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Hydrothermal Routes for the Synthesis of CdSe Core Quantum Dots

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1. Introduction

Semiconductor nanocrystals, 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, biodiagnostics,... (Costa-Fernandez et al., 2006; Lim et al. 2007; Medintz et al., 2005; Robel et al., 2006). CdSe QDs are probably the most extensively investigated colloidal II-VI semiconductor nanoparticles 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.

Presently, CdSe QDs can be prepared in a high quality by using the organometallic synthesis (Qu et al., 2002; Foos et al., 2006). The hot injection technique used in that synthesis procedure produces a “burst nucleation” event, which is a crucial factor for the narrow size distribution of the nanoparticles. A reaction temperature of ca. 300°C is generally required to decompose the precursors used for the production of CdSe QDs. The hot-injection process involves complex manipulation that may limit its application in the scaled-up production and control of particle size, due to the difficulty in controlling the reaction temperature. In addition, it is not easy to obtain the desired products with the expected fluorescence due to the rapid growth rate of nanocrystals, which leads to a quick temporal evolution of the optical properties.

The choice of the ligands used to stabilize the nanoparticles is also crucial to obtain samples with a narrow size distribution and to control the shape of the nanocrystals. Fatty acids, fatty amines, phosphines, and phosphonic acids turned out to be suitable ligands allowing controlling the structural and electronic properties of QDs (Foos et al., 2006; Owen et al., 2008; Peng et al., 2001). Preparation methods for the synthesis of high quality and nearly monodisperse CdSe QDs have typically utilized tri-n-octylphosphine oxide (TOPO) and tri-n-octylphosphine (TOP) as these compounds provide the most controlled growth conditions. The hydrophobicity of TOPO and other ligands on the CdSe surface renders these QDs only dispersible in organic solvents of low polarity. However and especially for bio-applications, the ligands covering the surface of the as-synthesized CdSe nanoparticles are not suited for

their further application and a modification of the surface properties is required. The most common method to render nanoparticles water-dispersible is to modify their surface with thiol-containing bi-functional ligands, such as thioacids and thioamines (Aldeek et al., 2011). This functionalization can lead to increases in hydrodynamic radii, as well as to instability when ligand exchange is not complete. Moreover, a loss of photoluminescence quantum yields (PL QYs) is often observed. QDs can also be encapsulated by a shell of material such as polymer, micelle or bead that makes them more dispersible in aqueous media. Such encapsulation significantly increases the diameter of the QD-based material, which may not be desirable in some applications such as biosensors and live cell imaging.

Because of this, the synthesis of QDs in aqueous solution is still pursued in hopes of providing a material that is easily fabricated and functionalized. During many years, the synthesis of CdSe in aqueous media has been investigated with limited success due to the low quantum yields and poor crystallinity of the nanoparticles produced. Moreover, the fluorescence of the CdSe QDs obtained by this approach cannot be controlled over a wide range. Direct synthesis of CdSe QDs in water is however a promising alternative route to organometallic reactions and facilitates the use of the dots in biological systems. Hydrothermal synthesis offers also the following advantages: (1) lower reaction temperatures with comparable PL QY; (2) does not use toxic and expensive organometallic reagents; (3) surface functionalization during synthesis without further treatment; (4) comparatively smaller sizes (3-8 nm) than those obtained after encapsulation of hydrophobic QDs with amphiphilic lipids or polymers (generally > 20 nm); (5) more reproducible.

Thus, it is still a challenging task to develop a method for preparing CdSe QDs with the desired quality under mild and environmentally friendly conditions using a low-cost and simple method.

In this review, we summarize the aqueous solution-based syntheses of CdSe nanocrystals developed in recent years and the applications of these nanocrystals.

2. CdSe photoluminescence

CdSe QDs exhibit size-dependent absorption and photoluminescence spectra which result from three-dimensional carrier confinement. The size of CdSe QDs can be used to tune the optical gap across a major portion of the visible spectrum. For example, the optical gap can be tuned from deep red (1.7 eV) to green (2.4 eV) by reducing the dot diameter from 20 to 2 nm. (Alivisatos, 1996).

PL studies have also demonstrated the important role of states in the nanocrystal energy band gap associated with the surface and/or defects.

The PL spectrum of CdSe QDs may be composed of two bands:

- the high energy band (band-edge emission) can be explained by different recombination mechanisms, such as recombination of the delocalized electron-hole (e-h) pairs or recombination through localized states, possibly of surface origin
- the low energy band in the near-IR-red spectral range originates from donor-acceptor recombination involving deep defect states associated to vacancies (Klimov et al., 1996) (Figure 1).

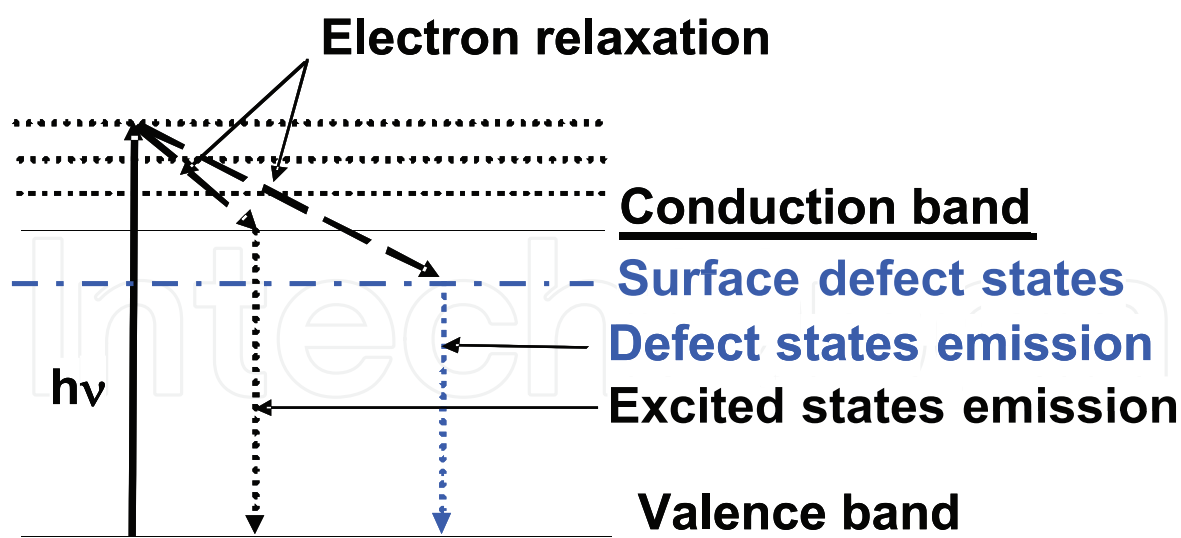


Fig. 1. Schematic diagram illustrating basic emission properties of CdSe quantum dots.

3. Synthesis of CdSe nanoparticles in aqueous phase

3.1 Syntheses without ligand or with weakly-coordinating ligands

Many properties of CdSe, such as electrical and optical properties, are mainly controlled by the particles size, size distribution, phase, and morphology. Recent efforts to synthesize nanostructures with well-defined geometrical shapes and organize them as two- or three-dimensional assemblies have further expanded the possibility of developing materials for optoelectronic devices and sensing. The first part of this chapter will be quite entirely devoted to the preparation of low-dimensional CdSe nanomaterials as extensions of the zero-dimensional CdSe quantum dots that will be described in details in the following paragraphs.

Solvothermal synthetic methods have initially been developed by using organic solvents such as pyridine or ethylene diamine at high temperature for the preparation of CdSe nanoparticles (Yu et al., 1998). Treatment of cadmium oxalate CdC_2O_4 with Se at 140°C in chelating solvents such as ethylene diamine, diethylene triamine or triethylene tetramine afforded CdSe nanorods in pure hexagonal phase with lengths up to 100-500 nm and diameters ranging from 6 to 20 nm (Figure 1).



Fig. 2. Synthesis of CdSe nanoparticles from cadmium oxalate and Se(0)

The morphology of CdSe crystallites can be controlled by the solvent. Uniform disklike particles with a size of 40 nm were prepared using the same synthetic protocol but performing the reaction in pyridine as solvent.

By changing the synthetic route, the same authors demonstrated one year later that spherical CdSe nanoparticles with an average diameter of 7 nm could be prepared in the ethylene diamine using CdCl_2 and Se associated to sodium metal (Figure 3). Crystalline

CdSe nanoparticles produced by this solvothermal method have a hexagonal structure. Upon excitation at 488 nm, a sharp emission was observed at 600 nm indicating a quantum confinement (Xie et al., 1999).

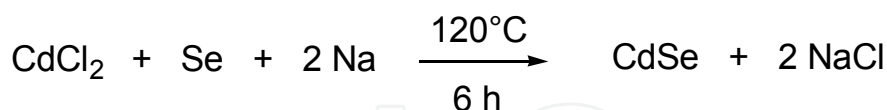


Fig. 3. Synthesis of CdSe nanoparticles from CdCl₂, Se(0) and Na(0)

The synthesis in aqueous media has further been investigated because it has been identified as a cheaper and cleaner route to CdSe nanoparticles.

