

Aqueous synthesis of semiconductor nanocrystals

By

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1. Historical overview

Water is a natural medium for all forms of life. This is one reason why any solution-based techniques and processes proceeding in aqueous media are considered to be environmentally friendly and safe in comparison to others which demand, e.g. organic solvents or melts. In the field of the synthesis of colloidal semiconductor nanocrystals (NCs), which consist mainly of water insoluble II–VI and IV–VI compounds, the use of chemical precipitation reaction in aqueous media was historically the number one choice [1]. In the earlier work a commercially available colloidal silica sol (13 nm in diameter) was used as a carrier and stabilizer of the CdS [1] and ZnS [2] colloidal solutions as well as CdS–ZnS co-colloids [3]. The reported mean size of the NCs was relatively big, e.g. 37 nm diameter for CdS, as determined by fractional filtration through micropore filter, thus the optical spectra reported showed no serious deviations in comparison to the corresponding bulk materials [1]. Very soon the possibility of use of styrene/maleic acid anhydride copolymer (Brus group) or phosphates and polyphosphates (Henglein, Grätzel and Nozik groups) as stabilizers was recognised and colloidal (free of SiO₂) solutions of CdS [4–6], ZnS [2, 7], PbS [5], Cd₃P₂ [8], Zn₃P₂ [8], Cd₃As₂ [9], CdTe [10] and ZnTe [10] NCs were synthesized. Blue shifts of the absorption edge and the emission bands in comparison to the corresponding bulk materials were observed and reported. The theoretical background for this shift to higher energies/shorter wavelengths, the quantum confinement effect was introduced by brothers Efros [11] and Brus [12]. Further development of the stabilizing techniques included the use of short chelating peptides of general structure (g-Glu-Cys)_n-Gly to control the nucleation and growth of CdS crystallites [13], micelles and vesicles [14] and finally the use of various short-chain thiols [15, 16]. The attempts to reach as small as possible sizes and as high as possible monodispersity of the NCs led to the establishment of the exciting field of ultra small molecular-like semiconductor clusters with definite size, structure and characteristic optical properties [16, 17], e.g. [Cd₁₇S₄(SCH₂CH₂OH)₂₆] [16, 17] and [Cd₃₂S₁₄(SCH₂CH(OH)CH₃)₃₆]·(H₂O)₄ [18]. These clusters correspond to minima of the free energy vs. particle size dependence owing to their closed

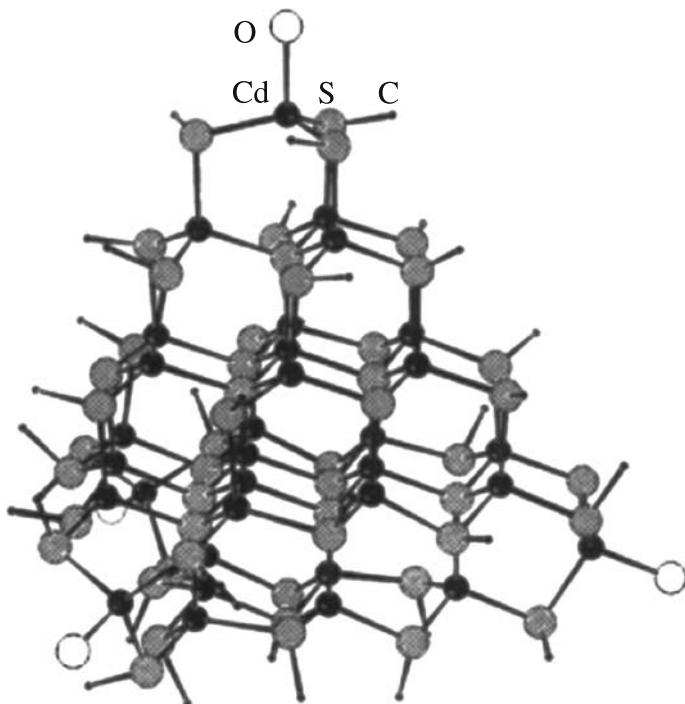


Fig. 1. Structure of a $[\text{Cd}_{32}\text{S}_{14}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_3)_{36}] \cdot (\text{H}_2\text{O})_4$ cluster as derived from the single-crystal X-ray data. Reproduced from [18], © 1995, with permission from American Chemical Society

structural shells (the concept of so-called “clusters of magic size” in the earlier literature [19]) and are naturally “100% monodisperse”. They can be crystallized in macroscopically large single crystals allowing their investigation by single-crystal X-ray analysis, including the exact determination of the atomic coordinates. Figure 1 shows the inner structure of a $[\text{Cd}_{32}\text{S}_{14}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_3)_{36}] \cdot (\text{H}_2\text{O})_4$ cluster representing a piece of the zinc blende lattice in the shape of a tetrahedron.

