

Lecture 4. Semiconductor Nanocrystals and Quantum Dots

The purpose of the lecture: to familiarize students with semiconductor nanocrystals and quantum dots.

Expected results: students getting information about semiconductor nanocrystals and quantum dots.

STRUCTURE OF SEMICONDUCTOR NANOCRYSTALS

There are three basic types of semiconductor nanoparticles:

1. Intrinsic, in which the number of electrons in the conduction band is equal to the number of “holes” in the Highest Occupied Molecular Orbital (e.g., Si, Ge, Ga, and SdS nanoparticles)
2. N-type doped, in which the number of electrons in the conduction band is greater than the number of holes in the HOMO (intrinsic nanoparticles doped with As or P)
3. P-type doped, in which the number of electrons in the conduction band is smaller than the number of holes in the HOMO (intrinsic nanoparticles doped with B, Ge, and Al)

In general, semiconductor nanoparticles can be classified according to their shape, including, but not limited to, ordered nanowires, nanorods, nanobelts, nanotubes, nanohelices, and nanorings. Different types of semiconductor nanoparticles have potential applications in photodetectors, light-emitting devices, solar cells, biological labeling, medical diagnostics, etc. These applications are facilitated by the nanoparticles’ unique optical and electronic properties, which depend on the size, shape, and crystal phase.

Therefore, fabrication of semiconductor nanocrystals with well-defined shapes and desired crystal structures in a controlled manner is of key importance in designing and tailoring the properties of semiconductor nanocrystals. MnS nanoparticles are extensively used p-type semiconductors with wide band energy (3.7 eV), varied crystal structures, and promising novel magneto-optical properties. The n-doped nanoparticles are being used in the area of energy conversion and environmental cleanup, but their use in medicine is not fully known.

STRUCTURE OF QUANTUM DOTS

Quantum dots are semiconductor nanocrystals with a core-shell structure and a diameter that typically ranges from 2 to 10 nm. The shell is usually ZnS, while the core usually composed of elements from groups IIeVI, such as CdSe, CdS, or CdTe; groups IIIeV, such as InP or InAs; or groups IVeVI, such as PbSe. This core-shell structure confers QDs the status of an artificially fabricated atom in which charge carriers are confined in all three dimensions, similar to the electrons in real atoms. Quantum dots therefore exhibit properties (quantized energy levels and shell structures) described by the electron wave functions whose evolution is governed by the Schrodinger equation and Pauli’s exclusion principle.

SYNTHESIS OF SEMICONDUCTOR NANOCRYSTALS AND QUANTUM DOTS

TPOP/TOP PROCEDURE FOR NANOCRYSTALS

The commonly used procedure for synthesis of semiconductor nanoparticles (ZnO as an example) consists of two steps:

1. First is the synthesis of a single source precursor, such as bis (benzoate) zinc (reaction between benzoic acid and diethyl zinc) for ZnO or bis (dialkylamidedithiocarbamate) zinc (reaction between diethylamine and carbon disulfide and diethyl zinc) for ZnS nanoparticles.
2. The precursor is subjected to thermal decomposition in the presence of trioctylphosphineoxide (TPOP) and trioctylphosphine (TOP) for 1e20 nm nanoparticles. The TPOP/TOP procedure has been used extensively for various semiconductors.

The nanocrystals produced are hydrophobic in nature; thus, further functionalization may be needed to enhance their biocompatibility.

THE CO-PRECIPIATION METHOD FOR NANOCRYSTALS

In co-precipitation, fractional precipitation of a specified ion results in the precipitation not only of the target ion but also of other ions existing side by side in the solution. Some of the most commonly used substances used in co-precipitation are chlorides, hydroxides, carbonates, sulfates, and oxalates.

SYNTHESIS OF QUANTUM DOTS

The synthesis procedure for QDs varies according to their core components, buffers, and the synthesis solution used. Danek et al. (1994), Talapian et al. (2001), and Qu and Peng (2002) developed an

organometallic method to produce highly fluorescent CdSe dots with a quantum efficiency of approximately 50%. Qu and Peng (2002) found that if the Cd:Se ratio was increased to 1:10, the fluorescent quantum yield increased to 80%. Wang et al. (2010) synthesized InP QDs from a high-temperature organic solution system, and then transferred the QDs into an aqueous phase through a ligand-exchange process using trichloro-striazine modified mPEG.

Huang et al. (2013) and Ma et al. (2009) have used alloyed bichalcogenide nanocrystals of type $ME_xE_0^y$ (M is metal, E and E₀ are different chalcogen atoms, $x + y = 1$) such as ZnSeS, CdSeS, and CdSeTe in a one-step synthesis of QDs. The photoluminescence can be tuned through the visible range by varying the alloy composition. In these reactions, L is oleic acid and P is TOP, TOPS, or TOPSe.