SYNTHESIS OF CdSe CRYSTAL USING HOT INJECTION METHOD

S. Mahajan¹, Meenu Rani², R. B. Dubey³ and Jagrati Mahajan⁴
ECE, Hindu College of Engg., Sonepat, India¹,²,³, PIET, Panipat, India⁴,
sudhirmahajanbe53@rediffmail.com¹, meenu.sharma1234@gmail.com²,
rbdubeyster@gmail.com³, jagritimahajan2000@gmail.com⁴

Abstract - CdSe semiconductor is highly luminescent crystals which are synthesized using hot injection method. The band gap of nano crystals are controlled by gradual incorporation of sulphur to CdSe nano crystals by applying asymmetric composition of reactants. The maximum emission wavelength of the grown nano crystals are varied by controlling the concentration ratio of VI group element Cd with Se in the reactant mixture. We use the colloidal hot injection method to synthesize CdSe quantum dots. The shape of resulting nano-crystals can be altered by changing time and temperature of the reaction.

Keywords:- Nano-crystals, hot injection, TOPO, precursor, quantum dot.

Introduction

Semiconductor nano-crystals, also called quantum dots (QDs), are fluorescent inorganic particles with typical diameters ranging from 1 to 10 nm. Due to their quantum confinement, QDs show unique and fascinating optical properties that are advantageous in the fields of photovoltaic devices, light-emitting diodes, biological imaging and biodiagnostics. CdSe QDs are probably the most extensively investigated colloidal II-VI semiconductor nano-particles because (i) their band gap can be tuned across the visible spectrum by variation of their diameters, and (ii) of the advances made in their preparation [1]. The technological applications of colloidal nano-crystals such as light emitting diodes (LEDs) [2], lasers, solar cells [3] and biological labelling [4-6] have generated substantial interest in nano-particle synthesis because the electronic and optical properties [7] of metals and semiconductors are determined by crystallite size in nano-range. CdSe NCs have attracted considerable interest in the field of nano-science because their luminescence wavelength can be tuned in the visible range by simply changing their sizes. In the past decade, several synthesis studies focusing on controlling the size, shape and crystal structure of CdSe NC shown in Figure 1(courtesy from [ref. 12]). The size of particles and their mono-dispersity are controlled by the nucleation and growth in nano-size regime [8]. Various methods are developed to prepare CdSe NCs. These methods can be broadly divided into two groups: namely, organic synthetic methods and methods using aqueous media. Compared with the organic phase routes, the synthesis methods using aqueous media are simple, green and highly reproducible and the products exhibit good water solubility, stability and biological compatibility. Here, CdSe tetrapods are synthesized using the hot-injection method, in which the trioctylphosphine selenide precursor and the shape-inducing cetyltri-methyl-ammonium bromide surfactant are injected into a cadmium oleate-containing solvent at 190 °C. At a synthesis temperature of 160 °C, the resulting quantum dot particles are find to grow more slowly in heat transfer fluids. With synthesis time, the selectivity to tetrapods increased, and the arms grew proportionally in width and length. The use of heat transfer fluids provides a convenient means to control growth of shaped nano-particles.

Quantum dot

A quantum dot (Q-dot) are the semiconductors made by nano-particles that are used for many applications like in electro-optical devices, spectral bar coding and light filtering[9]. Such materials have electronic properties intermediate between those of bulk semiconductors and those of discrete molecules. The quantum dots have been studied in transistors, solar cells [3], LEDs [2], and diode lasers.

The quantum dots are semiconductors whose electronic characteristics are closely related to the size and shape of the individual crystal. Normally, smaller size crystals have larger band gap and greater energy difference between the highest valence band and the lowest conduction band. Therefore, more energy is necessary to excite the dot, and has
The height and energy between different energy levels varies inversely with the size of Q-dot [10]. The quantum dots of the same material, but with different sizes, can emit light of different colours. The physical reason is the quantum confinement effect. The larger dots have lower energy in the fluorescence spectrum. The smaller dots emit bluer higher energy light [11]. The lifetime of fluorescence is determined by the size of the quantum dot. Larger dots have more closely spaced energy levels in which the electron-hole pair can be trapped. Hence, electron-hole pairs in larger dots live longer causing larger dots to show a longer lifetime. Similar to a molecule, a quantum dot has both a quantized energy spectrum and a quantized density of electronic states near the edge of the band gap. Quantum dots can be synthesized with larger shells. The shell thickness has shown direct correlation to the lifetime and emission intensity. A main advantage with quantum dots is that, because of the high level of control possible over the size of the crystals produced, it is possible to have very precise control over the conductive properties of the material.

Table 1: Properties of Q-dots

<table>
<thead>
<tr>
<th>Property</th>
<th>QDots</th>
</tr>
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<tbody>
<tr>
<td>Absorption Spectra</td>
<td>Broad spectra with a first size dependent excitation peak</td>
</tr>
<tr>
<td>Emission Spectra</td>
<td>Symmetric, &lt;40 nm for CdSe</td>
</tr>
<tr>
<td>Photobleaching</td>
<td>High resistant</td>
</tr>
<tr>
<td>Size</td>
<td>10-20 nm</td>
</tr>
<tr>
<td>Blinking Interval</td>
<td>500 ms</td>
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</table>

Fig. 1 shows the properties of CdSe nano-crystals (NCs) obtained by the hot-injection solvothermal synthesis: a) Colloidal suspensions of CdSe NCs under weak daylight (top) and under UV excitation leading to brilliant luminescence (bottom), b) CdSe/TOPO-HAD NCs (6.0 nm in diameter) self-assembled on a TEM grid, c) Optical absorption spectrum, d) Resonant tunneling spectrum.