CdSe nanoparticles with sizes ranging from 70 to 100 nm can simply be produced by reacting metallic Cd with Se in an autoclave at 180°C for 24 hours. Cd(0) was found to react with H₂O at high pressure and temperature to generate Cd(OH)₂ and H₂. Dissolved Se is reduced by H₂ to produce Se²⁻, which reacts with Cd(OH)₂ to give CdSe nanocrystals (Figure 4). Interestingly, CdSe nanocrystals produced at that high temperature have a cubic phase structure (Peng et al., 2001).

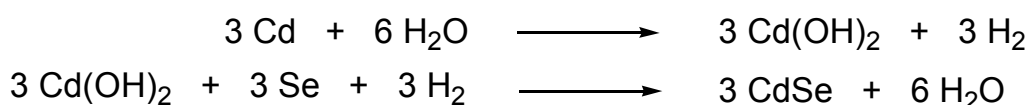


Fig. 4. Synthesis of CdSe nanoparticles from Cd(0) and Se(0)

Ethylene diamine can also be used as surface ligand for the stabilization of CdSe QDs prepared under hydrothermal conditions (100°C, 10 hours, autoclave) from CdCl₂ and sodium selenosulfate Na₂SeSO₃. Cubic zinc blende CdSe nanoparticles with an average diameter of 12 nm were further used for the preparation of CdSe-oligonucleotide probe. Because the surface ethylene diamine ligand is positively charged at neutral pH, these dots were found to associate with the negatively charged phosphate skeleton of the DNA molecule (Huang et al., 2009).

Triethanolamine (TEA) was also recently used as capping ligand to prepare CdSe nanoparticles. Selenide Se²⁻, produced by reaction of Se with sodium borohydride NaBH₄, reacts at room temperature with CdCl₂ in the presence of TEA (Cd/TEA = 1/20) to yield CdSe nanocrystals with an average diameter of ca. 8 nm. The amine group of TEA binds to surface Cd atoms, while the OH groups provide hydrophilicity (Dlamini et al., 2011).

High quality CdSe nanorods and fractals can be prepared from Na₂SeO₃ and Cd(NO₃)₂ at temperatures varying from 100 to 180°C and using hydrazine N₂H₄ as reductant (Figure 5). Na₂SeO₃ is first reduced into Se(0) by N₂H₄. Through a disproportionation reaction in the basic solution, Se is next converted into Se²⁻ and SeO₃²⁻. Se²⁻ finally reacts with Cd(NH₃)₄²⁺ to yield CdSe (Peng et al., 2002).

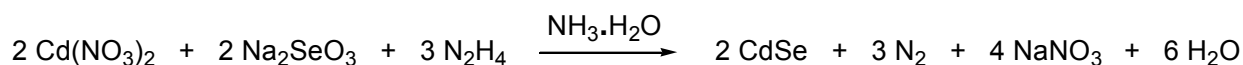


Fig. 5. Synthesis of CdSe nanoparticles from Cd(NO₃)₂ and Na₂SeO₃ using hydrazine as reducing agent

CdSe fractals with wurtzite structure were produced using $\text{NH}_3 \cdot \text{H}_2\text{O}$ as complexing agent and operating at low temperature. Using the stronger complexing agent EDTA and working at higher temperature afforded nanorods with pure zinc blende phase.

Close results were obtained using cetyltrimethylammonium bromide (CTAB) as surfactant and operating at 180°C for 10 hours. Dendritic structures and nanoparticles are produced in the absence or at low CTAB concentration, while high CTAB concentration favored the production of nanorods with wurtzite structure (diameter of 40-60 nm and lengths between 200 and 500 nm). In that surfactant-assisted hydrothermal system, CTAB adsorbs to the surface of newly nucleated nanoparticles. As a result, the growths on same faces were shut down, and the *c*-axis direction was kept as preferential orientation (Chen et al., 2005).

CdSe nanochains can be produced through a hydrothermal method using $\text{Cd}(\text{OH})_2$ nanoflakes as sacrificial template. $\text{Cd}(\text{OH})_2$ was first produced by basic hydrolysis of $\text{Cd}(\text{NO}_3)_2$. the quite perfect hexagonal nanoflakes obtained have a side length of ca. 200 nm. These nanoflakes were further selenized using Na_2SeSO_3 at 160°C for 10 h (Figure 6).

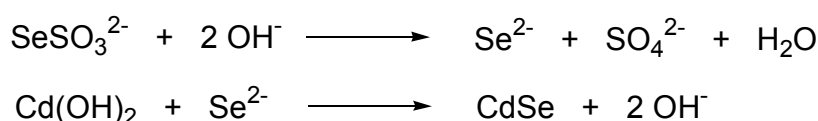


Fig. 6. Preparation of CdSe nanochains from $\text{Cd}(\text{OH})_2$ nanoflakes

Wurtzite CdSe nanoparticles produced arranged in open nanochains, which maintain the external skeleton of $\text{Cd}(\text{OH})_2$ nanoflakes. The preferential reaction of Se^{2-} with the edges of $\text{Cd}(\text{OH})_2$ nanoflakes where there is a large curvature and a high chemical reactivity, was used to explain the formation of nanochains (Chen et al., 2006).

$\text{Cd}(\text{OH})_2$ nanowires prepared by treatment of CdSO_4 with NaOH followed by hydrothermal treatment (180°C , 12 h) in the presence of sodium dodecylbenzene sulfonate (SDBS) were also used for the preparation of CdSe nanoparticles. Selenization of these nanowires was accomplished by treatment with Se powder and hydrazine in ethylene diamine at 180°C for 20 hours. The 30 nm diameter CdSe particles in cubic phase were evaluated as photocatalyst for the degradation of organic dyes such as Safranin T and Pyranine B. Under irradiation of 365 nm UV light, CdSe nanoparticles exhibit higher photocatalytic activity than CdS, CdO and $\text{Cd}(\text{OH})_2$ (Li et al., 2009).

Using *N,N*-dimethyloctadecylammonium bromide cadmium acetate ($\text{C}_{18}\text{-Zn}$) and Na_2SeSO_3 , the ionic liquid lithium *bis*((trifluoromethyl)sulfonyl)amide ($\text{LiN}(\text{Tf})_2$) as template and performing the reaction for two days at 180°C , CdSe nanorods with a diameter of 10 nm and a length of 30-50 nm could be prepared. These nanorods tended to auto-organize into chain-like patterns up to 1 μm or more in length and exist in a mixture of cubic and hexagonal crystalline phase forms. Interestingly, in the absence of ionic liquid, 10-30 nm wide CdSe nanoparticles in pure cubic phase were obtained (Tao et al., 2010). The surface photovoltaic response of CdSe nanorod-chain assemblies was observed at wavelengths in the range 320-800 nm and was found to be 40 times higher compared with that of CdSe nanocrystals. Moreover, the intensity of the photocurrent of CdSe nanorods was about 10 times that of CdSe nanocrystals and these nanorods have therefore great promise as photoelectric sensor.

Four different morphologies (taper microrods, nanotetrapods, fringy nanostructures and fasciculate nanostructures) were recently prepared from $\text{Cd}(\text{NO}_3)_2$, Na_2SeO_3 and ethylene

diamine tetraacetic acid tetrasodium salt (EDTA) as both a chelating agent and a reductant. At elevated temperature, SeO_3^{2-} is first reduced by EDTA to $\text{Se}(0)$, which disproportionates at basic pH to give Se^{2-} and SeO_3^{2-} . The authors demonstrate that the important factors that influence the morphology of CdSe crystals are the concentration of NaOH, the reaction temperature and, to lesser extent, the concentration of SeO_3^{2-} . At low NaOH concentration, the formation of Se^{2-} is slow, which favors the anisotropic nucleation and growth of the CdSe structure along the c-axis (formation of rods). With an increased quantity of NaOH, the concentration of Se^{2-} becomes higher, providing more CdSe building units that grow on nanorods (Liu et al., 2010).

A solvothermal route using a mixture of triethylene tetramine (TETA) and de-ionized water was also developed for the synthesis of CdSe microspheres with an average diameter of 5 μm . $\text{Cd}(\text{NO}_3)_2$ and Se were used as precursors and TETA played the role of reducing agent and surfactant. CdSe particles obtained after the solvothermal reaction performed at 180°C for 12 hours were further treated at 580°C for 4 hours to get pure CdSe in wurtzite structure. When the reaction was conducted with hydrazine in place of TETA as reductant, CdSe nanorods and dendrites were obtained (Yang et al., 2010).

Two papers have also been dedicated to ultrasonic-assisted synthesis of CdSe nanoparticles. The implosive collapse of bubbles generated from acoustic cavitation generates hot spots with transient temperatures of ca. 5000 K, pressures over 1800 kPa, and cooling rates in excess 10^{10} K.s^{-1} . Hence, sonochemistry is becoming a very attractive method for the preparation of nanomaterials.

Depending on the sonication conditions, amorphous or wurtzite CdSe nanocrystals can be produced using $\text{Cd}(\text{NO}_3)_2$, Na_2SeO_3 , NH_3 and N_2H_4 as starting materials (Figure 7).

