X-ray diffraction on core-shell nanoparticles for a precise structure determination


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The interest in semiconductor nanoparticles has strongly increased during the last decades. This is partly due to their potential for applications but also to the fact that their properties are of high interest in fundamental research. In particular particles with sizes below 5 nm are striking since they build the bridge from molecular to solid state physics. One aspect for working out a proper picture of nanoparticles is the precise determination of their geometric parameters. A method well suited for this is x-ray diffraction (XRD). Yet, the analysis of the data is a crucial point and requires special care. Many approaches use common solid state techniques to fit the data, like, e.g., the Rietveld refinement. But due to the fact that only several hundred atoms make up one particle, a solid state based analysis must fail in determining detailed structural characteristics. Moreover, core-shell particles cannot be considered at all with the conventional data analysis techniques.

Since techniques that assume an infinite and quasi-fixed crystal structure fail, new approaches must allow for more or different degrees of freedom. In our case, this concerns the shape of the particles, surface strain and relaxation, and stacking sequences differing from those of the bulk structure. With the software package DIFFEVE it is possible to directly determine these intrinsic parameters [1]: An entire nanoparticle is modeled and its diffractogram is calculated via the Debye formula. To take into account particle distributions, like a size or stacking fault distribution, the diffraction data of an ensemble of several particles are averaged. The whole procedure is embedded in an evolutionary algorithm to automatically refine the model. As one is independent of any constraints in setting up the atomic models, core-shell particles can easily be realized as well.

Here we show XRD measurements on CdSe/ZnS core-shell particles and several refined diffractograms, which were calculated from different nanoparticle models. The nanoparticles were wet-chemically synthesized (for details see [2]) and the experiment was performed at beamline BW2 at HASYLAB. To minimize the background scattering, the sample was drop-coated on a silicon wafer and transferred into a helium-flooded chamber for the measurement. The helium atmosphere also reduces radiation damage in the sample. At a photon energy of 9645 eV a $\theta$-2$\theta$-scan from $\theta \approx 0.6$ to 47° was performed.

Fig. 1 shows one example for such a measurement (empty dots). Additionally, the calculated diffractograms for four different atomic models are presented. The agreement of the different calculations with the experimental data improves from bottom to top. For the bottom-most diffractogram the simplest possible model was assumed, a bare CdSe sphere having bulk-structure and without a ZnS shell. All main peaks cannot be reproduced very well, both in shape and intensity. The fit becomes hardly better when a CdSe sphere with an epitactic ZnS shell is used. Only, the intensity ratio of the triple peak (q = 2.7 Å$^{-1}$ – 3.7 Å$^{-1}$) improves a little. Proceeding to the third refined model, a CdSe cylinder without a shell or stacking faults, one can recognize that this fit reproduces the shape of the first peak slightly better but worsens the agreement of the triple peak with the data. However, the situation improves when an epitactic shell is added to this cylindrical model, stacking faults are considered and the shell atoms are allowed to shift from their original position in radial direction. This best fitting particle ensemble was obtained for a CdSe core size of 4.0 nm x 4.0 nm for diameter and height, respectively and with a 0.6 nm thick shell around. The shell was allowed to relax its lattice parameters in the fit and which resulted in values of 95 % of those of bulk CdSe. This indicates significant strain in the shell, since the difference of the lattice parameters for ZnS and CdSe bulk material differs by 10 %. Moreover, a stacking fault probability of about 2 % was found in the refinement. This corresponds to a 20 %-probability for one stacking fault per particle.
In summary, we could demonstrate that it is possible to obtain precise structural information on very small core-shell nanoparticles from XRD measurements, provided that a careful analysis is being applied. While conventional methods are sufficiently accurate for particles larger than 10 nm, the analysis of very small nanoparticles requires new techniques. Not only stacking faults, size distributions and other ensemble parameters can be addressed with our method, but a reasonable simulation of small core-shell particles is enabled as well.

We thank the beamline staff at BW2 for technical assistance. This work was supported by the DFG (SFB 410, TP C5 and B8) and the by Volkswagen-Stiftung (Project I/78909).

![Graph](image)

Figure 1: Measured diffraction pattern of CdSe/ZnS core-shell nanoparticles together with calculations of four different simulated atomic models, plotted vs. $q = 4\pi/\lambda \sin(\theta)$.

References