

Dynamic Fluctuations in Ultrasmall Nanocrystals Induce White Light Emission

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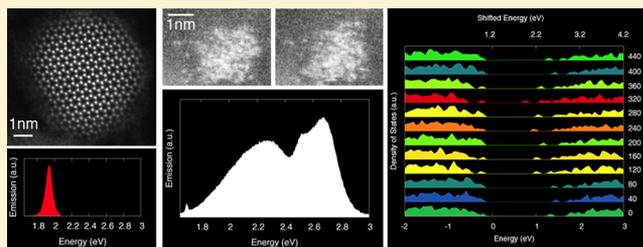
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S Supporting Information

ABSTRACT: Individual ultrasmall CdSe nanocrystals have recently been found to emit white light, but the ultimate origin of the phenomenon has remained elusive. Here we use a combination of state-of-the-art experiment and theory to show that excitation sets the ultrasmall nanocrystals into a fluxional state. Their energy gaps vary continuously on a femtosecond time scale, so that even an individual nanocrystal can emit across the entire visual range. In addition, we observe the outer layers of the larger monochromatic emitting nanocrystals to be fluxional. Such fluxionality should be considered when optimizing nanocrystals for applications. Thus, small is indeed different, but ultrasmall is different yet again.

KEYWORDS: Nanocrystals, quantum dots, fluxionality, scanning transmission electron microscopy, density functional theory



Nanotechnology depends on the fact that as structures are made smaller they acquire new properties. For semiconductor nanocrystals, one consequence of smallness is quantum confinement.¹ The resulting size-tunable optical properties of nanocrystals are of major interest for lighting and solar cell applications and as an alternative to fluorescent dyes in biological imaging.^{2–6} The quest to fully exploit quantum confinement brought with it a push to synthesize progressively smaller and monodisperse nanocrystals. As their size was reduced into the ultrasmall sub-2-nm range, new properties emerged. In particular, nanocrystals that exhibit blue-shifted monochromatic light emission at larger sizes begin to show broad spectra when made ultrasmall.^{7–12} White light emission from ultrasmall CdSe nanocrystals^{13–16} is a particularly interesting case of such broad emission because of its potential for solid-state lighting.⁸ The origin of white light has been attributed to surface or trap states, but the sudden appearance of a *continuum* of emission wavelengths from individual nanoclusters has not been explained.

In this Letter, we combine aberration-corrected scanning transmission electron microscopy (STEM) and finite-temperature density functional theory (DFT) simulations to elucidate the mechanism of the white light emission. Figure 1 documents the size and structure dependence of the optical properties of CdSe nanocrystals. Monochromatic emission from red to green is seen to correlate with increasingly smaller diameters of wurtzite nanocrystal (Figure 1a–f). Around each wurtzite core

a fluxional surface layer of approximately a nanometer in thickness exists, appearing as a blurry layer in the images (Figure 1a,c,d) because of the rapid rate at which the surface structure changes. These motions are clear in the movies available online (see Supporting Information, movies si_002.qt, si_003.qt, and si_004.qt).

Moving into the ultrasmall regime produces the broad white-light emission spectrum shown in Figure 1g. Single particle optical spectroscopy indicates that individual CdSe nanoparticles emit white light.⁵ The STEM observations confirm that the size distribution of the particles is far too narrow to produce such a spectrum through quantum confinement alone. On the basis of their sub-2 nm sizes, one would expect quantum confinement to produce only colors in the blue to ultraviolet range. On the other hand, it has been suggested that white light emission involves surface or defect states in the gap,¹⁶ but again defect and surface states cannot explain the sudden appearance of a continuous spectrum of transition energies spanning the visual range when the diameter is reduced below 2 nm.

Successive frames (Figure 1g,h) from a Z-contrast STEM movie (see Supporting Information, movie si_005.qt) of a white-light-emitting nanoparticle show it wriggling continu-