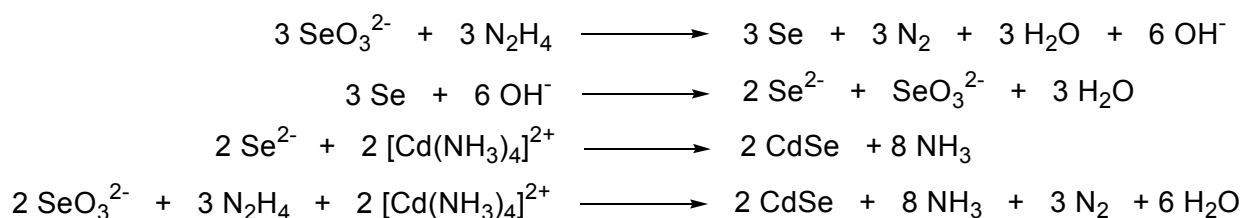


Fig. 7. Ultrasonic-assisted synthesis of CdSe nanocrystals

Particles thus prepared have small diameters (ca. 5-6 nm) but tend to aggregate. Amorphous CdSe nanoparticles have a luminescence 5-times higher compared to hexagonal CdSe (excitonic emission at 556 nm and broad emission centered near 670 nm). This luminescence was found to be pressure sensitive due to a solid-solid phase transition (Ge et al., 2002).

A sonochemical route was also developed for the preparation of CdSe hollow spherical structures (Figure 8).

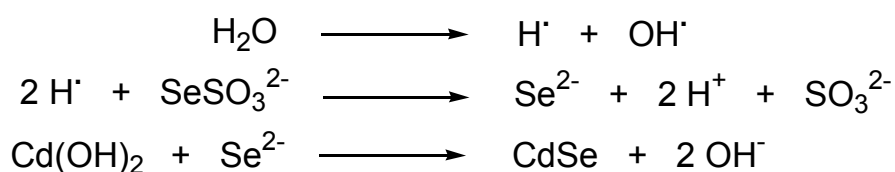


Fig. 8. Generation of Se^{2-} under sonication and preparation of CdSe nanocrystals

$\text{Cd}(\text{OH})_2$ produced by reaction of CdCl_2 with aqueous NH_3 or triethylamine generates CdSe nanoparticles upon reaction of H^\bullet with sodium selenosulfate. Amorphous $\text{Cd}(\text{OH})_2$, which acts as an *in situ* template, was found to direct the growth of the primary CdSe nanoparticles formed and their assembly into hollow spheres of ca. 120 nm in diameter (Zhu et al., 2003).

Finally, γ -irradiation has been used to prepare CdSe nanocrystals. Electrons or H^\bullet radicals produced after γ -ray irradiation of water at room temperature reduce SeO_3^{2-} into Se^{2-} , which could react with $[\text{Cd}(\text{NH}_3)_4]^{2+}$ to produce cubic CdSe nanocrystals with an average diameter of 4 nm (Figure 9) (Yang et al., 2003).



Fig. 9. γ -Irradiation assisted synthesis of CdSe nanoparticles

3.2 Citrate-capped CdSe QDs

The weakly coordinating trisodium citrate ligand (Figure 10), which stabilizes nanoparticles through electrostatic interactions, has numerous times been used to cap CdSe QDs prepared in aqueous solution.

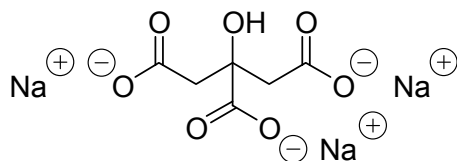


Fig. 10. Chemical structure of trisodium citrate

First syntheses of citrate-capped CdSe QDs were performed under microwave irradiation because the microwave process provides a uniform thermal activation that is ideal for nuclei formation and growth of nanoparticles.

Citrate-capped CdSe QDs were first prepared by Rogach *et al.* using $\text{Cd}(\text{ClO}_4)_2$ and *N,N*-dimethylselenourea at pH = 9 (Figure 11).

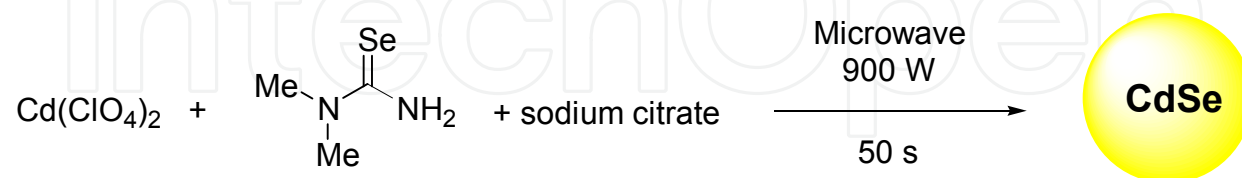


Fig. 11. Synthesis of CdSe nanoparticles from $\text{Cd}(\text{ClO}_4)_2$ and *N,N*-dimethylselenourea under microwave irradiation

Using a Cd/Se ratio of 4/1 affords CdSe nanocrystals with ca. 4.0 nm diameter. By varying the Cd-to-Se ratio (from 16:1 to 4:1), it is also possible to prepare CdSe QDs of different sizes (1-5 nm). These nanocrystals exhibit excitonic emission located between 550 and 600 nm but also trapped emissions between 650 and 800 nm. The PL QYs are weak (0.1-0.15%) but can be enhanced to 4.2% by introduction of a CdS shell at the periphery of

QDs by decomposition of thioacetamide. Correspondingly, the trapped emission of bare CdSe QDs is strongly depressed for the core/shell CdSe/CdS nanocrystals because the shell passivates nanoparticles surface defects, thus leading to the localization of photoexcited charge carriers in the CdSe core. The surface of these nanocrystals was successfully modified with 2-mercaptopropyltrimethoxysilane. By addition of sodium silicate, CdSe or CdSe/CdS QDs could be incorporated into silica spheres of 40-80 nm diameter (Figure 12) (Rogach et al., 2000).

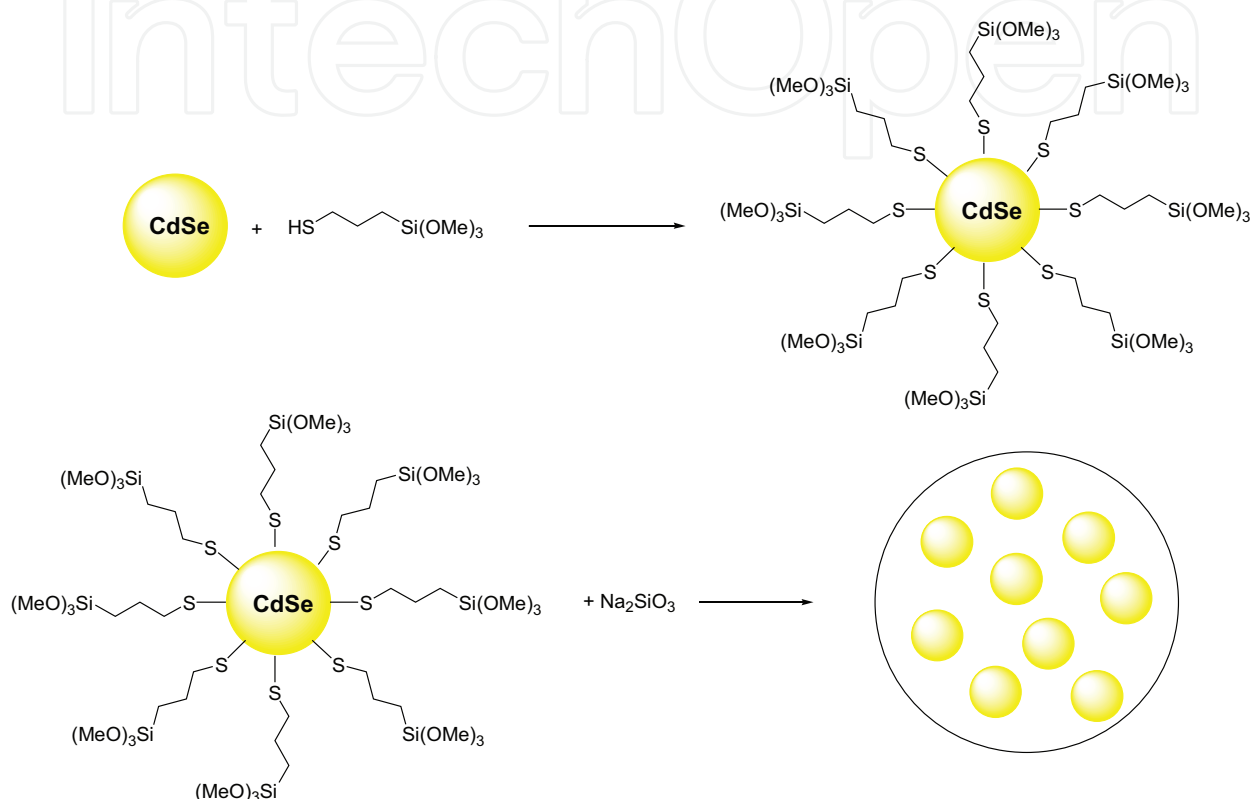


Fig. 12. Preparation of silica nanospheres containing CdSe QDs

The same group reported one year later a strong increase of PL QY of CdSe QDs through photoetching. Exposure of CdSe/CdS QDs dispersions in water to ambient light for several days (intensity 0.12 mW) afforded dots with PL QYs reaching values of 25-45%, while no increase in PL was observed for the samples stored in the dark. The photoetching was accompanied by a blue shift of the PL peak, and the blue-shift was more marked for the largest particles (up to 30 nm for yellow-emitting CdSe QDs) (Wang et al., 2003).