Hot-injection method

The method to prepare CdSe nano-crystals involved the injection of a cool solution of precursor molecules into hot liquid TOPO (300°C) [12]. The precursor solution consisted of CdMe2 and Se in trioctyl phosphine (TOP). The injection leads to the instantaneous formation of nuclei of CdSe (denoted as (CdSe) c. the formation of new nuclei is prevented due to a drop in temperature to about 170°C. The result is a suspension of reasonably monodisperse nuclei together with considerable amounts of free Cd and Se precursors. Increasing the temperature to higher values, but below 300°C, leads to slow growth of the existing nuclei but not to new nucleation. With increasing growth temperature the size of the resulting CdSe nano-crystals increases. The omnipresent TOP molecules slow down the growth considerably by coordinating the surface Cd atoms, thus forming a steric barrier for reactants. The slow growth at relatively high temperatures allows the nano-crystals to anneal and to form nearly defect-free wurtzite lattices, which are identical to the bulk lattice. The use of alkyl phosphine oxide molecules with shorter alkyl chains as the coordinating solvent leads to a much faster growth, which becomes uncontrolled at a sufficiently temperature 230°C for butyl phosphine oxide. After the synthesis, the nano-crystals can be separated from the growth solution by adding a non solvent, and can then be re-dissolved in a suitable organic solvent to form stable colloidal suspensions. The TOPO molecules remain attached to the surface Cd atoms, and the suspensions are stearically stabilized. Such CdSe nano-crystal suspensions have remarkable optical properties as shown in Fig. 1. The hot-injection solvo thermal method represents a clear break with previous wet-synthetic methods, in the sense that neutral organo metallic precursors were used in a coordinating alkyl solution with a high boiling point, instead of ionic precursors in water or another polar solvent. The use of TOP-Se and CdMe2 precursors was inspired by the work of Steigerwald et al. carried out in the late 1980s, in which organometallic precursors were reacted in inverse micelles at room temperature to yield CdSe clusters and nano-crystals of various sizes [12]. The small CdSe clusters could be isolated and subsequently grown to larger sizes (3-4 nm) by treatment at higher temperatures (200°C) in coordinating solvents (e.g., ethyl-pyridine, alkyl- phosphine, or alkyl-phosphine oxides). Thus, nucleation and growth were separated resulting in a very reasonable size dispersion (<8%) of CdSe nano-crystals. The photoluminescence quantum yield at room temperature was very low.
Table 2 shows the modifications to the original hot-injection solvothermal method for the synthesis of colloidal CdSe nanocrystals, where NC = nanocrystal, T\textsubscript{inj} = growth temperature, V\textsubscript{inj} = injection volume, QY = photoluminescence quantum yield at room temperature, HAD = hexadecylamine, TBP = tri-n-butyphosphine, ODA = octadecyamine, SA = stearic acid, PA = phosphonic acid, TDPA = tetradecylphosphonic acid, HPA = hexyl decylphosphonic acid.

![Scheme of the experimental setup for the synthesis of NCs](image_url)

**Results and discussions**

The synthesis of CdSe nano-particals is carried out by a single injection of premixed solution of Se in TOP and ODE solvents to the cadmium oleate solution heated at 300°C. In this, excess total cadmium relative to se ratio of 1~8 times. Following atom takes place:

\[
_{\text{cd}}(L) + \text{TOP} + \text{se} \rightarrow (\text{cdse})_{m}L_{n}\text{TOP}_{p}\text{K}
\]

Where \( L = \) oleic acid \( P = \) TOP or TOPO se and \( K = \) rate of reaction constant. A large chemical potential is require to add cd and se. The size and concentration of the nuclei and the growing nano-crystals are estimated from optical absorption measurements. It is obtained that the number of nano-crystals during growth remains constant, that new nucleation events do not occur during growth. The size of the nano-crystals during growth at different temperatures as shown Fig. 4. After a period of growth at 240°C, the size of the nano-crystals becomes a constant. If the temperature is raised, the nano-crystals start to grow again until a larger constant size is reached. The evolution of the crystal size in response to a sudden increase in temperature was very similar to that following injection of excess precursors. These observations indicate that equilibrium between the nano-crystals and the free monomers can occur in the TOP solution at a given
temperature and that the nucleation reaction is indeed endothermic.

Fig.4: Experimental observation of the growth evolution of nuclei into mature nano-crystals at 240°C

Conclusions

Hot-injection synthesis gives a versatile methodology for the preparation of highly luminescent colloidal nano-crystals with tunable size, shape, and surface passivation. By controlling the size of crystals, conductive properties of the material is controlled. Because of their small size, Q-dots display unique optical and electrical properties. The second important aspect of this type of synthesis is the separation of the nucleation and growth stages. Due to this, a high degree of mono dispersity can be achieved without the use of post-synthesis size-selective techniques. The ability to manipulate precisely the size, the shape, and the surface of nano-crystals has opened up a number of potential applications for these new materials: light-emitting diodes, low-threshold lasers, solar cells, optical amplifiers for telecommunications and biomedical tags. Hence, the rate at which progress is made on various fronts, the nano-science will have a greater impact in the near future.

References


www.nikoninstruments.com/information center “Quantum dots”.