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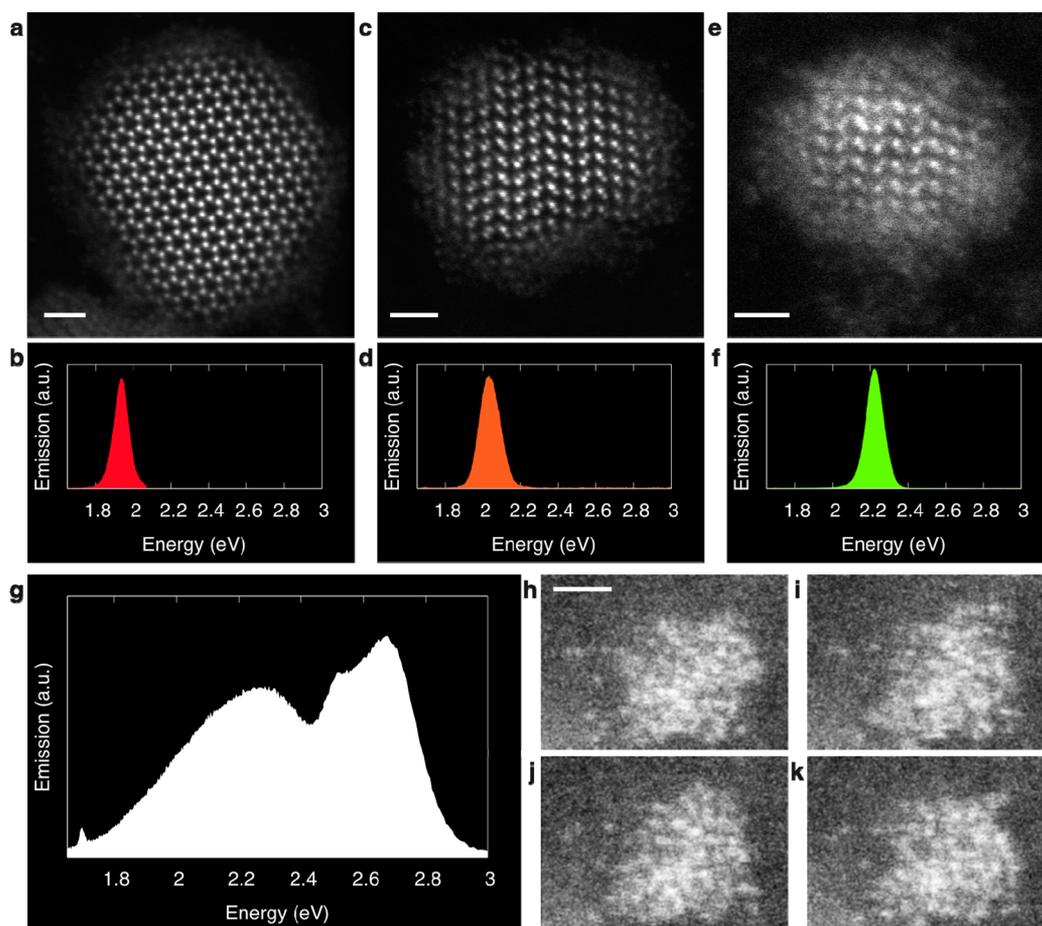


Figure 1. Atomic resolution Z-contrast STEM images and optical emission spectra from CdSe nanocrystals of 7 nm (a,b), 5 nm (c,d), and 3 nm (e,f) diameters. (g) White light spectrum emitted by ultrasmall sub-2 nm CdSe nanoclusters. (h–k) Successive frames from a STEM movie showing the continuous motion and disorder of the ultrasmall clusters. Scale bars are 1 nm.

ously. All the ultrasmall CdSe nanocrystals behave this way, regardless of the accelerating voltage (60–300 kV). The disordered fluxional surface layers seen around the larger nanocrystals appear to have consumed the entirety of the ultrasmall white light emitting CdSe particles. They therefore cannot be regarded as crystalline, and hence we should more correctly refer to the white-light emitting structures as nanoclusters. Note that energy transfer from the fast electron beam is quite sufficient to be the cause of the continuous fluxional motion (see Supporting Information).

The white light spectrum spans from 1.7 to 3 eV and is produced by exciting the nanoclusters with ultraviolet light. An electron excited by the absorption of a 3 eV ultraviolet photon must therefore lose up to 1.3 eV of energy to vibrations before emission in the visible spectrum can occur. For a 75-atom cluster, such an energy amounts to 17 meV per atom added to the existing thermal energy of the cluster at room temperature. For comparison, at the melting temperature of bulk Si individual atoms possess a kinetic energy of 22 meV.¹⁷ Furthermore, the melting point of nanoclusters decreases rapidly as their size decreases.^{18–23} Clearly something other than simple quantum confinement is causing the white emission. The only common property of the white light emitting nanoclusters seen by STEM is their dynamic amorphous structure. We therefore turn to density functional theory (DFT) calculations to test if such fluxionality could result from photoexcitation and cause the white light emission.

