

Project Title: Optical Determination of Crystal Phase in Semiconductor Nanocrystals

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Executive summary:

Optical, electronic, and structural properties of nanocrystals fundamentally derive from crystal phase. However, standard crystallographic characterization techniques like X-ray diffraction yield poorly resolved phase signatures when the nanocrystal size is small and when crystalline lattices are polytypic. We report the identification of unambiguous optical signatures of cubic and hexagonal phases in II–VI nanocrystals using a combination of steady-state absorption spectroscopy and first-principles electronic-structure theory. We show that certain spectral features allow rapid identification of crystal phase during nanocrystal growth, allow determination of crystal phase in very small nanoparticles, and semi-quantitatively predict polytypic nanocrystal structures. We expect that this provides a tool for nanomaterials in liquid dispersions, compatible with continuous readout to improve the precision of nanocrystal engineering and improve our understanding of nanocrystal reactions.

Key Challenges:

Semiconductor nanocrystals (NCs) are light-absorbing, light-emitting materials with diverse applications e.g. in bioimaging, light-emitting devices, and solar cells. They exhibit unique optical and electrical properties tunable by composition, size, shape, and crystal phase. To predict and understand the electronic and optical properties of these complex materials is a critical challenge both for experiment and theory. A major advance has been the discovery that NC size and concentration quantitatively correlate with features of steady-state absorption spectra that can be measured rapidly in solution. Unfortunately, crystal phase remains challenging to measure in high-throughput. Distinguishing ZB and WZ is critically important because phase is a key design parameter for tuning NC structure and optical properties.

Why it matters:

Distinguishing ZB and WZ is critically important because phase is a key design parameter for tuning NC structure and optical properties. Phase-specific synthesis methods now allow growth of size-tunable NCs with either pure ZB or pure WZ phases for CdS, CdSe, and CdTe (CdE) compositions. A major outcome is that NC shape can be chosen by phase, as the highly symmetric ZB phase tends to yield spheres, tetrahedrons, or cubes, whereas the WZ phase tends to yield rod and disk-shaped nanocrystals. The two phases can be combined to yield unique structures such as tetrapods with ZB cores from which four WZ rods extend outward in a tetrahedral geometry, and different chemical components can be incorporated in the different domains.

Accomplishments:

We introduce a new methodology for crystallography of NCs. We demonstrate that polymorphic ZB and WZ NCs can be reliably distinguished based on optical signatures measured through steady-state absorption spectroscopy from samples dispersed in liquids. Focusing on CdSe and using a combination of experiment and parameter-free electronic-structure theory, we demonstrate that distinct absorption features at energies much higher than the band-edge transitions clearly distinguish WZ from ZB crystal structures. This allows high-throughput optical assessment of crystal phase. This technique also provides unambiguous signatures for NCs with very small sizes (~ 2 nm) for which XRD patterns provide vague phase information.

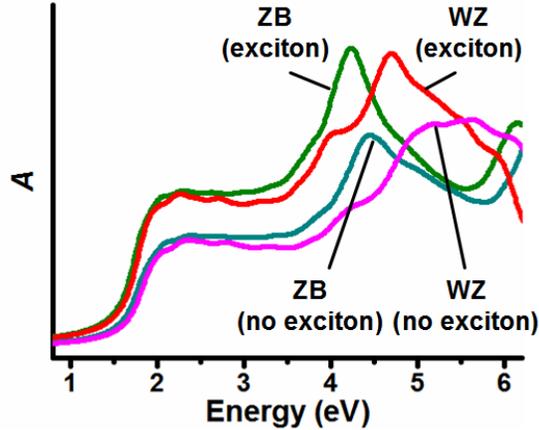


Figure 1: Optical absorption spectra for bulk WZ and ZB CdSe computed using the independent quasiparticle approximation (no exciton) and the BSE approach that takes excitonic effects into account (exciton). The influence of excitonic effects can be seen as a redistribution of spectral weight. However, this effect is smaller than observed for many other semiconductors due to the large electronic screening in CdSe.

