varying quenching centers.[26] This model has also been used to explain observed spontaneous spectral diffusion (sudden shifts in emission energy) from the fluorescence of single nanocrystals. The discovery of memory effects in both blinking and spontaneous spectral diffusion has also implicated some dynamic process involving nearly degenerate surface or ligand states.[27−29] Additionally, Voznyy applied density functional theory to show that the bidentate nature of carboxylic acid ligands leads to nearly degenerate bonding configurations.[15] These surface ligands can transition from different bond configurations at elevated temperatures introducing new states into the bandgap. This mechanism could yield the switchable long-lived trap state required by the MRC model.[15] However, not all nanocrystal ligands are bidentate, and one would expect greater control over blinking by modulating the organic passivation. Our recent experiments pose an alternative source of dynamics.

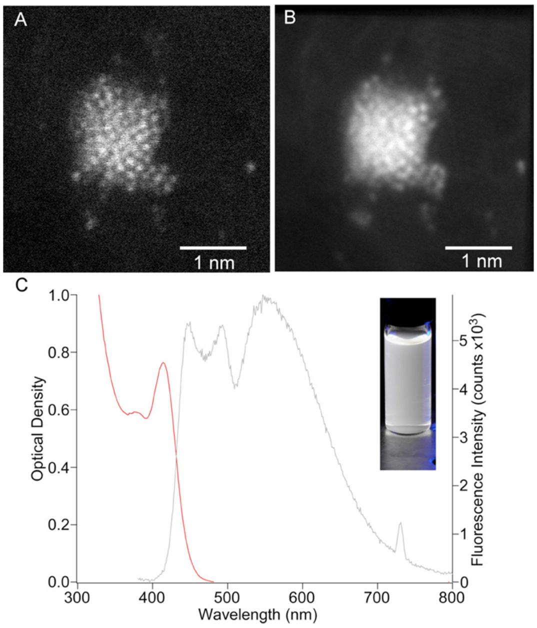

Figure 3. White light-emitting CdSe nanocrystals. (A) Single frame from a scanning transmission electron microscope (STEM) movie collected at 60 kV of a white light nanocrystal showing a disordered atomic structure. (B) Frame-averaged STEM image of the same movie with drift-correction showing motion-induced blurring. (C) Absorption (red) and fluorescence (gray) of white-light-emitting CdSe nanocrystal with a photograph of the fluorescence from a sample in solution.

Direct Observation of Surface Dynamics. Since 2001, we have been utilizing atomic number contrast scanning transmission electron microscopy (Z-STEM) to study the structure of nanocrystals.[30] With the advent of aberration correction, it became possible to obtain atomic-resolution images showing the ionic periodicity of the crystal lattice, enabling direct identification of the surface facets in the image. This led to the determination of the subtle effect ligands have on nanocrystal faceting as well as the determination of facet-directed shell growth.[31,32] Unfortunately, the direct determination of the atomic structure at the surface was consistently thwarted by the presence of an amorphous surface coating. In 2005, we became interested in determining the structures of sub-2-nm CdSe nanoparticles, which exhibit broad white-light fluorescence.[33] Although one set of images suggested that these sub-2-nm nanocrystals may be wurtzite, further attempts to image these clusters yielded seemingly random, spherical clusters of atoms.[33] However, once the images were collected in rapid succession, it became clear that the atoms in the cluster fluctuate under the electron beam.[34] Figure 3 shows a single (A) and a frame-averaged (B) STEM image of a sub-2-nm CdSe nanocrystal. The blurring in Figure 3B is due to the movement of the atoms.

