OPTICAL DETERMINATION OF CRYSTAL PHASE IN SEMICONDUCTOR NANOCRYSTALS

Allocation: Blue Waters Professor/190 Knh; Illinois/550 Knh
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EXECUTIVE SUMMARY

Semiconductor nanocrystals are highly interesting and diverse material systems with unique electronic and optical properties that are even tunable as to size, shape, composition, and internal structure. Currently, the fundamental connection between crystal structure and optical properties is not well understood, hampering wide-spread and efficient use of these nanocrystals in societally important applications such as light-emitting diodes, solar cells, bioimaging, and consumer electronics. In order to establish a connection between structure and optical properties, we use a combination of cutting-edge experimentation and first-principles theoretical spectroscopy. Our work shows that by understanding the absorption spectrum at energies well above the absorption onset, it is possible to efficiently distinguish optically between two different crystal structures of CdSe materials, wurtzite and zincblende, both in bulk crystals and nanocrystals. This may rapidly accelerate development of these materials by allowing fast and accurate structural characterization with small quantities as well as samples in liquids.

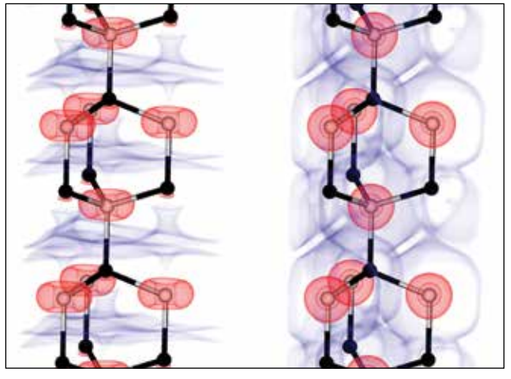

Figure 1: Visualization of wave functions of electronic energy states in bulk WZ CdSe at the kappa point (left) and the gamma point (right) of the Brillouin zone. Atoms and bonds are shown in ball-and-stick format with Cd in black and Se in grey. Isosurfaces are shown in red for the top 95% of the squared wavefunction to depict high localization and the lowest 5% in blue to depict nodes.

RESEARCH CHALLENGE

Semiconductor nanocrystals are diverse material systems currently used in light-emitting devices, solar cells, bioimaging, and consumer electronics. Their unique electronic and optical properties and the fact that these properties are tunable by changing the size, shape, composition, and internal structure of the nanocrystals, make them highly interesting material systems to a broad community of researchers and diverse commercial sectors from optical devices to medical diagnostics. Among the most fundamental questions is the *connection* between crystal structure and optical properties, as answering that question would allow control of functionality through structural properties that are accessible to synthesis. Despite highly interesting implications for materials design of semiconductor nanocrystals, this connection is not fully understood today, hampering a more widespread and more efficient use of semiconductor nanocrystals for many of the above-mentioned applications.

Establishing such a connection is extremely challenging since, in experiment, clarifying the crystal structure typically relies on X-ray crystallography. This technique is, however, not well-suited for samples in solution, for process analysis, for micro-scale reactions, or for high-throughput synthesis. In addition, X-ray diffraction patterns are less clear for very small or mixed-crystal nanocrystals. Application of fast and reliable optical techniques is highly desirable but is, so far, impossible since spectral features in the vicinity of the optical absorption onset are too similar across different crystal structures to allow reliable distinction.

METHODS & CODES

In order to extend the spectral range of interest beyond the absorption onset, we use a combination of cutting-edge experimentation and first-principles theoretical spectroscopy. This allows us to clarify important structure–property relationships for CdSe nanocrystals in two different crystal structures, wurtzite and zincblende. Here, we focus on the computational aspects of the project: We use many-body perturbation theory to explore the influence of quasiparticle effects on optical properties of CdSe. More specifically, single-quasiparticle effects are described using the HSE06 hybrid exchange–correlation functional. From the solution of the Bethe–Salpeter equation for the optical polarization function we conclude that excitonic effects are small in bulk CdSe due to the large screening of the electron–electron interaction.