Starting from the very early publications, the photoluminescence (PL) from semiconductor NCs was paid a lot of attention. It was shown, for example, that weak fluorescence of CdS NCs with maximum at 620–660 nm can be efficiently quenched in presence of nitrobenzene, various anions and cations [1, 2]. It was also shown that doping of the CdS NCs with Ag^+ or Cu^{2+} resulted in the increase of the fluorescence in comparison to the undoped samples [1]. One of the very interesting examples of fluorescence enhancement (“activation”) in phosphate-stabilized CdS NCs was their treatment with NaOH and subsequent addition of excess of Cd^{2+} ions [20]. The precise control of the pH was found to be necessary as well. This treatment resulted in the many fold increase of the band gap photoluminescence, which was attributed to the formation of broad-band gap material, $\text{Cd}(\text{OH})_2$, as a shell on the luminescent CdS core nanoparticles. This approach was essentially the first successful realization of the type I core-shell NCs, well-known and widely used nowadays (see the Chapter of P. Reiss of this book).

As a rule (with the exception of molecular-like, or magic-sized [19] clusters) the size distribution of the colloidal NCs prepared in water is relatively broad, and several post-preparative approaches were introduced to optimize it. One of the most important and widely used nowadays techniques, not only for water-soluble NCs, is the size-selective precipitation from solvent–non-solvent mixtures which was firstly introduced for CdS NCs [21]. The method is very simple and exploits the difference in solubility of smaller and larger particles [21, 22]. A typical example of carrying out the size-selective precipitation on a nanoparticle colloid is as follows: a sample of as-prepared nanoparticles with a broad size distribution is dispersed in a solvent and a non-solvent is added dropwise under stirring until the initially optically clear solution becomes slightly turbid. The largest nanoparticles in the sample exhibit the greatest attractive van der Waals forces and tend to aggregate before the smaller particles. The aggregates consisting of the largest nanoparticles can be isolated by centrifugation or filtration and re-dissolved in any appropriate solvent. The next portion of non-solvent is added to the supernatant to isolate the second size-selected fraction, and so on. The procedure can be repeated several times and allows for obtaining up to 10 or more size-selected fractions from one portion of the crude solution. Moreover, each size-selected fraction can be subjected again to size selection to further narrow the size distribution. Figure 2 shows an example of post-preparative size fractionation for CdTe NCs. All size-selected fractions possess sharp excitonic transitions in the absorption spectra which is a direct evidence of their narrow particle size distributions. TEM and HRTEM investigations show that a carefully performed size-selective precipitation allows for achieving size distributions of 5–10%. In some specific cases also exclusion chromatography [23, 24] and gel electrophoresis [25] were utilized for the size fractionation.

The introduction of the hot-injection synthesis in high-temperature boiling coordinating organic solvents (often referred to as TOP–TOPO synthesis, from initially used coordinating solvents trioctylphosphine, TOP and trioctylphosphine

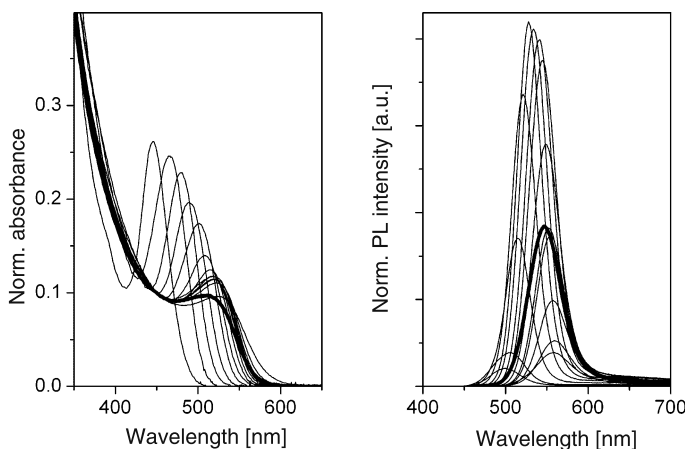


Fig. 2. Absorbance and photoluminescence of the size-selected fractions of the thioglycolic acid-capped CdTe nanocrystals. The spectra of the initial crude solution are highlighted in bold

oxide, TOPO) in 1993 made a revolution in colloidal synthesis of the NCs [22]. The CdSe NCs of different sizes synthesized by this approach became an object of numerous studies in the last 15 years. The methods of core passivation by wide-band gap inorganic shells were further developed [26], and synthetic approaches allowing shape control of NCs were introduced [27]. Resulting materials allowed first applications of colloidal NCs, among others in light-emitting diodes (LEDs) [28], photovoltaics [29] and bio-labelling [30]. A recent overview on semiconductor NCs synthesized in organic solvents can be found in [31] as well as in the Chapters of P. Reiss and Kudera/Carbone/Manna/Parak of this book.