The topic of fluctuating nanoparticles under an electron beam is not new and has been commented on previously.[35,36] Generally, the energy of the electron beam heats up small atomic clusters, causing the atoms to reorganize into new configurations.[37] The difference here is that we can now image single atoms under relatively low beam energies, in this case 60 keV.[38] In this 'gentle STEM' regime, knock-on damage should be significantly reduced as one can generally image organic structures with minimum damage. However, regardless of beam energy (60−300 keV), the atoms in the clusters were seen to fluctuate continually during imaging. Rather than dismissing what we observed as an artifact of STEM imaging, we proposed that the energy imparted by the electron beam is on the same order as an ultraviolet (UV) photon.[34] In the same manner that the electron beam induces atomic motion, the absorption of a UV photon by a small nanocrystal could also destabilize the crystal structure. This energy imparted by the beam can be approximated using the stopping power of bulk CdSe (1.38 eV/nm) for a 100 keV electron, which gives 2.8 eV per electron for a 2 nm nanocrystal. The energy imparted by a UV photon can be as much as the Stokes loss or the energy difference from the excitation energy to the emission energy, which is ~1.3 eV for a 2 nm nanocrystal. For a 54-atom CdSe cluster, this gives 34 meV per atom from the electron beam and 24 meV per atom from the UV photon. The effective temperature can then be calculated using (3/2)kT plus room temperature in K. This gives an approximate temperature of about 700 K for the electron-excited particle and 500 K for the UV-photon-excited particle. Density functional theory (DFT) simulations of the time evolution of a similarly sized CdSe crystallite were performed to test this idea.

With the use of heat to simulate the absorption of energy by the nanocluster, the atomic displacement of the atoms and the resultant energy gaps were calculated for a small CdSe cluster. Just as in the STEM movies, the DFT movies show the crystal in a disordered state and undergoing continuous random atomic fluctuations. In a similar fashion to what Voznyy observed, each new configuration of the atomic structure modifies the effective band gap.[34] If a portion of these states are radiative, then the nanocluster fluorescence would emit over the entire visible spectrum, matching the experimental spectrum of the nanocrystals (Figure 3C). The surface ligands then tune the efficiency of a certain subpopulation of states yielding a balanced white light fluorescence.

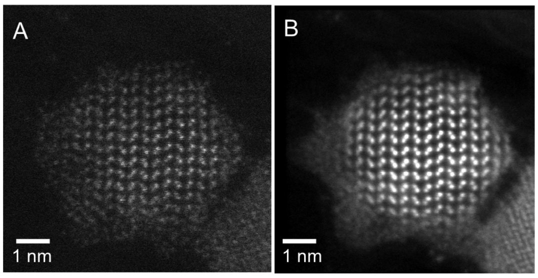

Figure 4. Image of a fluxional surface. (A) Single frame and (B) a frame-averaged image from a drift-corrected scanning transmission electron microscope movie of a 5-nm CdSe nanocrystal, illustrating the surface blurring due to atomic fluctuations.

To determine exactly at what diameter fluxionality begins to manifest, we obtained movies of 3-, 5-, and 7-nm-diameter CdSe nanocrystals. As the diameter increases, a bulk-like region of crystalline stability is observed surrounded by about 1 nm of fluctuating surface. The fluxional surface can be seen in the STEM images of a 5-nm CdSe nanoparticle in Figure 4. What appears to be a static amorphous layer in Figure 4A is actually constantly fluctuating and becomes blurred once successive frames of the STEM movie are averaged (Figure 4B). The size where the stable crystal core appears also coincides with the emergence of band edge luminescence. Therefore, *fluctuations observed in the STEM are not limited to sub-2-nm nanoclusters, but are ever-present for all sizes of nanocrystals.*

Possible Origins of the Fluxional Surface. One of the size-dependent properties of nanoparticles is the melting temperature. Theoretical treatments for nanoparticle melting include the surface-tension-based phase equilibrium model described by Buffat and Borel as well as the liquid-drop model described by Nanda *et al.*[39,40] The melting temperature for a nanoparticle (T_{mp}) according to the Buffat-Borel model eq 1 is

$$T_{mp} = T_{mb}\left[1 - \frac{4}{L\rho_s d_p}\left\{\gamma_s - \gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right\}\right] \quad (1)$$

where T_{mb} is the bulk melting temperature, L is the molar latent heat of fusion, ρ_s and ρ_l are the density of the solid and liquid, d_p is the particle diameter, and γ_s and γ_l are the solid and liquid surface tensions. This model assumes equilibrium between a spherical solid particle, a liquid particle of equal mass, and a vapor phase, and it invokes a surface-only liquid phase (premelting). The liquid drop model predicts nanoparticle melting by scaling the material-dependent cohesive energy with the melting temperature. The size-dependent melting temperature is calculated as

