

Chapter VI

Conclusion

Size dependence of crystalline structure and electronic properties in organic-passivated CdSe nanocrystals, with size ranging from 18 to 42 Å, was investigated by means of powder X-ray diffraction, extended X-ray absorption fine structure, and synchrotron photoemission spectroscopy. Major study in this thesis is motivated by the unique characteristics of nanometer-scale materials dominated by size and surface effects, which are distinguishable from the bulk. Colloidal CdSe nanocrystals are often used in scientific research and technical application, owing to their advantages of easy preparation, high stability, as well as narrow size distribution.

Nanocrystals have been attracted much interest in crystalline structure due to their unique properties and their potential for various applications. Systematic studies on powder X-ray diffraction of CdSe nanocrystals presented the gradual phase transformation and a nonuniform lattice distortion using the Debye formula and a simple model fit. When the particle size decreases, CdSe nanocrystals exhibit a phase transformation from predominant wurtzite structure into high zinc-blende stacking fraction by creating stacking faults. The existence of phase transformation can be understood by the thermodynamic approach,

which predicts the critical temperature of phase transition increasing as decreasing particle size.

A simple model, considering an ellipsoidal shape particle, a mix of defect-free nanocrystals with pure wurtzite or pure zinc-blende structure, a distorted wurtzite unit cell, atomic form factors, and Debye-Waller factor, was used to fit diffraction patterns of CdSe nanocrystals; the obtained results shows an increase in lattice parameter c and a decrease in lattice parameter a with the reduction of size. Extended X-ray absorption fine structure studies, which introduce a relationship between bond lengths and lattice parameters, show that the size-dependent variations of the axial and equatorial bond lengths $R^{(1)}$ and $R^{(2)}$ have the corresponding behaviors to those of c and a , respectively. The contraction in $R^{(2)}$ and a can be related to surface tension due to particle size effect and surface reconstruction contributed from organic passivation. For $R^{(1)}$ and c , on the other hand, their size dependence would be explained as the net result under competition of lattice contraction and atomic relaxation near the stacking fault interface.

The electronic structure of nanoparticles is sensitive to both size and surface effects due to quantum confinement and a number of atoms at the surface. Photoemission investigation with synchrotron radiation on the core level and valence band of organics-passivated CdSe nanoparticles reveals a measurable dependence of the energy shift on dot size. Both core-level and valence-band edge shift towards higher binding energy when nanoparticles become smaller; however, the energy shift in the valence-band edge is larger than that in the core level. The core-level shift of nanoparticles passivated with TOPO/HDA can exclusively be attributed to the photoemission final-state effect describing an electrostatic interaction between the photohole and the dielectric background,

and, on the other hand, the energy shift in the valence-band edge should include an additional effect from quantum confinement.

After CdSe nanoparticles have a treatment of pyridine, the energy shift becomes smaller compared to the nanoparticles passivated with TOPO/HDA. A dynamic effect in the final state, which is characterized by a finite lifetime of the photohole depending on the coupling between nanoparticle and its neighbors, was introduced to elucidate the observed energy shift for nanoparticles treated with pyridine.

The surface states of nanocrystals play considerable roles to influence the PL efficiency. We performed synchrotron photoemission spectroscopy to explore the surface characteristics of two series of colloiddally synthesized CdSe nanocrystals with OPA and those with OA. Our Investigations indicate that the unpassivated surface Se atoms with dangling bonds are responsible for luminescence quenching. However, the PL efficiency exhibits a strong dependence on the amount of unpassivated surface Se atoms but independent of particle size, which is incongruous with our knowledge. Further study is needed to understand this behavior.

Conclusion remarks

The structural and electronic characteristics of CdSe nanocrystals have been systematically investigated by various synchrotron tools, which are influenced by surface passivation. The nature of the surface ligands is one of the most crucial parameters determining surface modification (relaxation and/or reconstruction). It is also the parameter that can dominate the coupling between nanocrystal and its neighbors. Although some physical mechanisms need to be

Chapter VI / Conclusion

further clarified, our results suggest that the surfactants can significantly affect and modify the structural and electronic properties in quantum confined systems, and the adequate and effective passivation is quite important for scientific research and technical applications.