First steps toward successful aqueous alternative to the organometallically synthesized CdSe-based NCs were done by Nozik's [15] and later by Weller's [32] groups in their developments of CdTe NCs. In the former work CdTe NCs were synthesized using the mixture of 3-mercaptopropan-1,2-diol and hexametaphosphate as stabilizers, and their size-dependent properties including absorption, band gap emission, energy level diagrams and extinction coefficient were reported. The latter work introduced CdTe NC synthesis in the presence of various thiols (2-mercaptoethanol or 1-thioglycerol (TG)) solely and included, in addition to the size-tunable optical spectra, the TEM and X-ray diffraction (XRD) data of NCs. The following efforts in the field resulted in as high as 20% photoluminescence quantum efficiency (PL QE) of thioglycolic acid-capped CdTe NCs achieved by their proper post-preparative surface modification [33], in the demonstration of LEDs operating with these NCs [34, 35], and in their bio-conjugation with albumin [36]. Nowadays, aqueous syntheses of II–VI semiconductor NCs like CdS [16], CdSe [37], CdTe [38, 39], $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ [40], HgTe [41] and ZnSe [42] by employing different short-chain thiols as stabilizing agents represent a useful alternative to synthetic routes in highly boiling organic solvents [22, 43–45], providing brightly emitting NCs with PL QE

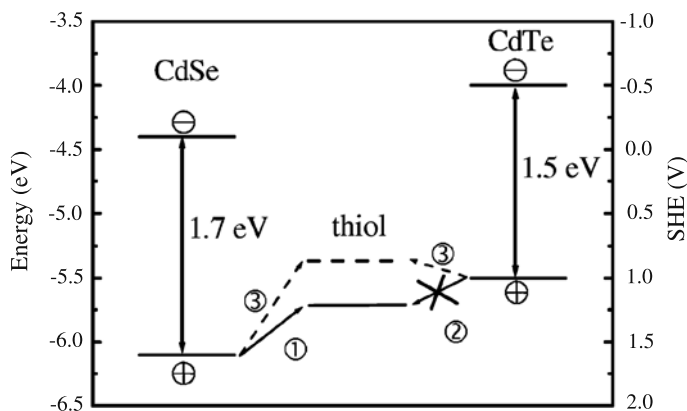


Fig. 3. Positions of bulk CdSe and bulk CdTe band edges shown both on a vacuum scale and with respect to a standard hydrogen electrode reference. The standard potential expected for a thiol that does not quench the CdTe exciton luminescence is given by a solid line between CdSe and CdTe. Hole trapping can occur from CdSe (process 1) but not from CdTe (process 2). The dashed line indicates the assumed position for the standard potential of a thiol that quenches the luminescence of both CdSe and CdTe (process 3). Reproduced from [46] © 2004, with permission from American Chemical Society

of 40–60%. The use of different thiols allows for the kinetic control of the NCs synthesis, to passivate surface dangling bonds, and to provide stability, solubility and surface functionality of the nanoparticles. It is of interest that thiol capping, although providing stable colloidal solutions of CdS and CdSe NCs, does not result in strong band gap emission of these nanoparticles. The reason for this, for the case of CdSe NCs, was addressed in [46] and is schematically explained in Fig. 3. The energy difference between the tops of the valence bands of bulk CdSe and CdTe is approx. 0.5 eV and this difference is even more pronounced in the case of CdS and CdTe (ca. 1.0 eV) [47]. Hole trapping from the semiconductor NCs on a thiol and subsequent PL quenching is energetically favorable only if the thiol redox energy level is situated at higher energies than the valence band top. As seen from Fig. 3, this probability is high for the CdSe (and should be even higher for CdS). This problem may be overcome if the appropriate inorganic passivation of the emitting NC core is done. One of the examples is the ZnSe(S) NCs in which sulfur-enriched shell may provide efficient wide-band gap associated screening of the hole trapping effect and by this the dramatic enhancement of the band gap PL of ZnSe NC core is observed, as will be discussed below.

In spite of the typically low PL QE of the core-only thiol-capped CdS and CdSe NCs, the interest to these nanoparticle systems synthesized by aqueous approaches remains to be high. For CdS NCs, capping with thiols has been proved to be successful in the above-mentioned formation of the molecular-like clusters [16, 17, 48], in the synthesis of NCs as functionalized building blocks for the sophisticated self-assembled structures with gold nanoparticles [49] or bio-conjugates [50, 51], and as model NCs for studies of the stability and size distributions in the nanoparticle assemblies [52]. Alternative synthetic approaches to water-soluble CdS NCs mainly addressed their biological applications, including syntheses in presence of D- and L-penicillamine [53], specially engineered peptides [54] or DNA [55]. Thiol-based synthesis of CdSe NCs also provided extremely small, molecular-like clusters [37]; the interest to larger CdSe NCs synthesized by this method has been fueled very recently as to the light-absorbing and photosensitizing species in solar cells [56]. Citrate-stabilized CdSe NCs have been developed [57], with a reasonably efficient band-edge emission being strongly increased upon photoactivation [58, 59].