The photooxidation of the QDs surface in the presence of oxygen was demonstrated to play a crucial role in the photoactivation process. Electrons propelled to the conduction band upon light-activation react with O₂ to generate reactive-oxygen species like O₂^{•-}, while holes trapped on the surface oxidize Se into SeO₂. This results in the gradual erosion of the unwanted topographic features on the surface and in smooth, which yields highly luminescent nanoparticles where the nonradiative decay of excitons no longer dominates. It is finally worth mentioning that the photoactivation was found to be the more efficient for CdSe/CdS capped by a thin silica shell. Indeed, the porosity of the silica shell results in the enhanced adsorption

of O_2 molecules from the solution which are therefore readily available for the photocorrosion reactions and therefore for the photoactivation process (Wang et al., 2004).

Using the same starting materials ($Cd(ClO_4)_2$, $Me_2NCSeNH_2$), microwave irradiation, and a $[Cd]/[Se]$ ratio of 4 permits to finely tune the size of the dots with the temperature, while a $[Cd]/[Se]$ ratio of 8 allows to prepare QDs with the highest PL QY. By varying the temperature from 60 to $180^\circ C$, nanocrystals with diameters ranging from 2.5 to 4.0 nm were readily prepared. Of course, CdSe QDs prepared at high temperature possess the best optical properties (no trapped-state emission) due to their good crystallinity and narrowing of size distribution. The PL QY measured for bare CdSe QDs prepared at $180^\circ C$ with $[Cd]/[Se]$ of 8 was found to be 9.9%. PL lifetimes were also increased for CdSe QDs prepared at high temperature. To passivate the unsaturated surface dangling bonds, sequester excitons within the core and thus increase PL QYs to 20–40%, a ZnS shell was successfully introduced at the periphery of CdSe QDs by thermal decomposition of $Zn(ClO_4)_2$ and thioacetamide CH_3CSNH_2 (Figure 13) (Han et al., 2010).

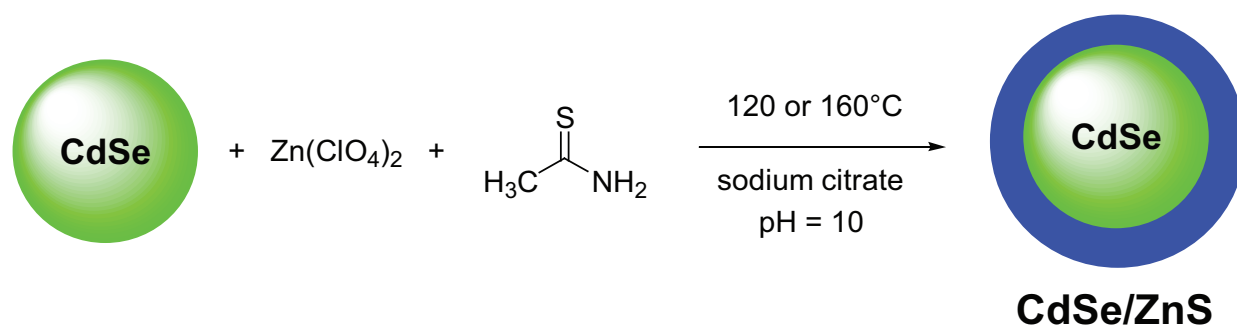


Fig. 13. Preparation of core/shell CdSe/ZnS QDs under microwave irradiation

The first high temperature synthesis of citrate-capped CdSe QDs was described in 2007 by Williams *et al.* Mixing $Cd(ClO_4)_2$, *N,N*-dimethylselenourea and sodium citrate at room temperature followed by heating to $200^\circ C$ for 15 min. produced CdSe nanocrystals. Using a $[Cd]/[Se]$ ratio of 8/1 and a $[Cd]/[Citrate]$ ratio of 1.04, the PL QY of the CdSe QDs was found to be modest (1.5%) but could be increased to 7% by adding a CdS shell through thermal decomposition at $200^\circ C$ of thioacetamide. The authors demonstrated that the mean diameter of the nanocrystals can be tuned by changing the process variables. The particle size increased with increasing reaction time, temperature, and the Cd/Se ratio. Surprisingly, increasing the loading in citrate had the same effect and this may indicate that nucleation and growth processes in high-temperature liquid water differ from classical CdSe QDs syntheses. The mean diameter of CdSe dots was finally found to decrease with increasing pH (from 9 to 11) because at high pH the coordination between the citrate ligand and Cd surface atoms strengthens and Ostwald ripening is therefore slowed (Williams et al., 2007).

The same authors reported two years later an improved synthetic procedure for the preparation of CdSe QDs based on the rapid injection at $200^\circ C$ of selenourea to cadmium perchlorate. Using that methodology, smaller nanoparticles were produced (3.5 versus 5.0 nm using a Cd/Se/Citrate ratio of 8/1/9.5). Moreover, the widths of the PL emission peaks were found to be smaller than those obtained when mixing the reagents at room temperature. Without any post-synthetic treatment, citrate-capped CdSe nanoparticles have

a PL QY over 5%. The dependence of the PL emission peak position on the Cd:Se ratio during the synthesis was also demonstrated. Contrary to results obtained using the cold-precursor loading method, a decrease in nanoparticle diameters as the Cd:Se molar ratio increased was observed (Williams et al., 2009).

Photo-irradiation with a high pressure mercury lamp at room temperature was also developed to prepare 4 nm-sized CdSe nanocrystals from $\text{Cd}(\text{OAc})_2$, Se and Na_2SO_3 (Figure 14) using sodium citrate and cetyltrimethylammonium bromide used as capping agents. The optical properties of the CdSe nanocrystals have not been reported probably due to their important size polydispersity (Yan et al., 2003).

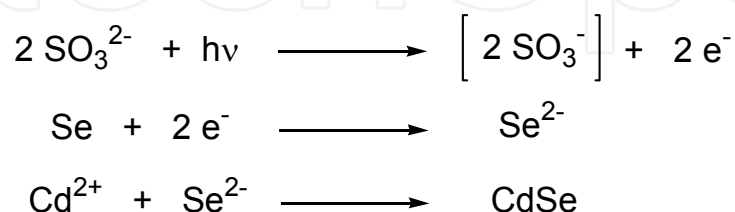


Fig. 14. Photo-assisted synthesis of CdSe nanoparticles

Because classical syntheses of CdSe QDs in aqueous solution at temperatures below 100°C generally afford nanocrystals with poor PL QYs (< 0.15%), laser-assisted synthesis has been developed. Heating a mixture of $\text{Cd}(\text{NO}_3)_2$ and *N,N*-dimethylselenourea in the presence of sodium citrate while irradiating with a Nd:YAG laser at 532 nm affords CdSe QDs emitting between 561 and 590 nm depending on the temperature used during the synthesis. UV-vis spectroscopy monitoring of the reaction demonstrated that photoetching or photooxidation of the surface of the CdSe QDs dominates the growth of the nanocrystals during the first half-hour of the reaction before nanoparticles growth through Ostwald ripening takes control. To improve PL QYs, a CdS shell was first introduced at the periphery of CdSe cores using thioacetamide as sulphur source and the crude solution illuminated for 24 h with a 100 W Xe-Hg lamp to photopassivate the core/shell CdSe/CdS QDs. The PL QY of the obtained QDs reaches 60% and the full-width-at-half-maximum (fwhm) of the PL emission peak is below 35 nm, indicating a narrow size distribution.

By varying the [Cd]/[Se] ratio from 2 to 12, this simple method allows the preparation of CdSe/CdS QDs with sizes between 3.7 and 6.3 nm that emit in a wide range in the visible region (green to red) (Lin et al., 2005).

Illumination with ambient light has also been used to improve the PL QY of core/shell CdSe/CdS QDs. CdSe cores were first prepared by bubbling H_2Se , generated from NaHSe and H_2SO_4 , into a solution of CdCl_2 and sodium citrate adjusted to pH = 9. CdSe/CdS QDs were prepared from the crude citrate-capped CdSe QDs by bubbling H_2S (Figure 15).

By varying the temperature of the reaction medium or the heating time during the preparation of the cores from 20 to 94°C, CdSe QDs with cubic structure and emitting between 500 and 570 nm could be prepared. After introduction of the CdS shell and upon illumination for 30 days, core/shell CdSe/CdS QDs with diameters below 4.0 nm, with PL QYs over 20% and with narrow luminescence band (fwhm of ca. 40 nm) were prepared (Deng et al., 2006).