We use density functional theory to compute Kohn-Sham states and eigenvalues as starting electronic structures for the solution of the Bethe-Salpeter equation. Exchange and correlation are described using the generalized-gradient approximation by Perdew, Burke, and Ernzerhof and the electron-ion interaction is described by the projector-augmented wave method. Wave functions are expanded into a plane-wave basis up to a cutoff energy of 520 eV (400 eV for NCs). For bulk WZ and ZB CdSe we use the atomic geometries provided by the Materials Project and all atomic geometries of CdSe NCs are relaxed until the Hellman-Feynman forces are below 10 meV/Å. In order to correct the DFT band-gap error due to the neglect of quasiparticle effects, we use a scissors operator that rigidly shifts the conduction bands to open up the bandgap to 1.76 eV (WZ) and 1.74 eV (ZB), respectively. We verify that this approach accurately describes higher energy bands as well as their dispersion by comparing to data computed using the HSE06 hybrid exchange-correlation functional. In order to achieve an accurate description of optical properties (including excitonic and local-field effects) from first principles, we solve the Bethe-Salpeter equation for the optical polarization function. After constructing the excitonic Hamiltonian that includes statically screened Coulomb attraction and unscreened exchange terms, the dielectric function is computed using a time-propagation technique (see results in Fig. 1). In order to converge these optical spectra with respect to BZ sampling, we use $8 \times 8 \times 6:7 \times 7 \times 5:19.4 \times 19.4 \times 15.6$ (bulk WZ) and $10:5:30$ (bulk ZB) hybrid k-point meshes and apply a small random shift to lift degeneracies. For NCs we use $2 \times 2 \times 2$ Gamma-centered Monkhorst-Pack k-point grids and do not take excitonic effects into account due to the large computational cost. All calculations are carried out within the Vienna Ab-initio Simulation Package and an in-house Bethe-Salpeter equation implementation.

Our experimental collaborators synthesized a size series of CdSe NCs using high-temperature organic phase procedures that yield quasi-spherical particles. As shown in **Figure 2a** and **2b**, distinctive signatures of WZ and ZB crystal phases were evident from powder XRD by comparison with bulk standards, although distinctive features were not apparent for the smallest NCs with E_0 near 2.7 eV (~ 2.0 nm NC diameter). **Figure 2c**

shows the ultraviolet-visible absorption spectra of these NCs dispersed in hexane in the 1.55–6.20 eV region (200–800 nm). Several well-known features of the quantum confinement effect are apparent for both ZB and WZ, including a shift of E_0 transitions to higher energies with decreasing NC size, highly discrete transitions near the band-edge, and a nearly featureless, monotonic rise in absorbance with increasing energy. Interestingly, the band-edge spectral regions are very similar when comparing ZB and WZ particles, but we observe large deviations in the high energy region of the spectrum between 4–6 eV. We designate peaks in this spectral region as E_1 in convention with their bulk origins, and demonstrate that their energies uniquely correlate with crystal phase: $E_{1,ZB}$ is ~ 4.9 eV, and $E_{1,WZ}$ is ~ 5.1 eV.

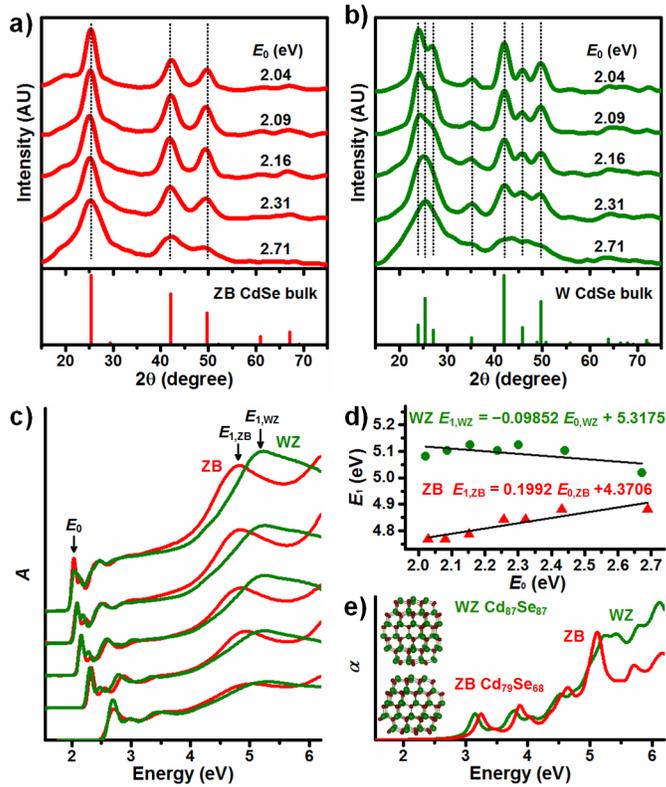


Figure 2: Phase-dependent absorption spectra of CdSe NCs. (a,b) XRD patterns of CdSe NCs with five different E_0 transitions, matching for ZB (a) and WZ (b). Bulk patterns are shown below the experimental spectra. (c) Experimental absorption spectra of ZB and WZ CdSe NCs, with matched E_0 transitions. Prominent crystal phase-specific E_1 bands are apparent at ~ 4.9 eV and ~ 5.1 eV for ZB and WZ, respectively. (d) Measured relationship between E_0 and E_1 for ZB (red triangle) and WZ (green circle) CdSe NCs with linear fits (black lines), showing little quantum confinement effects for E_1 in comparison to E_0 , and showing a greater size-dependent shift of E_1 for ZB compared with WZ. (e) Density functional theory-simulated absorption spectra of ZB (red) and WZ (green) CdSe NCs, showing similar E_0 transitions and phase-distinct E_1 bands in the 5–6 eV range. The structures used in the simulations are depicted in the plot inset.

