2-6-4. Quantum Dots and Semiconductor Nanoparticles

Overview

Semiconductor nanoparticles with sizes below about 10 nm, known as quantum dots (QDs), exhibit size-dependent optoelectronic properties due to the quantum size effect and have been intensively investigated for applications in various photofunctional devices. In the early stages, QDs were synthesized through precipitation reactions in aqueous solutions, which made precise size control difficult. More recently, synthetic methods employing precursor decomposition reactions in high-temperature organic solvents have been widely adopted, enabling the preparation of monodisperse QDs. High-quality binary QDs such as CdSe and PbS can be synthesized, though their high toxicity restricts their broader practical application. As alternatives, low-toxicity multinary QDs such as $Ag(In,Ga)S_2$ have attracted increasing attention, and extensive efforts have been devoted to achieving higher quality through precise control of both size and composition.

Current Status and Frontiers

Semiconductor nanoparticles smaller than 10 nm exhibit unique optoelectronic properties distinct from bulk semiconductors due to the strong confinement of charge carriers. This phenomenon is known as the quantum size effect. Nanoparticles in this regime are called quantum dots (QDs), whose properties vary greatly with particle size.[1,2] In 2023, Ekimov, Brus, and Bawendi received the Nobel Prize in Chemistry for their pioneering work on QDs. QDs have already been applied in liquid crystal displays (quantum dot TVs) and fluorescent bioimaging probes. Furthermore, research is actively progressing toward new devices such as high-efficiency solar cells, photocatalysts, and quantum information technologies.

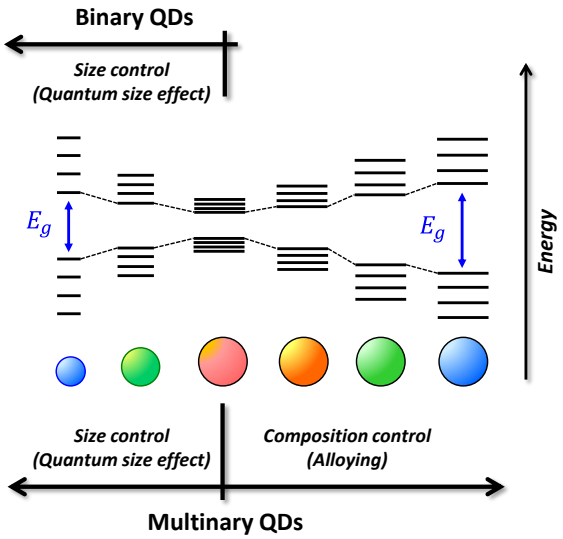

Figure 1. Size- and composition-dependent E_g of binary and multinary QDs.

When the diameter of QDs becomes smaller than twice the exciton Bohr radius (a_B), the quantum size effect becomes prominent. In this regime, the energy levels available to electrons and holes are quantized, leading to an upward shift of the conduction band minimum and a downward shift of the valence band maximum (Fig. 1). Consequently, the energy gap (E_g) of QDs increases as particle size decreases, causing a blue shift of the absorption spectra.

In the early stages, the synthesis of QDs involved precipitation reactions of metal

chalcogenides, such as CdS formed by reacting Cd^{2+} and S^{2-}, in aqueous solutions containing polymer stabilizers (e.g., hexametaphosphate, polyvinyl alcohol), producing colloidal dispersions. Although these methods were simple, the reactions proceeded too rapidly, preventing control over crystal growth and precise size tuning. A major breakthrough came in 1993 when Bawendi and co-workers developed the hot-injection method.[3] By rapidly injecting precursors into a hot organic solvent, they temporally separated nucleation and growth stages, enabling the synthesis of high-quality, monodisperse CdSe QDs. Since then, this method has become the standard, allowing the use of precursors previously unsuitable at room temperature and thereby accelerating the development and quality enhancement of QDs. Notably, binary CdSe QDs exhibit sharp band-edge photoluminescence peaks, which are tunable by E_g, and have been applied in liquid crystal displays.

Binary QDs such as CdSe and PbS remain extensively studied because reliable liquid-phase synthesis methods have been established to obtain high-quality QDs. Although some binary QDs have already been used in commercial device, their toxicity severely limits broader applications. Consequently, alternative materials are actively being developed, particularly low-toxicity I–III–VI semiconductors composed of group 11, 13 and 16 elements (e.g., $CuInS_2$, $Ag(In,Ga)S_2$, $Ag(In,Ga)Se_2$).[4] These multinary QDs enable tuning of E_g through both size and composition (Fig. 1). Furthermore, I–III–VI QDs exhibit high tolerance to non-stoichiometric compositions, allowing control of photoluminescence by adjusting the ratio of group 11 to group 13 elements. For instance, $Ag(In,Ga)S_2$ QDs with Ag-deficient compositions exhibit sharp band-edge emissions when their surfaces are coated with a GaS_x layer to form core/shell-structured $Ag(In,Ga)S_2@GaS_x$ QDs. As the Ga/In ratio increases, the E_g increases and the emission peak is blue-shifted. Advances in liquid-phase synthesis have enabled precise tailoring of multinary QD properties, making their photoluminescence characteristics comparable to conventional binary QDs.

References

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Future Perspectives and Directions

Multinary QDs can achieve optoelectronic properties tailored to specific devices by controlling both size and composition. Ongoing advances in the development of low-toxicity multinary QDs are expected to broaden their scope of practical applications.

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