Because of the higher affinity of Cd for thiol compounds than for carboxylate functions, citrate-capped CdSe QDs can easily be modified with thiol-bearing compounds. This strategy was successfully used for the surface modification of core CdSe and core/shell CdSe/CdS QDs with monothiolated β -cyclodextrin (mSH- β -CD). Core CdSe were classically prepared by reaction of $\text{Cd}(\text{ClO}_4)_2$ with *N,N*-dimethylselenourea at 100°C and the CdS shell introduced at the periphery of citrate-capped CdSe QDs by thermal decomposition of thioacetamide. Both dots were modified by the cyclodextrin simply by adding mSH- β -CD to the citrate-capped CdSe core QDs at 75°C and stirring for 6 to 24 hours under N_2 (Figure 16).

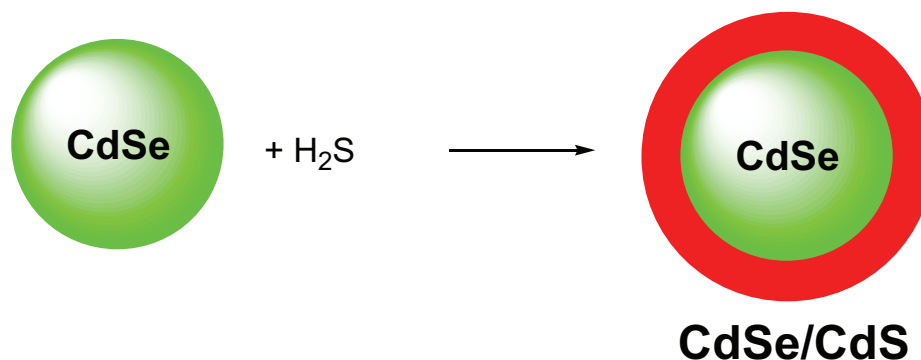
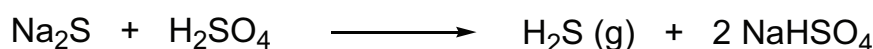
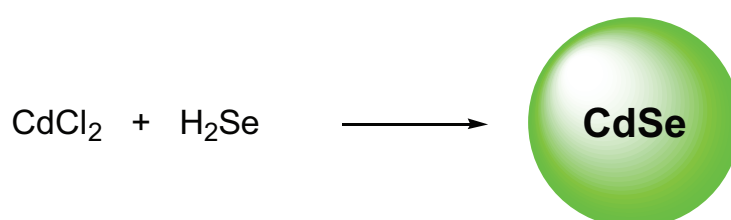
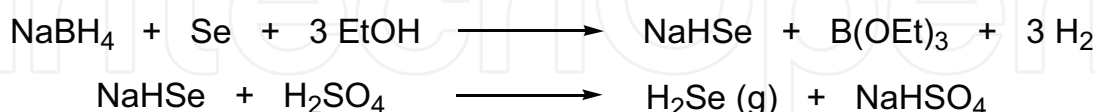


Fig. 15. Synthesis of core/shell CdSe/CdS QDs

Only band-edge emission at 597 nm was observed for CdSe/CdS QDs, while band-edge and trap-state emissions, at 550 and 700 nm respectively, could be detected for CdSe QDs. The PL QYs of these dots were found to be modest (0.65% and 3.7% for CdSe and CdSe/CdS, respectively) but could be markedly improved simply by exposing water dispersions of the nanocrystals to room light over 1 week in sealed tubes. PL QYs increased from the original 0.65% and 3.7% to 7.8% and 46.2%, respectively for CdSe and CdSe/CdS. The numerous hydroxyl groups of surface-bound mSH- β -CD conferred to the QDs high water dispersibility at pH values between 5 to 9 and high ionic strength media. The surface-anchored mSH- β -CD was also found to retain its host capability for small hydrophobic molecules in aqueous media. The fluorescence of the β -CD-modified CdSe core QDs could be selectively tuned by introducing different redox-active substrates (e.g. fluorescence quenching with ferrocene and fluorescence enhancement with benzoquinone) and these nanocrystals have therefore great promise for sensing (Palaniappan et al., 2006).

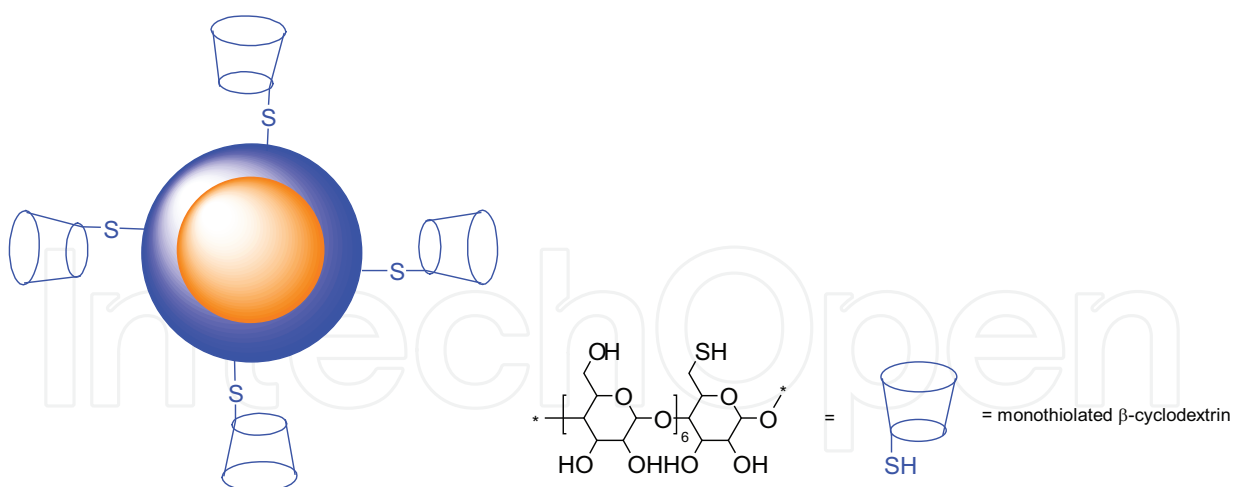


Fig. 16. structure of cyclodextrin-capped CdSe/Cds QDs

3.3 Thioacids, thioamines and thioalcohols as stabilizers

Organic molecules with both thiol and carboxylic acid, amine or alcohol functional groups have been widely adopted as capping molecules for CdSe nanoparticles in aqueous phase. The thiol group coordinates to surface Cd atoms, whereas carboxylate, ammonium or alcohol groups contribute to the electrostatic stabilization of the colloidal nanoparticles as well as to their further surface modification for various applications.

CdSe QDs stabilized by 4-mercaptobenzoic acid and possessing an average diameter of ca. 2 nm can easily be prepared by reaction of $\text{Cd}(\text{OAc})_2$ with sodium hydrogenoselenide in DMF at room temperature. These nanoparticles exhibit a strong exciton absorption at 430 nm and were successfully used for the preparation of poly(vinylpyridine) (PVP)/CdSe thin films by layer-by-layer deposition using hydrogen bond interaction (Hao et al., 2000).

Parallel methods based on an aqueous route were also successfully developed using various thioacids or thioalcohols as capping ligands. A paper published in 2000 reviews comprehensively the early work devoted to the aqueous-phase synthesis of thiol-capped II-VI semiconductor nanocrystals (Eychmüller et al., 2000).

Rogach *et al.* described in 1999 the first aqueous preparation of CdSe QDs using thioacids (thioglycolic acid (TGA) or thiolactic acid) or thioalcohols (2-mercaptoethanol, 1-thioglycerol) as stabilizers (Rogach et al., 1999). Reactions were conducted at 100°C using a $\text{Cd}^{2+}/\text{Se}^{2-}/\text{stabilizer}$ ratio of 2/1/4.8 based on the conditions used for the preparation of CdS and CdTe nanoclusters (Rogach et al., 1996; Vossmeier et al., 1995). The growth of nanocrystals via Ostwald ripening using thioalcohols as capping agents was found to be significantly reduced (1.4-2.2 nm) compared to those prepared with TGA (2.1-3.2 nm). Photoluminescence of all the QDs prepared was found to originate from deep surface traps (from 600 nm for thioalcohol stabilized CdSe QDs to near IR for TGA-capped CdSe QDs) and PL QYs were weak (< 0.1%).

A deep trap emission centered at 560 nm originating from incompletely surface-passivated QDs was also observed using Na_2Se instead of NaHSe and performing the reaction with 3-mercaptopropionic acid (3-MPA) as capping ligand. The authors studied the fluorescence quenching of these 1.5-2.0 nm-sized CdSe QDs by various gold nanoparticles and

demonstrated that the quenching rate of Au nanorods is more than 1000 times higher stronger than that of Au nanospheres (Nikoobakht et al., 2002).