$$T_{mp} = T_{mb}\left(1 - \frac{\beta}{d}\right),\ \beta = \frac{z\nu_0\gamma}{0.000365T_{mb}} \quad (2)$$

where β (nm) is a material-dependent constant, z is a coefficient dependent on the melting mechanism, ν_0 is the atomic volume, and γ is the coefficient of surface energy, while 0.000365 is calculated from the slope of the cohesive energy (eV/coordination number) and the melting temperature (K). The challenge in applying these models to predict the melting point accurately is their reliance on bulk constants that are assumed to remain unchanged for nanoparticles.

Experimental methods for measuring nanoparticle melting are limited to X-ray or electron diffraction techniques, where loss of measurable diffraction peaks is equated to melting. Goldstein *et al.* measured the size-dependent melting temperature for CdS nanocrystals using *ex situ* heating and electron diffraction.[41] If one extrapolates their results below 2 nm, the CdS nanocrystals would exist as a liquid near room temperature. Figure 5 shows several calculated melting curves for CdSe nanocrystals utilizing modified versions of eqs 1 and 2. The Buffat-Borel equation was modified using a size-dependent surface tension, while two different values for β were calculated using cohesive energies from the literature. Details for this set of calculations can be found in the Supporting Information. The most conservative of these models suggests that sub-2-nm CdSe nanoparticles could exist at a near-liquid state at room temperature. This mirrors what we observe in the STEM for CdSe; the fluid motion of the atoms under the electron beam resembles that of a liquid. Furthermore, for larger nanocrystals we could be observing surface or premelting.[42,43] In this case, melting occurs first at the surface followed by either a persistent liquid skin that prevents the particle melting until reaching T_m or a gradual thickening of this layer until the entire particle is molten.[44]

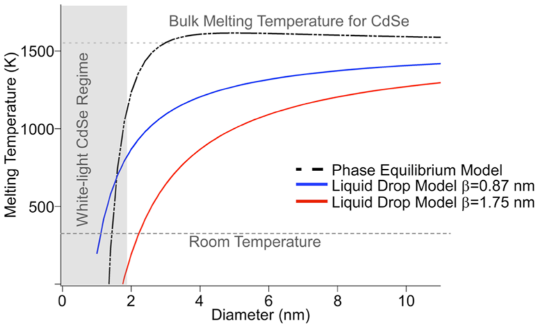

Figure 5. Size-dependent melting temperature of CdSe nanocrystals calculated from models based on bulk and experimentally determined size-dependent values.

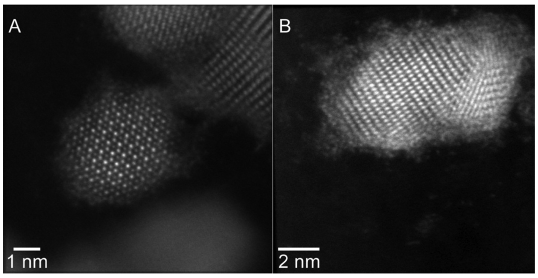

Figure 6. Frame-averaged STEM image of an oleic acid-capped CdSe nanocrystal (A) and a phosphonic acid-capped CdTe nanocrystal (B).

How long can the surface remain in this state of constant motion before a permanent defect is introduced or the particle disintegrates completely?

Alternatively, surface vacancies or surface adatoms could lead to a weakened disordered layer that could be highly susceptible to fluctuations. The stoichiometry of CdSe nanocrystals has been measured by inductively coupled plasma atomic emission and/or mass spectroscopy (ICP-AES/MS) and Rutherford backscattering spectroscopy, both indicating that they are nonstoichiometric.[45−47] Specifically, nanocrystals synthesized using metal phosphonates are cation-rich, with the excess cations coating certain facets of the nanocrystal.[46] These surface adatoms would be intrinsically less stable due to lower coordination with their nearest-neighbor atoms.