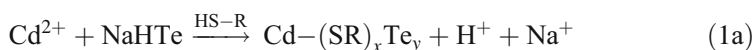
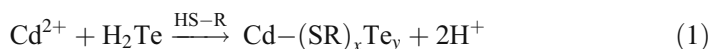
Much of the literature based on the aqueous synthesis of the lead chalcogenide materials has concentrated on synthesizing PbS particles employing different surface ligands and demonstrating a degree of control over the final shape and morphology of the material. Using a wide variety of techniques such as electrochemistry, various polymer and mixed polymer systems and chemical synthesis in restricted spaces of various geometries, different shapes of PbS NCs such as hollow spheres [60], cubes [61–63], rods [64], belts [65], wires [65] and stars [66] have been reported. However, with few exceptions [67], water-based synthesis routes have not resulted in efficiently emissive PbS NC materials.

In what follows, we will focus on the description of the most successful examples of aqueous thiol-capped colloidal NCs, possessing strong band gap emission and by this being promising for the broad nano(bio)technological applications: the most widely studied CdTe NCs emitting in visible and near-infrared, UV-blue-emitting ZnSe NCs, and finally near-infrared-emitting HgTe and alloyed $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs.

2. CdTe nanocrystals

The basics of the aqueous synthesis of thiol-capped CdTe NCs has been described in details in [32, 38, 39]. In a typical standard synthesis [38], $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (or other soluble Cd salt) is dissolved in water in the range of concentrations of 0.02 M or less, and an appropriate amount of the thiol stabilizer is added under stirring, followed by adjusting the pH by dropwise addition of a 1 M solution of NaOH. The solution is placed in a flask fitted with a septum and valves and is deaerated by N_2 bubbling for 30 min. Under stirring, H_2Te gas is passed through the solution together with a slow nitrogen flow. Alternatively, an excess of H_2Te may be passed through the deaerated solution of the NaOH with known concentration forming equimolar NaHTe solution. After this the estimated amount of NaHTe solution can be taken out and injected in the reaction flask. It should be noted that NaHTe solutions are inherently very unstable and become pink due to the oxidation. The use of only freshly prepared NaHTe solution is recommended.

CdTe NC precursors are formed at the stage of Te precursor addition (Reaction 1 or 1a); formation and growth of NCs (Reaction 2) proceed upon refluxing at 100°C under open-air conditions with a condenser attached.



A schematic drawing of the typically used experimental setup is shown in Fig. 4, although the specific design of this setup may vary from one group to another.

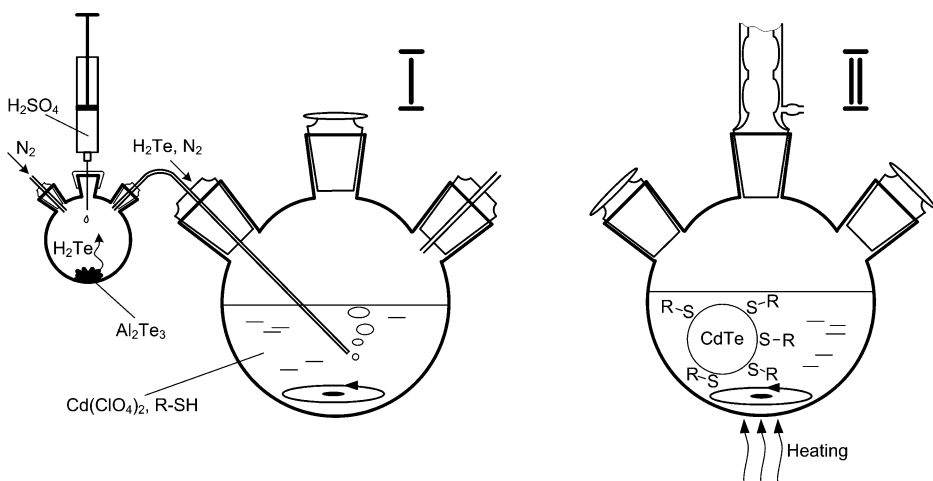
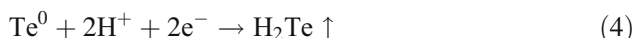
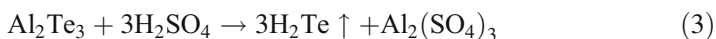


Fig. 4. Schematic presentation of the synthesis of thiol-capped CdTe NCs. First stage: formation of CdTe precursors by introducing H_2Te gas into the aqueous solution of Cd precursors complexed by thiols. Second stage: formation and growth of CdTe NCs promoted by reflux. Reproduced from [38], © 2002, with permission from American Chemical Society

Important part of this setup is the connecting tube for introducing the H_2Te gas, which should be as short as possible and made of glass or another inert material. The use of glass joints and connections is strongly recommended due to the high reactivity of H_2Te gas with rubber and common polymer tubes. The use of relatively small and well-deaerated flask for the generation of H_2Te may also help to reduce undesirable losses of this gas. Special precautions should be taken against the possible leakage of the non-reacted H_2Te . Exhaust traps filled with NaOH solution are proven to be efficient for this purpose. We note that the synthetic procedure described above is easily up-scalable. Indeed, even in laboratory conditions the Reactions (1) and (2) may be routinely performed in a few litres volume and by this, yield up to several grams or even tens of grams of CdTe NCs (estimated for dry weight).