By varying the $\text{Cd}^{2+}/\text{NaHSe}/3\text{-MPA}$ ratio (optimal ratio determined = 8/1/20) and performing the reaction at pH = 9.5 under microwave irradiation (temperature = 140°C), the low energy band of emission from trap states could markedly be reduced. Alloyed CdSe(S) QDs with a gradient of sulfur concentration from the core to the surface were formed due to the decomposition of the 3-MPA ligand under microwave irradiation and release of sulfide ions S^{2-} in the reaction medium. The PL QY of the CdSe(S) QDs was found to be 25% in water and full-width-at-half maximum was about 28 nm (Qian et al., 2005).

Small-sized CdSe QDs (diameter of ca. 2 nm) were also produced under high-intensity ultrasonic irradiation. H^\bullet radicals formed during the sonochemical process reduce Na_2SeSO_3 into Se^{2-} which reacts with CdCl_2 and thioglycolic acid at pH = 11 to produce CdSe@TGA QDs (Figure 17). Using a Cd/Se ratio of 0.67, the first excitonic peak was located at ca. 450 nm. The photoluminescence properties of the dots were not described by the authors (Han et al., 2006).

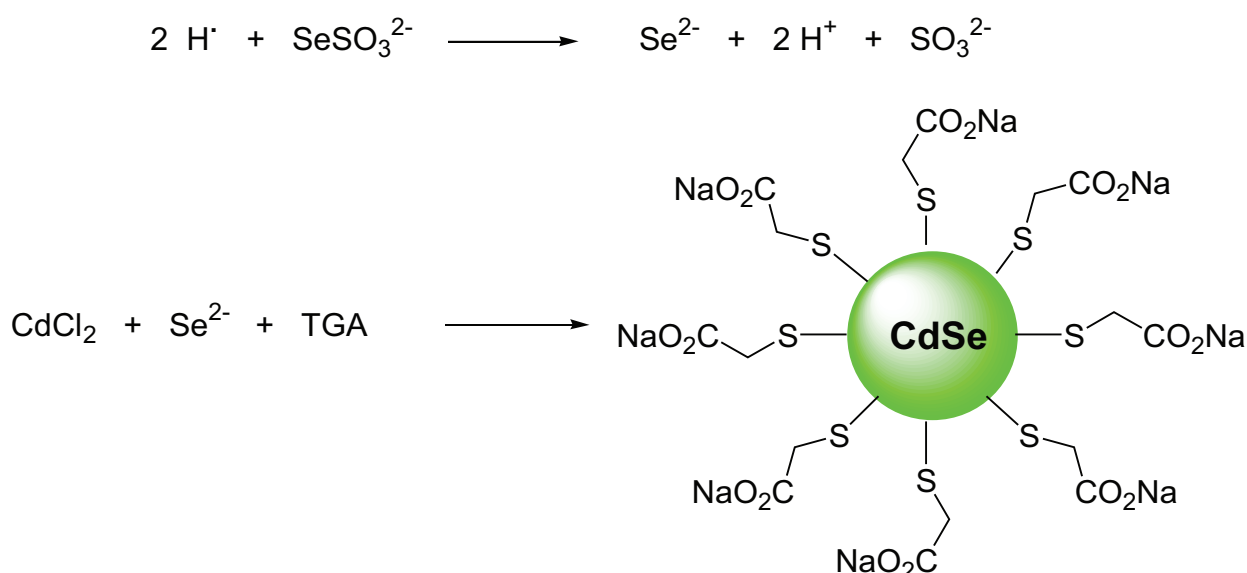


Fig. 17. Synthesis of CdSe@TGA QDs under ultrasonic irradiation

The amphiphilic 11-mercaptoundecanoic acid (MUA) was also used to disperse CdSe QDs in aqueous solution. The synthesis performed under standard conditions ($\text{Cd}/\text{Se}/\text{MUA} = 2/1/4.8$; pH = 11) in refluxing water for 2 h afforded CdSe with an average diameter of ca. 6 nm. A sharp excitonic peak was observed at 327 nm but the emission, centered at 550 nm, was found to be broad. CdSe@MUA QDs were successfully used as specific fluorescent probe for lysozyme (limit of detection of $0.115 \text{ mg}\cdot\text{mL}^{-1}$) (Zhong et al., 2006).

The same synthetic protocol was used for the preparation of CdSe@TGA QDs emitting at 525 nm. The dots could successfully be linked with bacterial cells (*Escherichia coli* and *Staphylococcus aureus*) using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) as coupling reagent (Figure 18). A sensitive and rapid fluorescence method was developed for counting these bacteria (detection of 10^2 - 10^7 CFU/mL total count of *E. coli* and *S. aureus* in 1-2 h; limit of detection: 10^2 CFU/mL) (Xue et al., 2009).

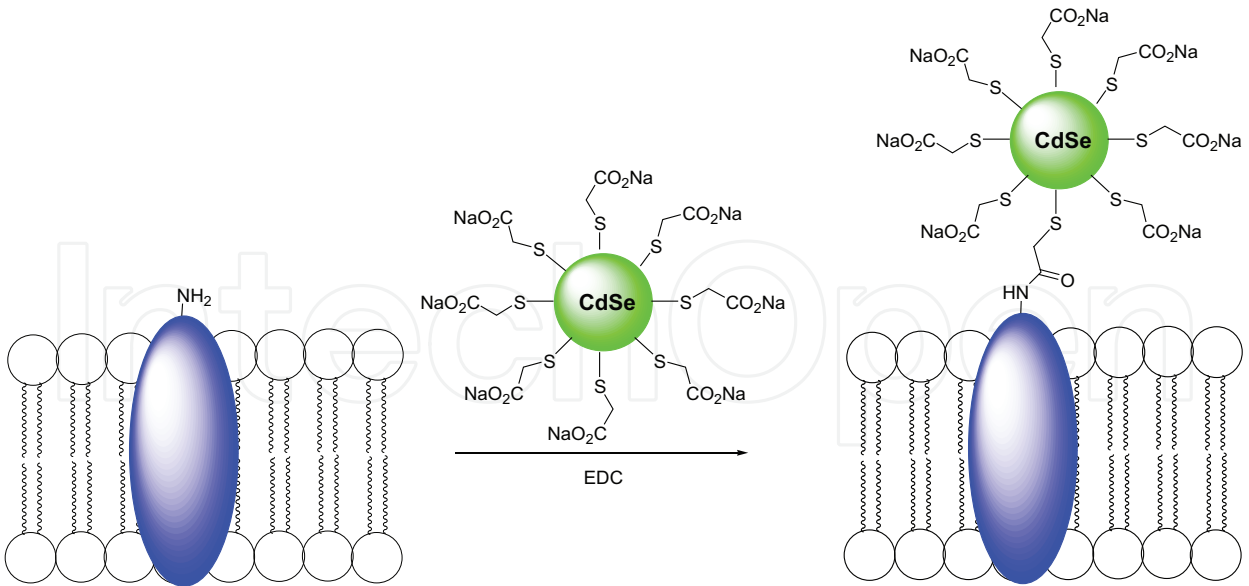


Fig. 18. Principle of EDC-mediated bacterial membrane coupling with CdSe@TGA QDs

Our group has also studied the influence of the thioalkyl acid during the aqueous synthesis of CdSe QDs and demonstrated that the particle growth and thus the photophysical properties of the nanocrystals are related to the structure of the capping ligand. The growth at 100°C of CdSe QDs was markedly decreased with 6-mercaptohexanoic acid (MHA) and MUA compared to MPA yielding particles with diameters of 2.8, 2.5 and 1.9 nm, respectively for MPA, MHA, and MUA ligands. The PL emission of these QDs was dominated by low-energy bands arising from the recombination of trapped charge carriers (Figure 19). By changing the Cd/Se/MPA from 2/1/4.8 to 8/1/8 and performing the reaction under pressure at 150°C for 1 hour in a Teflon-lined stainless steel autoclave, good quality (PL QY of 12%) green-emitting alloyed CdSe(S)@MPA QDs could be prepared (Aldeek et al., 2008).