It has also been proposed that the ligand shell, specifically one composed of phosphonic acid, can form a disordered surface coating on the nanocrystals. Utilizing vibrational sum frequency generation and X-ray photoelectron spectroscopy, Frederick *et al.* measured the ordering of octylphosphonate ligands on the surface of CdSe nanocrystals.[48] While a generally ordered monolayer of the phosphonate was found for large, ∼5-nm-diameter CdSe, this order was observed to decrease with decreasing particle diameter. Of particular relevance to this Perspective are the reported adsorbed cadmium−phosphonate complexes that exist in this surface layer, which were not observed for stearic acid-capped CdSe. In this case, what we could be imaging in the STEM are surface-associated cadmium phosphonate complexes. To test this possibility, we synthesized CdSe nanocrystals using oleic acid as the capping ligand and observed the same fluxional surface in the STEM, indicating that the observed phenomenon is not qualitatively ligand dependent (Figure 6A).

Lastly, the fluxional layer could be the skeletal remains of a once-oxidized surface. Using X-ray photoelectron spectroscopy, Bowen-Katari *et al.* showed that the surface of CdSe oxidizes to form SeO_2.[49] This molecule then sublimes from the surface of the nanocrystal creating vacancies. Prior to imaging in a STEM, it is common to heat the sample under high vacuum conditions to prevent the buildup of carbon contamination during imaging. Any SeO_2 adsorbed to the surface of the nanocrystal could be removed during this procedure. CdTe, however, should oxidize to form TeO_2 at the surface, which is unlikely to sublime. Figure 6B shows a phosphonic acid-passivated CdTe nanocrystal also exhibiting a fluxional surface. The observation of the fluxional surface for CdTe and a lack of a measurable oxygen signal from electron energy loss spectroscopy measurements suggest that surface oxidation does not create an unstable surface that fluctuates in the STEM.

Implications of a Fluxional Surface. *Nanocrystal Stability.* The stunning STEM movies quickly raise the question: how long can the surface remain in this state of constant motion before a permanent defect is introduced or the particle disintegrates completely? For organic-capped nanocrystals, this will largely depend on how efficiently the surface ligands can recoordinate or adapt to the surface dynamics, while competing with oxygen and water. Once the surface becomes unpassivated under excited conditions, the oxidation and dissolution at the surface would rapidly increase and work its way deeper into the nanocrystal core. Improved surface stability should be obtainable by utilizing strongly coordinating bidentate ligands.

> For nanocrystal blinking and spectral diffusion, a dynamic surface offers potential support for some current models.

Dynamic Surface States and Charge Trapping. Surface fluxionality also introduces a new level of complexity when modeling charge transfer mechanisms that are often mediated by surface states; the energy levels of the surface states are now time dependent. Charges trapped on the surface will experience an evolving energy surface dependent on the configuration of the charged atom relative to its nearest neighbors. In the context of a nanocrystal-based photovoltaic, the ability of surface charges to leave the nanocrystal is now constantly changing and measured charge-transfer rates are not from a single surface-state transition but from a time-averaged dynamic state. Similarly, charge injection into the nanocrystal for electroluminescent light-emitting diodes becomes equally as complicated because the injected electron and hole will also impart energy that could initiate surface mobility.

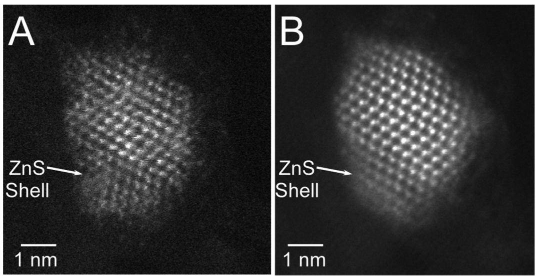

Figure 7. Single frame (A) and frame-averaged, drift-corrected STEM image (B) of a CdSe/ZnS core/shell nanocrystal showing enhanced motion blurring for the shell region.