Carving out an ultrasmall Cd₂₇Se₂₇ nanocrystal from bulk wurtzite CdSe and relaxing it already gives some hints as to the sensitivity of the electronic structure. Before relaxation, the nanocluster has no energy gap; after relaxation it adopts a less crystalline structure and a gap opens up. This result is consistent with previous theoretical work on magic-sized Cd₃₃Se₃₃.²⁴ Heating the relaxed cluster up to room temperature (300 K) using quantum mechanical molecular dynamics (MD) the cluster disorders further. The atoms move continuously, but after some time the motions look less wild. Relaxing the structure after the atomic motions have calmed down somewhat results in a structure lower in energy than the cluster relaxed from wurtzite. Therefore, we conclude that the ultrasmall nanoclusters are intrinsically disordered.

To account for the additional vibrational energy imparted after the absorption of an ultraviolet photon, we performed MD at 500 K (see Supporting Information). The extra energy makes the motion of the atoms more rapid and violent. Snapshots from the simulation are shown in Figure 2a–d, and the full movie is available online (see Supporting Information, movie si_006.qt). The atoms appear to move around as they do in the microscope.

The densities of states (DOS) calculated at 40 fs intervals during part of the 500 K MD simulation are shown in Figure 2e. From this figure it is immediately clear that the continuous structural fluctuations result in correspondingly fluctuating energy gaps. The DOS have been colored according to the

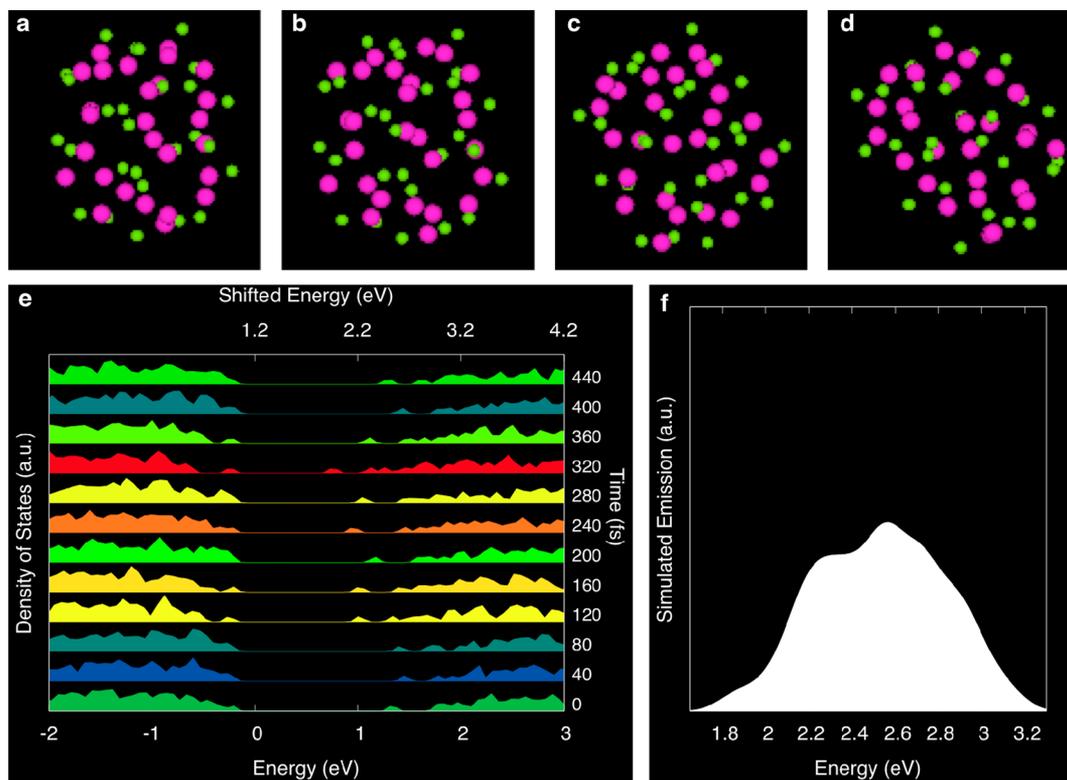


Figure 2. Density functional simulations of ultrasmall CdSe. (a–d) Snapshots from a 500 K quantum MD simulation of a Cd₂₇Se₂₇ cluster. (e) DOS calculated at 40 fs intervals during the 500 K simulation. The zero of the bottom energy axis has been set to the DFT Fermi level. The top axis has been shifted 1.2 eV to account for the well-known underestimation of the band gap by DFT. Each DOS has been colored according to the energy of the lowest unoccupied state on this recalibrated axis. (f) An emission spectrum simulated from 20 DOS calculated at intervals of 40 fs.