H_2Te gas can be generated for the synthesis of CdTe NCs as well as other tellurides, like HgTe [41, 68] or ZnTe [10] by at least two different methods: chemical decomposition of Al_2Te_3 powder or lumps according to Reaction (3), and electrochemical reduction of Te electrode in acid media according to Reaction (4).



The use of Reaction (3) is the simplest way, if Al_2Te_3 is available. However, the limited amount of suppliers and the continuously increasing price for this reagent limit its availability for a lot of groups dealing with the synthesis of corresponding NCs, stimulating a search for alternative sources, e.g. NaHTe solution obtained by reduction of Te powder with NaBH_4 [69, 70]. Although this method provides an alternative for Te source in the synthesis of CdTe NCs, the direct injection of H_2Te gas is an easier, more controllable, cleaner and more reproducible way to produce high-quality CdTe NCs. To avoid the use of Al_2Te_3 , electrochemical method (Reaction (4)) can be used to produce H_2Te gas, which has been known since the beginning of last century [71] and was recently generalized and reported in detail by Hodes et al. [72, 73]. The use of the electrochemically generated H_2Te gas for successful synthesis of both CdTe and HgTe NCs has been reported recently [39, 68, 74]. The tellurium cathode may be easily formed by melting of tellurium powder inside a glass tube and subsequent cutting the tube end. The reaction proceeds in a glass cell (or flask) and in the simplest case can be controlled by common power supplier instead of potentiostat, which makes the approach easily available for a broad scientific community. The electrochemical method also allows for control of H_2Te amount by measuring the charge passed through the cell, is applicable for the continuous generation of this gas, and can be easily scaled up.

Originally introduced [32] molar ratio of the main reaction components, $\text{Cd}:\text{Te}:\text{R-SH}$ (R-SH stays for thiol stabilizer) being 1:0.5:2.45 was widely used with only slight deviations as “standard” synthetic approach [38]. As stabilizers, the wide family of short-chain (up to 4 carbon units) thiols possessing at least one or several functional groups (amino, carboxylic, hydroxylic, etc.) were employed [38]. Most popular are thioglycolic (or mercaptoacetic) acid (TGA), mercaptopropionic acid (MPA) and 2-mercaptoethylamine (or cysteamine). Both TGA and MPA allows the

synthesis of the most stable (typically, for years) aqueous solutions of CdTe NCs possessing negative charge due to the presence of surface carboxylic groups. Cysteamine-stabilized NCs possess moderate photostability (although they may be stable for years as well being kept in darkness) and attract an interest due to surface amino-functionality and positive surface charge in neutral and slightly acidic media. Other thiol stabilizers are mainly used when some specific functionalities are envisaged, the overview of them may be found in [38]. The improvement of the standard synthesis of aqueous CdTe NCs focused on the optimization of the thiol:Cd ratio and pH. Upon testing different TGA:Cd ratios between 2.45 (as it was used in the standard synthesis of [38]) and 1.1, it was realized by several groups [75–77] that decreasing the TGA:Cd ratio leads to a drastic increase of the PL QE of the CdTe NCs. In an attempt to understand this influence on the properties of the NCs, the experimental data were compared with the results of a numerical simulation of the solution composition [76]. The results of this simulation show that the increase of the PL QE of CdTe NCs with the decrease in the TGA concentration can be attributed to the increase in the relative concentration of the Cd–SR complex (i.e. uncharged 1:1 complex of cadmium with TGA). This tendency has a natural limit at very low values of the TGA:Cd ratio (approaching 1) when the amount of stabilizer in the system becomes insufficient to stabilize NCs from aggregation. There is a competition of at least two different factors during the synthesis: (i) upon decrease in the concentration of TGA, the surface quality of the NCs improves as a result of the increase in the relative concentration of 1:1 Cd–SR complex in comparison with other possible complexes in solution and (ii) a sufficient amount of TGA as a stabilizer has to be present in solution to provide stability and surface passivation of the growing NCs. As a result, the optimum TGA:Cd ratio allowing to produce CdTe NCs emitting with PL QE 40–60% at room temperature as-prepared is slightly higher than 1 and the experimentally obtained optimal values are 1.30 [76], 1.32 [75] and 1.20 [77]. This tendency is of general use, for example, the synthesis of CdTe NCs employing 1-thioglycerol as a stabilizer at R–SH:Cd ratio of 1.3:1 provides as-prepared samples with PL QE in the range of 25%, which exceeds the initially reported (3%) values [32, 38] by almost an order of magnitude.