Blinking and Spectral Diffusion. For nanocrystal blinking and spectral diffusion, a dynamic surface offers potential support for some current models. Since the surface states are in constant flux during excitation, it is plausible that certain atomic arrangements correspond to 'ON' or 'OFF' states. Atomistically, prior to excitation, the surface is presumably resting in a stable reconstructed configuration, perturbed only by ambient thermal energy. Once light is absorbed, the surface atoms are set in motion, sampling different atomic configurations. Once the excitation source is removed, the surface will relax to a local low energy configuration, which may be metastable. Following this description, the rate of switching between 'ON' and 'OFF' would be determined by the speed at which different atomic configurations are sampled and by the probability distribution of 'ON' and 'OFF' configurations. Although the atoms seem to move fluidly on the time scale of the movies, this motion should be less random at faster time scales, as certain atomic configurations should be more stable than others. 'ON' and 'OFF' time variations would then depend on the probability that the surface will be in a configuration that is conducive to emitting a photon. Additionally, the spectral diffusion, or energy jitter observed even at cryo-temperatures, could be small variations in the bandgap energy caused by the surface dynamics.[29] Only certain surface atomic configurations contribute to the nanocrystal's bandgap, essentially causing the nanocrystal diameter to oscillate under excitation. This would also lead to size-dependent spectral diffusion as energy difference in a band gap for a monolayer ranges from ∼600 meV for small (2 nm) to ∼50 meV for large (5 nm) CdSe nanocrystals. Although measured spectral diffusion shifts are on the order of 0.1 meV, larger jumps out of the detection window were observed by Fernée *et al.*[29]

Memory Effects. Surface fluxionality could also explain excitation-induced memory effects. After excitation, the energy fueling fluxionality will be reduced, and the particle will relax into a local minimum energy configuration. Without the energy to overcome large energy barriers, this will effectively lock the surface atomic structure in a configuration dependent on the previous excited state ('ON' or 'OFF'). Therefore, subsequent blinking states will at least remain weakly correlated until a defect in the surface is formed.

Core/Shell Nanocrystals. With respect to a fluxional surface, the shell serves simply to reduce the overlap of the electron/hole wave functions with the dynamic surface states. In practice, this is difficult to do since shell growth typically favors a particular facet. Nonetheless, recent success at limiting or eliminating blinking by growing thick shells or thick gradient shells suggests that it is possible to decouple the excitation dynamics partially from surface dynamics.[19,50] However, the dynamic surface adds a new wrinkle to core/shell structures. Since the core and shell material will have different bond energies, they should fluctuate differently. In essence, the shell could serve as a sink for the fluxional energy, yielding enhanced luminescence efficiency with only partial shell coverage. Figure 7B shows a frame-averaged STEM image of a thin-shelled CdSe/ZnS nanocrystal. The atomic lattice of the ZnS shell is significantly blurred due to atomic motion relative to the CdSe core. In contrast to the usual monolayer of motion, at least 3 layers of the shell, albeit asymmetrically, are in motion. It must be stated, however, that ZnS may very well interact more strongly with the electron beam, even with low beam energies. Further work will be required to investigate other material compositions.

SUMMARY AND FUTURE DIRECTIONS

From the theories developed to explain the complex photodynamics of nanocrystals, it is clear that one or several dynamic surface mechanisms exist rather than a static system of mid-gap states. Although ligand rearrangement has been proposed theoretically as a mechanism, our STEM data point to the possibility that the dynamic process may be the result of excitation-induced atomic motion at the nanocrystal surface. Localized trapped charges at the surface encounter a changing energy surface as the atoms move in and out of different configurations. Whether these processes involve just the surface atoms or both surface atoms and ligands, they must be understood for proper control over fluorescence efficiency and intermittency. Further, a fluxional surface has profound implications for photocatalytic mechanisms, which are often tied to a specific surface configuration. This Perspective should spur the search for experimental methods to examine the atomic surface configuration in the ground and excited states of the nanocrystal.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Experimental procedures, size-dependent melting temperature calculations, and STEM movies (Figure 3: nn403478h_si_002.avi; Figure 4: nn403478h_si_003.avi; Figure 5: nn403478h_si_004.avi; Figure 6: nn403478h_si_005.avi; Figure 7: nn403478h_si_006.avi). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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