Figure 2d depicts the measured relationship between the E0 and E1 peaks for CdSe NCs, extracted through the second derivative of each spectrum. The two phases are highly distinguishable by E1 peak energy for all of the NCs, even for those with E0 transitions near 2.7 eV (460 nm), whereas distinguishing features are washed out in XRD spectra for small NCs due to their broad scattering bands (Figure 2a and 2b). Figure 2e shows CdSe NC spectra simulated using density functional theory that clearly show that transitions in the 5.0–5.5 eV range are similar to those in the experimental spectra, with the ZB peak at lower energy than the WZ peak. For these simulations optical transition-matrix elements were computed within the longitudinal approximation. These quasi-spherical WZ or ZB CdSe NCs were composed of 147-174 atoms, and passivated by pseudo-hydrogen atoms to saturate dangling bonds. The NCs are smaller than those tested experimentally, due to the large computational cost of DFT for large numbers of atoms. We also note that excitonic effects are not included in these calculations due to the extremely large computational cost of many-body perturbation theory for NCs. However, we verified that excitonic effects are small for bulk CdSe in both crystal structures and do not substantially impact the trends our conclusions are based on (also see Fig. 1).

Why Blue Waters

The present research requires DFT runs for systems with hundreds of atoms. This imposes challenging requirements for memory and data storage, as well as CPU hours that cannot be met by a system like the Campus Cluster. We ran many (on the order of 40-50) of these jobs for each of the 6 nanocrystals just to obtain relaxed atomic positions and optical properties on DFT level.

For the BSE runs, it is necessary to compute and analyze very large exciton Hamiltonian matrices. For bulk materials, we computed multiple matrices with ranks between 350k and 378k on Blue Waters in the past, leading to memory and storage demands between 0.5 TB and 1 TB for each individual matrix. Computing the matrix is a computationally demanding task itself that we accomplish using a well-parallelized Bethe-Salpeter code. The code uses an ensemble run to divide the work into about 40 to 60 24-hour single-node jobs, each of which is parallelized across all cores of a given node using OpenMP. In this phase of the work, the large and fast storage capabilities of Blue Waters are important: Once the matrix is written to disk we use a time-propagation approach that scales quadratically with the rank of the matrix to compute an optical absorption spectrum. This code is parallelized using MPI and the time-propagation scheme is then used to compute the optical absorption spectrum.

In addition, the scenario described above is not a “one-shot” calculation: Our research requires multiple of these runs and, hence, we need a machine such as Blue Waters that allows us to routinely carry out this work. Hence, for this work it is not massive parallelism that is most important, but it is the entire “Blue Waters package” that makes this machine necessary: High-performance CPUs that are very well integrated into large-memory nodes and connected to an excellent (large and fast) storage system are needed for this work.

List of publications:

Submitted:

Sung Jun Lim, André Schleife, and Andrew M. Smith, “Optical Determination of Crystal Phase in Semiconductor Nanocrystals”, Nature Communications

Plan for Next Year:

We have already begun (and will continue) to extend this work towards manganese-doped NCs and started atomic relaxations for these systems. These require spin-polarized DFT calculations and, hence, increased requirements for memory, storage, and communication systems, but most importantly also computer time.

Furthermore, we are in the process of investigating the influence of free carriers and intra-conduction-band optical transitions on the optical properties of these systems. For some NCs we will be exploring whether excitonic effects need to be included. This can only be done within the BSE approach and will increase the computational cost of these calculations tremendously.

Jobs run for this project will require between several ten to a hundred nodes of Blue Waters. The DFT calculations are not limited by memory requirements. For BSE runs we use numbers of nodes that balance between fast calculations and optimal memory use for any given run, leading to requirements between 20 and 40 GB of memory per node. We may explore using the new GPU-version of VASP and, if so, will seek help from the Blue Waters team to compile that code on Blue Waters.

Node hours: We anticipate using the entire Blue Waters Assistant Professor allocation.

Storage: We are not planning to exceed standard storage quota.

Estimated usage: We anticipate uniformly distributed usage across the year, likely increasing usage towards the end of the year.