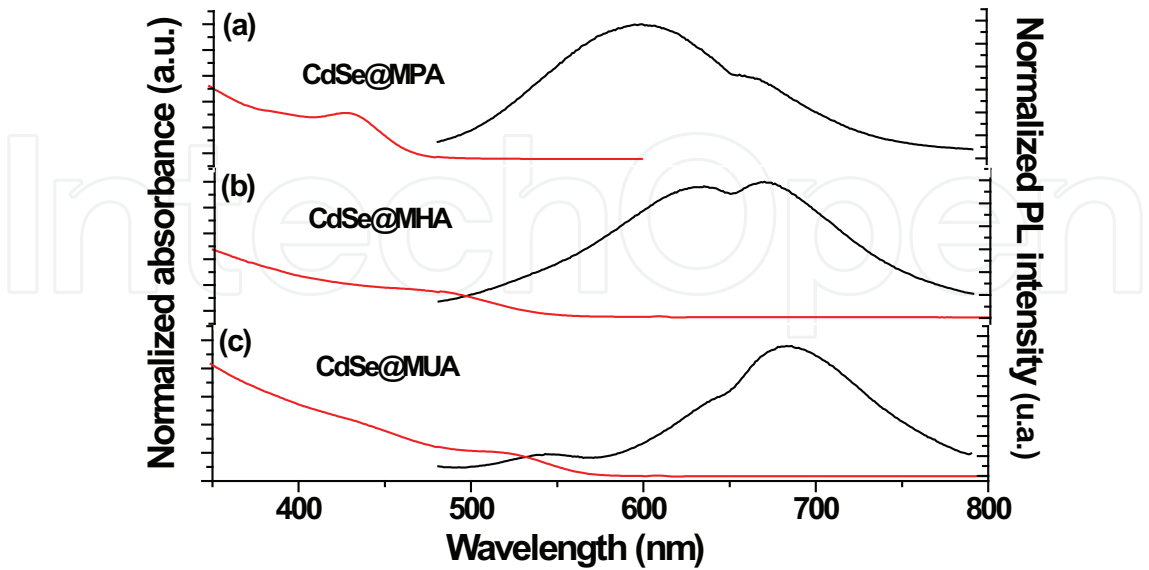


Fig. 19. UV-vis absorption (red) and PL (black) spectra of (a) MPA-, (b) MHA- and, (c) MUA-stabilized CdSe QDs prepared at 100°C for 15 h. PL spectra were recorded with an excitation at 400 nm.

The PL QY and the photostability of the green-emitting CdSe(S)@MPA QDs could be improved by epitaxial overcoat of a ZnO shell on the outerlayer of alloyed CdSe(S)@MPA QDs. Using Zn/Cd ratios of 0.2 or 0.4, the PL QYs of core/shell CdSe(S)/ZnO@MPA QDs reached 20 and 24%, respectively (Figure 20) (Aldeek et al., 2011).

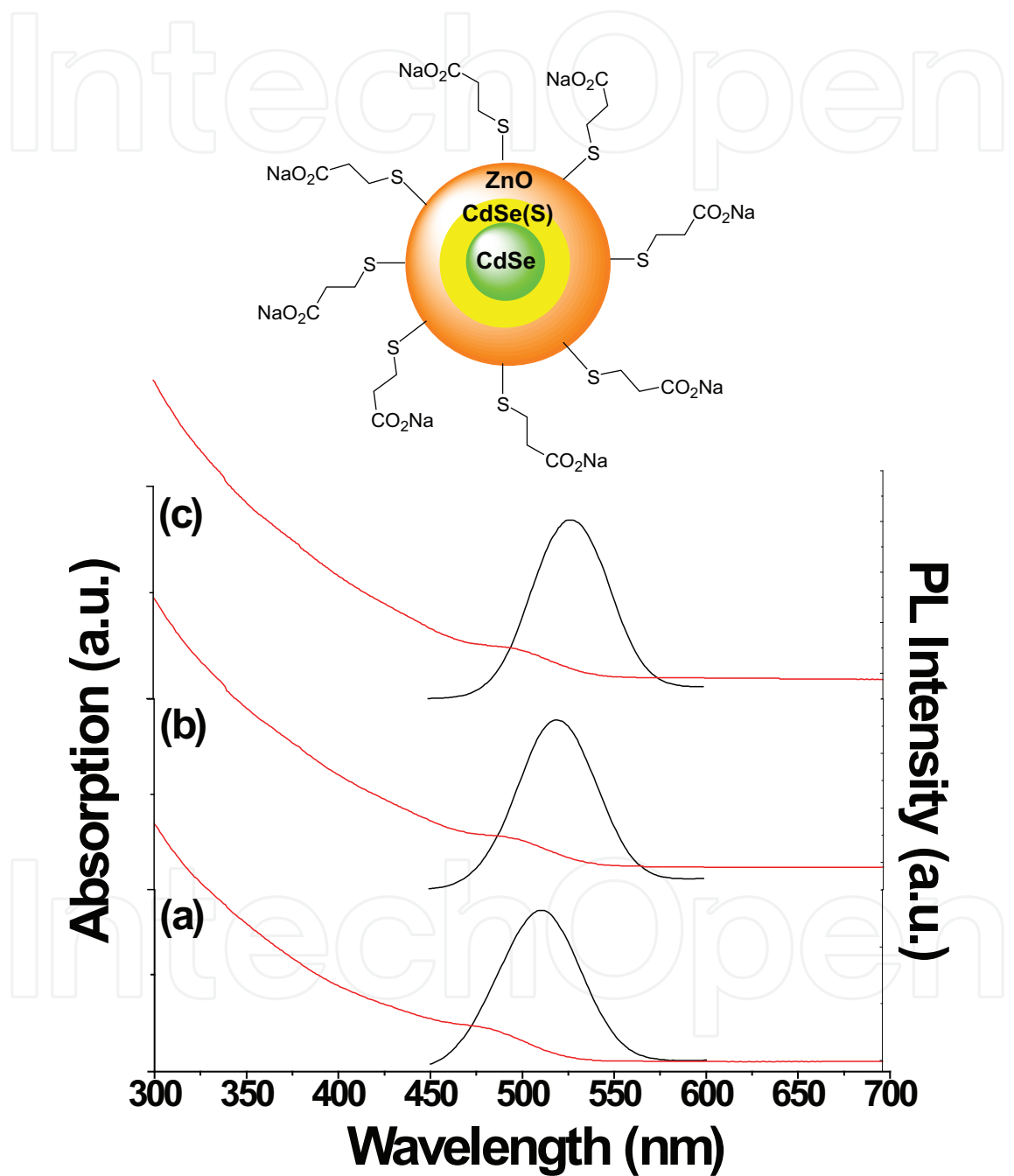


Fig. 20. UV-vis absorption (red) and PL (black) spectra of (a) core CdSe(S) QDs, (b) CdSe(S)/ZnO QDs (Zn/Cd = 0.2), and (c) CdSe(S)/ZnO QDs (Zn/Cd = 0.4).

The potential of these highly luminescent CdSe(S)/ZnO QDs for bioimaging applications was demonstrated by the labelling of *Schewanella oneidensis* biofilms (Figure 21).

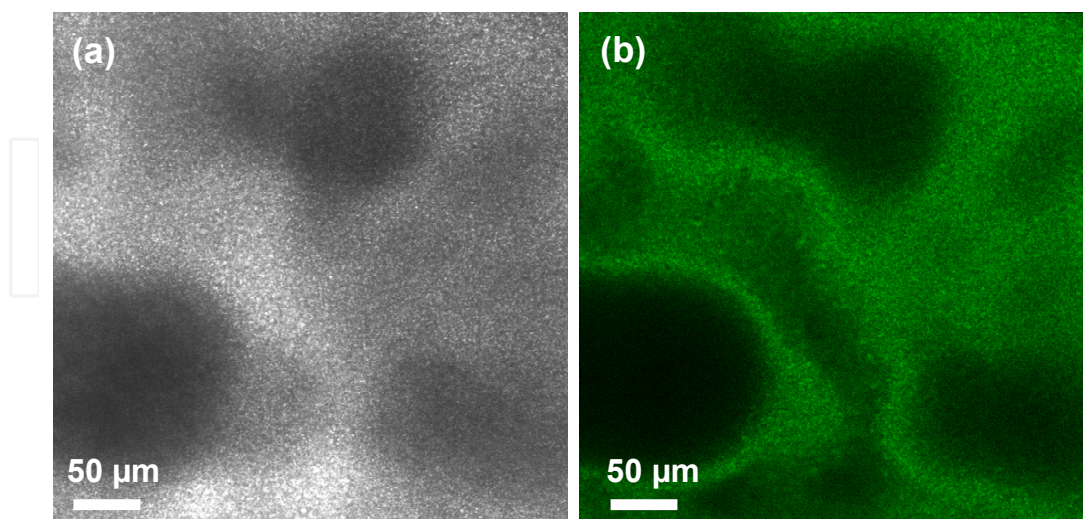


Fig. 21. Confocal microscopy images of a *S. oneidensis* biofilm treated with CdSe(S)/ZnO QDs: (a) transmission image, and (b) corresponding XY plane fluorescence image. Confocal microscopy images were obtained with laser excitation at 405 nm.

Hydrazine hydrate/Se complex as the source of selenium was also developed to prepared high quality CdSe@3-MPA QDs under ambient conditions (Figure 22).

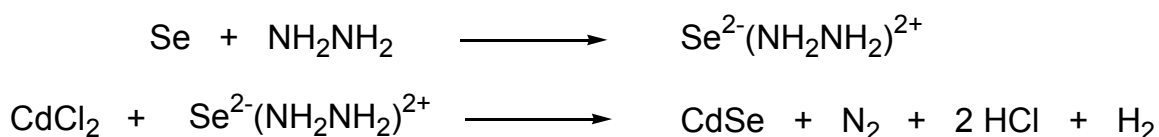


Fig. 22. Synthesis of CdSe QDs using a hydrazine/Se complex and CdCl₂

Using a Cd/Se ratio of 8/1, the size of the nanocrystals could readily be tuned from 1.6 to 3.5 nm by controlling the annealing time of the colloid at 100°C and nanocrystals emitting from blue to red were prepared (PL QY up to 40%) (Kalasad et al., 2009).