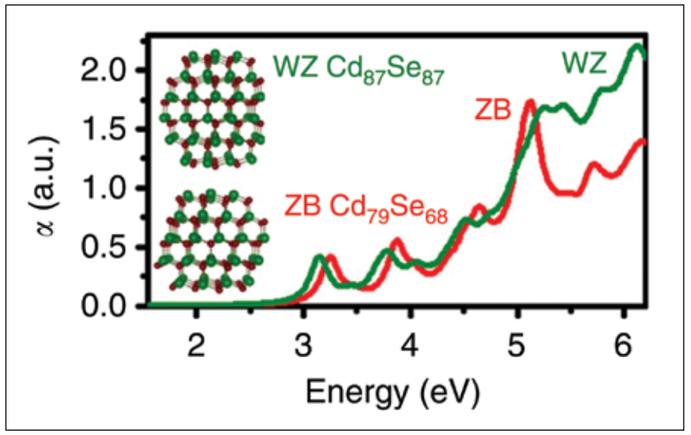

Figure 2: Absorption coefficient simulated using density functional theory for zincblende-phase (red) and wurtzite-phase (green) CdSe nanocrystals. Image credit: see [6].

This allows us to resort to a computationally more affordable density–functional theory description to extend this study toward optical properties of much more intricate hydrogen-passivated CdSe nanocrystals in both crystal structures. We use density functional theory to study both crystal structures and mixed-crystal nanocrystals where the wurtzite and zinc-blende phase are separated by a stacking fault. All calculations described here are carried out using the Vienna Ab Initio Simulation Package [1-3] as well as the Bethe–Salpeter equation implementation discussed in [4] and [5].

RESULTS & IMPACT

We report the experimental and computational identification of unambiguous optical signatures of cubic and hexagonal phases in II–VI CdSe nanocrystals: The main result of this work is that it is possible to efficiently distinguish between wurtzite and zincblende CdSe, both in bulk and nanocrystal form, *exclusively* using optical absorption spectra. Both computation and cutting-edge experimentation clearly show that it is key not only to focus on the absorption onset: While the onsets look very similar between both polymorphs, our work shows that high-energy spectral features in the 4–6 eV energy range are suitable to rapidly identify phase even in nanocrystals as small as about 2 nm. We found that this not only allows distinguishing the crystal phase of bulk CdSe but even to semi-quantitatively analyze wurtzite and zincblende contributions to nanocrystals that contain both structure types, separated by a stacking fault. Furthermore, the first-principles calculations carried out on Blue Waters explain the band-structure origin of these spectral features for both crystal structures. Our results pave the way for applying accelerated experimentation, possibly even high-throughput experiments, to nanocrystal samples in solution. Experiments carried out for this work additionally show that important ligands studied here are not affecting these conclusions.

WHY BLUE WATERS

Computing converged optical-absorption spectra of semiconductor nanocrystals is a computationally expensive task: Each nanocrystal consists of about 300 atoms, including passivating hydrogen atoms, and needs to be surrounded by a sufficiently large region of vacuum. In addition to densely sampling the Brillouin zone, a large number of valence and conduction bands needs to be included in order to achieve convergence of the computed optical spectra. These requirements lead to large matrices for the Kohn–Sham wave functions and solving the Kohn–Sham equations for such large systems can only be achieved using well-parallelized codes on fast supercomputers with fast interconnects. Such calculations are not a use case for the hardware infrastructures provided by cloud computing and, hence, are not possible on such high-throughput resources.

Instead, these calculations are exactly what Blue Waters is developed for: We benefitted from the fast CPUs, the large amount of memory per compute core, and extremely fast interconnects between nodes. Continuous access to such machines is absolutely critical for our research and cannot be accomplished by cloud services in the foreseeable future. Furthermore, Blue Water staff, e.g., Victor Anisimov, helped us identify and fix performance bottlenecks when writing and reading large wave function files, as was required especially in the early stages of this project. Only this combination of hardware and staff resources enabled the computational part of this research project.

PUBLICATIONS AND DATA SETS

Jun Lim, S., A. Schleife, and A. M. Smith, Optical determination of crystal phase in semiconductor nanocrystals. *Nat. Comm.*, 8 (2017), DOI: 10.1038/ncomms14849.