We note that the solution of Cd precursors at low TGA:Cd ratios may look slightly turbid. This fact is an additional indirect evidence of the domination of the uncharged, less-soluble Cd–SR complex. The turbidity of the solution does not disappear during refluxing, but this does not influence the ongoing Reaction (2); filtration of the final solution of CdTe NCs easily removes the insoluble precipitate. The precipitate of Cd–SR may play an additional role as a source of cadmium. Gradual dissolution of the Cd–SR complex during the NC growth provides a constant rate of transport of Cd ions to the particles. A slow flux of the cadmium precursor in turn provides the possibility of growing the NCs under diffusion control which, as has been predicted theoretically [78, 79] is preferable for narrowing the size distribution and may be a key factor for the dynamic improvement of the surface quality of the growing NCs.

The pH value is another important factor which strongly influences the PL QE of thiol-capped NCs post-preparatively [33, 70, 80, 81]. Thus, it is reasonable to assume that the pH will influence the quality of the NCs during the synthesis as well.

According to [38] the optimum pH value for the synthesis employing different capping ligands strongly depends on the nature of the stabilizer. For example, the recommended value in case of cysteamine is 5.6–6.0 (which is a natural value of cadmium perchlorate mixture with cysteamine, no adjustment of the pH by addition of NaOH solution is necessary in this case). In case of TGA the recommended value [38] was 11.2–11.8. For this stabilizer, it was found later [39, 76] that an increase of pH of the initial solution is followed by a considerable acceleration of the NC growth. Moreover, as a result of this acceleration one can choose the synthetic conditions allowing the “focusing” of the NCs growth in term of narrowing their size distribution. For example, NCs synthesized at pH 12.0 and TGA:Cd ratio 1.3 possess full width at half maximum (FWHM) of the PL band of 39 nm, PL QE 45% and a Stokes shift as small as 100 meV when CdTe NCs are approximately 3 nm in diameter and show a PL maximum at ca. 600 nm. Further growth proceeds more slowly and is accompanied by a slight broadening of the size distribution [76]. A relatively fast NC growth leads to their low quality reflected in low crystallinity of the resulting particles and a large amount of defects and surface states. On the other hand, a comparatively slow growth rate leads to a high content of sulfur (as a product of the TGA decomposition [52, 82]) in the NCs.

CdTe NCs synthesized in water can be transferred to non-polar organic solvents like toluene through a partial ligand exchange with a long-chain thiol (1-dodecanethiol) in the presence of acetone [83]. The transfer efficiency reaches 90% and depends on the component ratio of the 1-dodecanethiol/toluene/acetone mixture (typically 1:1:4 volume ratio), which in turn depends on the concentration of NCs and their average size. For any particular batch of NCs to be transferred, the correct ratio has to be found experimentally, with a typical variation of acetone content in the above-mentioned three-component system from 1:1:3 to 1:1:8. NCs can be transferred more efficiently when they are washed (e.g. by size selective precipitation) from the reaction by-products and the excess of short-chain thiol ligands. Thiol-capped CdTe NCs transferred into organics were used as photosensitizers of fullerenes [84, 85], as building blocks for NCs/polymer composites [83] and as core material for the synthesis of stable and brightly emitting core-shell CdTe/ZnS nanoparticles [86]. Their absorption and emission wavelengths have been shown to be tuned by surface modification in the presence of dodecanethiol [87]. Alternative methods of transfer of CdTe NCs from water to organic media include the use of polymerizable surfactants [88–90], tetra-*n*-octylammonium bromide [87] and ionic liquids [91].

Furthermore, thiol-capped CdTe NCs are also available in polar organic solvents. Mercaptoethylamine-capped CdTe NCs synthesized in water are readily re-soluble in dimethylformamide (DMF) after being precipitated by 2-propanol and dried. A direct synthesis in DMF is possible by taking cadmium lactate as a precursor and 1-thioglycerol as a ligand [82]. The synthesis proceeds at higher temperature, the growth of the NCs is faster and it takes only a few hours to obtain red-emitting samples. CdTe NCs precipitated from the crude solution immediately after synthesis by addition of excess of non-solvent (e.g. diethylether) are not only readily re-dissolvable in DMF, but also in methanol. To the best of our knowledge, this is the only example of II–VI semiconductor colloidal NCs being soluble in methanol as