energy of their lowest unoccupied state. In determining the color, 1.2 eV was added to the calculated Kohn–Sham energy gaps, which are well-known to be too small compared with measured values. The value 1.2 eV was chosen so that the first peak in the unoccupied DOS of the relaxed steady-state structures matches the energy at which absorption begins experimentally (see Supporting Information). The colors span the range from red to blue. We emphasize that the continuous emission spectrum arises from a continuously varying energy gap caused by the fluxionality. The bonds in the cluster are constantly and smoothly switching.²⁵ The evolving electronic states originate from different regions of the nanocluster, but the regions cannot be categorized as surface, bulk, or trap states (see Supporting Information).

The first unoccupied peak in each DOS is separated from the continuous band of unoccupied states that appear at higher energies. In some cases an additional isolated peak appears between the first peak and the continuous band of unoccupied states. If we consider that emission may occur from all of these, the range of potential emission energies expands. Figure 2f is the result of adding Gaussian peaks at each of these emission energies for 20 sets of DOS calculated at 40 fs intervals during the 500 K MD simulation, the first 12 of which are those shown in Figure 2e. The energy axis includes the 1.2 eV rigid shift to the conduction band to facilitate comparison to experiment. The plot simulates the time-averaged emission of an excited ultrasmall nanocluster. The simulated spectrum matches the width and general shape of the experimental emission spectra.

The perceived color of the time-averaged emission depends on the shape of the emission spectrum, not just the range of emission energies. Simulations with partial ligand coverage

produced levels of fluxionality similar to the bare clusters (see Supporting Information). Extensive simulations with ligands are not practical, however. Their presence most likely eliminates nonradiative recombination paths at the surface, but also modifies the fluxional nanoparticle's energy gap, which alters the emission spectrum. Experimentally, it is evident that the precise shape of the emission spectrum of ultrasmall CdSe depends on the mixture of ligands used in their synthesis.¹⁶ Different mixtures of ligands tint the spectrum in different ways, enhancing different regions of the visible range, and only the right balance of ligands produces white light. Other mixtures of ligands can make the spectrum appear different colors or reduce the emission intensity.^{26,27} All ultrasmall CdSe clusters, however, appear to emit broadly. In some cases, one peak is much stronger than the rest of the spectrum, but even in these cases a broad emission feature covering most of the visible range is present. The ligands also affect the emission of the larger nanocrystals. Only when correctly passivated do they appear to emit monochromatically. Poorly passivated nanocrystals have additional emission features, often referred to as deep trap emission, which may be related to fluxionality at their surfaces. Further effort is necessary to show how organic and inorganic passivation works on a fluxional surface.

In conclusion, the ultrasmall size marks the point at which the majority of atoms in a nanoparticle are at its surface. STEM observations and DFT simulations show that such a predominance of surface atoms can destabilize nanocrystals, causing them to take on a dynamic disordered structure. Furthermore, this fluxionality can lead to a dynamic electronic structure. In ultrasmall CdSe, it appears to lead to continuously changing energy gaps that are likely to result in their ability to

individually exhibit a white time-averaged emission spectrum. Fluxionality also exists at the surfaces of all the larger nanocrystals we have observed, and consequently, the ramifications exceed white light emission. This description of a nanocrystal surface is quite different from the concept of a stable trap state and may be relevant to understanding broad red-shifted emission from poorly passivated nanocrystals as well as nanocrystal blinking.^{26–29} Cotton³⁰ first advocated the use of the term fluxionality in connection with organometallic molecules in 1968. Fluxionality of ultrasmall nanoclusters has been invoked in the past in the context of catalysis^{22,23} and has been discussed by other authors.^{21,31} The present work indicates that fluxionality is the likely root cause of white-light emission from ultrasmall nanoclusters and that it persists at the surfaces of larger nanocrystals that emit monochromatic light. The concept may play a role in accounting for other features of white-light emission.¹⁶ When optimizing nanocrystals for any application, such as solar cells, light-emitting diodes, photocatalysis, or biological imaging agents, dynamic fluxionality could be a critical consideration.

■ ASSOCIATED CONTENT

📄 Supporting Information

Supporting Information includes a description of materials and methods and further discussion, as well as STEM movies, a movie of a DFT simulation, and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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