Mercaptosuccinic acid (MSA), bearing two carboxylic acid functions, was also used to stabilize CdSe QDs. The 4.2 nm-sized CdSe@MSA nanocrystals obtained after 2 hours heating at 90°C have a cubic structure and emit at ca. 540 nm. The fluorescence of these dots was found to be sensitive to Cu²⁺ ions (limit of detection 3.4 nmol.L⁻¹) but not to other physiologically important cations (Zn²⁺, Mg²⁺, Fe³⁺, ...) (Chen et al., 2011).

3.4 Aminoacids and small peptides as capping agents

Aminoacids and small peptides containing a thiol group like cysteine (Cys) and its derivatives and glutathione GSH (γ-Glu-Cys-Gly) have also been used to stabilize CdSe QDs in aqueous solution (Figure 23). When cadmium²⁺-cysteine complexes (Cys/Cd²⁺ = 3) were treated by NaHSe (optimal Se²⁻/Cd²⁺ ratio = 0.75) at pH = 10.5, CdSe@Cys QDs emitting at ca. 555 nm were obtained after 2 hours heating at 90°C. After interaction with bovine serum albumin (BSA), these QDs were used to label *E. coli* cells treated by lysozyme (Liu et al., 2009).

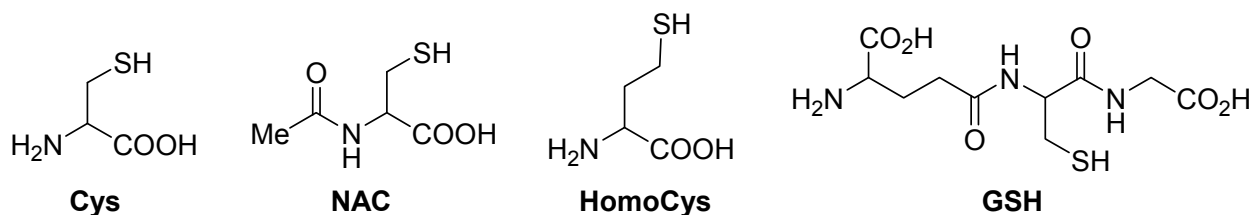


Fig. 23. Cysteine and cysteine derivatives used to stabilize CdSe nanoparticles

The size distribution and the stability of CdSe nanoparticles stabilized by cysteine or cysteine derivatives were also recently evaluated. CdSe nanocrystals were prepared at pH = 12 using a Cd/Se/Cys ratio of 4/1/8.8 at room temperature from CdSO₄ and Na₂SeO₃. Cysteine was found to be the best capping ligand for preparing small-sized (diameter between 1.4 and 1.8 nm) CdSe QDs with a narrow size distribution exhibiting a sharp excitonic peak at 410 nm. The nanocrystals were stable for at least 3 months in aqueous solution. The thiol group of Cys binds to the surface Cd atoms of CdSe nanoparticles. The secondary coordination was found to involve the amine group of Cys. The carboxylate group of Cys is only involved in the electrostatic stabilization of the colloidal CdSe nanoparticles and contributes to their long-term stability. The stability of CdSe nanoparticles prepared using Cys methyl or ethyl ester was maintained only for a short time confirming the crucial role played by the carboxylate group on the colloidal stability. *N*-acetylcysteine (NAC), which contains a nitrogen atom with very low nucleophilicity unable to coordinate with Cd surface atoms of the nanocrystals and thus which can only coordinate through its thiol function can be used to prepare CdSe nanoparticles but is unable to provide stability. Homocysteine, which coordinates only through the thiol function with the surface of CdSe nanoparticles because the amine group is located too far from the nanoparticles surface, can also restrict the initial growth of CdSe nanocrystals and help to maintain their short- and long-term stability (Park et al., 2010).

The same authors have recently demonstrated a strong influence of the Cys concentration on the optical properties and on the PL QYs of the CdSe QDs prepared. CdSe nanocrystals prepared at low Cys to precursor molar ratios (nCys/nCd ~ 1) exhibit intense PL QY (~ 18%) due to the presence of Cd-Cys complexes and cadmium oxides, which passivate the surface of the CdSe cores and reduce the non-radiative recombinations of excitons (Park et al., 2011).

Cysteine was also used as capping ligand for the preparation at room temperature of CdSe semiconductor magic-sized clusters (MSCs) using CdSO₄ and Na₂SeSO₃ as starting materials. The room temperature synthesis conditions ensured both very slow nucleation and growth, favoring focusing of the size distribution. As demonstrated by mass spectrometry, using a Cd/Se/Cys ratio of 1/0.25/8.8 and allowing the nanoparticles to grow for 7 days afforded (CdSe)₃₃ and (CdSe)₃₄ MSCs exhibiting a sharp first absorption peak at 420 nm. The sharpness of the first absorption peak indicates a very narrow size distribution. The average diameter of the nanoparticles produced was estimated to be 1.6 nm by TEM, by AFM, and by the optical absorption spectrum. The PL emission spectrum of the CdSe MSCs is composed of a sharp peak at 429 nm (excitonic emission) and of a broad longer-wavelength feature (surface trap emission) (Park et al., 2010).

Optical performances of glutathione-capped CdSe QDs were also recently studied. The dots were prepared from CdCl₂ and H₂Se in the presence of reduced GSH at pH = 11.5 and at 90°C and have diameters between 3 and 10 nm (Figure 24). A low concentration of GSH

during the synthesis (optimal $\text{Cd}^{2+}/\text{GSH}$ ratio = 1.42) favour the production of CdSe QDs with high PL QYs. Absorption, PL emission and PL QYs of CdSe@GSH QDs were monitored upon aging at room temperature in air and with and without illumination. PL QYs were found to increase with ageing but the increase was more marked under illumination. As demonstrated by XRD, photo-induced decomposition of the surface of the QDs under illumination generates CdO and Se which remove surface defects and improve PL QYs (the highest PL QY, 36.6%, was reached after 44 days storage) (Wang et al., 2011).

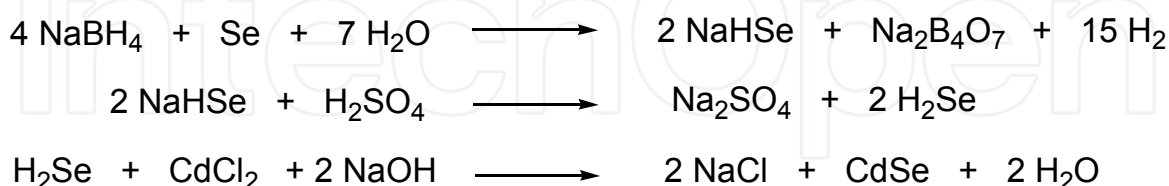


Fig. 24. Synthesis of CdSe QDs from H_2Se and CdCl_2

4. Conclusions and outlook

CdSe nanocrystals are important II-VI semiconductor materials with high luminescence quantum yields. The organometallic synthesis, injection of reagents into a coordinating solvent such as tri-*n*-octylphosphine oxide (TOPO) at high temperature (200-400°C), is an effective route to prepare high-quality CdSe QDs. The biological applications of these kinds of QDs have been hampered by their inherently low dispersibility in water. Then, new chemical strategies have been established to solve this problem. One is to synthesize in the aqueous solution, either by heating at 100°C, by the hydrothermal method or by microwave-assisted synthesis.

This review demonstrates that direct synthesis of CdSe nanocrystals in water is a promising alternative route to organometallic reactions because this process is economical and green and that the prepared fluorescent nanoparticles have high photoluminescence efficiencies. The most important feature is that the CdSe nanoparticles did not need further surface modification to be water-dispersible and that the surface functionalization with water-soluble ligands can be performed during the synthesis. Moreover, the size and the morphology of CdSe nanoparticles can conveniently be tuned by controlling the concentration of precursors, annealing temperature, and time of reaction.

Without any doubt, aqueous-based syntheses open up unique opportunities for CdSe quantum dots and CdSe-based nanomaterials that cannot be provided by any other synthesis techniques. Because of their size-tunable emission covering the whole visible spectrum, there are many reasons to believe that the low-dimensional CdSe nanomaterials synthesized by the aqueous route will be extremely useful for photonics, optoelectronics, and bio-imaging in the coming years. It is also reasonable to believe that the hydrothermal methods presented here could be used for large-scale fabrication of other semi-conductor nanoparticles.

5. References

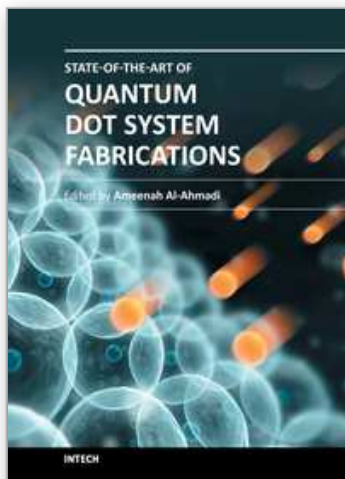
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