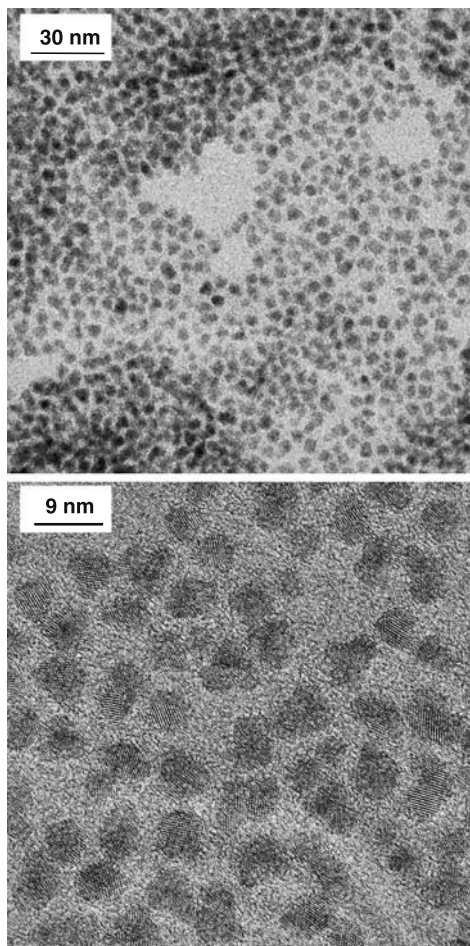


Fig. 5. TEM (top) and HRTEM (bottom) images of MPA-capped CdTe NCs, 5.5 nm average size, with PL maximum at 780 nm. Reproduced from [39], © 2007, with permission from American Chemical Society

synthesized. Indeed, methanol, among other short-chain alcohols is a commonly used non-solvent for size-selective precipitation of many types of organically and aqueously prepared NCs.

Typical TEM and HRTEM images of thiol-capped CdTe NCs with sizes from 2 to 6 nm can be found in [32, 38, 82]. Figure 5 shows TEM and HRTEM images of relatively large, 5.5 ± 0.5 nm CdTe NCs capped with MPA. In order to avoid aggregation on the TEM grid, which is common for aqueous solutions of thiol-capped NCs, the size-selected sample was transferred to toluene using partial ligand exchange with 1-dodecanethiol by applying the procedure of [83]. The images confirm the monodispersity of NCs; their non-spherical shape can be described within a recently proposed truncated tetrahedral model [92].

The sizes of thiol-capped CdTe NCs synthesized in aqueous solution can be determined from the so-called “sizing curve”: the function of the size of thiol-capped

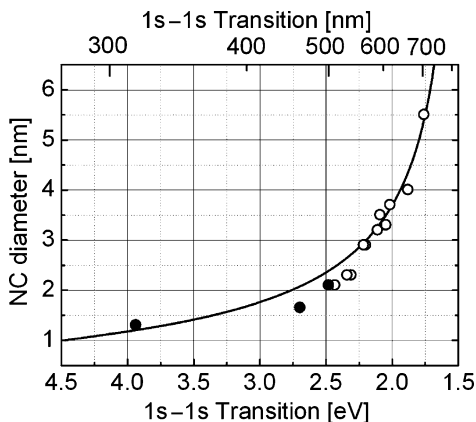


Fig. 6. Sizing curve for thiol-capped CdTe NCs synthesized in water. Filled circles represent sizes of NCs experimentally determined from powder XRD spectra; open circles represent sizes of NCs experimentally determined from TEM images. Solid line is a calculated dependence of the 1s–1s transition energy on CdTe NC size. Reproduced from [39], © 2007, with permission from American Chemical Society

CdTe NCs on the energy of the 1s–1s electronic transition estimated from the position of the first absorption peak (Fig. 6). The points (open circles) in Fig. 6 were derived from statistical analyses of NC sizes obtained by TEM measurements. For the smallest NCs (filled circles in Fig. 6) for which the precise TEM analyses are difficult we used the sizes derived from the powder XRD spectra as described in detail in [32]. Calculation of the 1s–1s transition energy of CdTe NCs (treated as spheres) as a function of their size has been done using an extended theoretical approach described in detail in [93], and is presented in Fig. 6 as solid line. The extension over the common effective mass approximation includes the implementation of the Coulomb interaction and finite potential wells at the particle boundaries in water as the surrounding dielectric medium. The physical parameters of bulk CdTe put into the model can also be found in [32]. The agreement between experiment and theory is quite well. We note that the sizing curve from [94] which is widely used in scientific community has been derived for CdTe NCs prepared by high-temperature organic syntheses and does not include data for small NCs (first absorption maximum at wavelengths shorter than 570 nm, Fig. 6) which are very easy to synthesize in water.

Thiol molecules can release S^{2-} in the course of the prolonged refluxing in the basic medium, which build into the lattice of the growing NCs. Thus, the positions of the powder XRD reflexes of CdTe NCs synthesized under prolonged refluxing in the presence of thioglycolic acid are intermediate between the values of the cubic CdTe and the cubic CdS phases [82]. Mixed $CdTe_xS_{1-x}$ NCs with some gradient of sulfur distribution from inside the nanoparticles to the surface are formed under these conditions. They represent a kind of core-shell system with a naturally CdS-capped surface created by mercapto-groups covalently attached to the surface cadmium atoms. Importantly, the synthesis of such kind of core-shell NCs occurs in one step, as the sulfur originates from the stabilizing thiol molecules and releases during the particle growth. At the bulk CdTe/CdS interface, the conduction band step, i.e. the

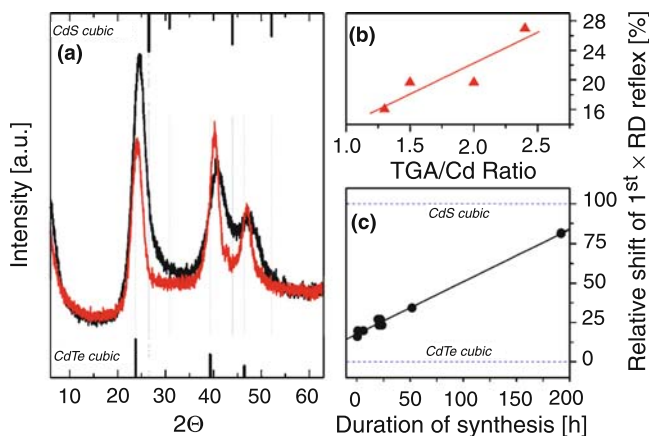


Fig. 7. XRD patterns of the CdTe NCs synthesized with a TGA:Cd ratio of 1.3 (red) and 2.45 (black) after 20 h of synthesis **(a)**. **(b)** Shows the influence of the TGA:Cd ratio on the relative position of the (1 1 1) XRD reflex of the CdTe NCs. **(c)** Presents the evolution of the relative shift of the (1 1 1) XRD reflex of the CdTe NCs during the synthesis. Reproduced from [39], © 2007, with permission from American Chemical Society

offset of the absolute band position, is close to zero, whereas the valence band step is ~ 1 eV [47]. The wave functions calculated for a CdTe/CdS system with the particle-in-a-box model [93] show a delocalization of the electron through the entire structure and the confinement of the hole to the CdTe core – the same phenomenon as reported for the organically synthesized core-shell CdSe/CdS NCs [43] providing their photostability and electronic accessibility.

The reduction of the amount of TGA at the synthesis stage leads to a reduction of the sulfur content in the NCs. XRD patterns of the CdTe NCs (Fig. 7) show that at a TGA:Cd ratio of 1.3 and a pH 12, a smaller shift of the reflexes toward the position corresponding to cubic CdS is observed. It can be explained by the fact that decreasing the amount of the stabilizer in solution and the acceleration of the NCs growth leads to a decreasing probability of TGA hydrolysis and, as a result, to a lower sulfur content. As discussed in [38, 95] the sulfur-enriched shell itself may be important for the improvement of the stability and luminescence properties of CdTe NCs. At the same time, a few monolayers of this shell is enough for the efficient protection of the NCs and further growth of CdS only reduce the NCs quality similar to the effect of the ZnS shell on the properties of CdSe NCs [96].

Typical absorption and PL spectra of size-selected [21, 38] fractions of TGA- and MPA-capped CdTe NCs are shown in Fig. 8. PL spectra of TGA-capped CdTe NCs are tunable in the range of 500–700 nm, while those of MPA-capped NCs are tunable between 530 and 800 nm. The MPA capping allows for a relatively quick and controllable growth of CdTe NCs up to 6 nm in diameter. The energy gap of bulk CdTe estimated from the absorption measurements at 300 K is 1.43 eV or ca. 867 nm [97]. The superior tunability of the absorption over the very broad spectral range is important for the use of thiol-capped CdTe NCs as absorbers in solar cells [98], for choosing optimal donor–acceptor pairs for FRET-based structures [99–101], as well

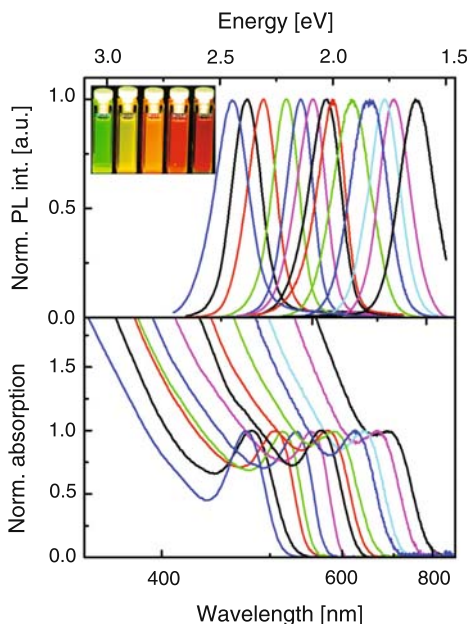


Fig. 8. A set of typical PL (top) and absorption (bottom) spectra of TGA-capped and MPA-capped CdTe NCs demonstrates their tuneability over a broad spectral range in the visible and near-infrared. Excitation wavelength is 450 nm. The inset shows a photograph of brightly emitting CdTe NCs of different sizes taken under UV lamp excitation. Reproduced from [39], © 2007, with permission from American Chemical Society

as for tuning an optimal resonance condition in nanoplasmonics systems [102, 103]. Narrow PL spectra in combination with their tuneability and high PL QE are of a special interest for bio-labelling applications [104], imaging [105] and LEDs [34] based on thiol-capped CdTe NCs.

The broad interest to thiol-capped CdTe NCs has triggered a search for improvements and specific adaptations of their conventional synthetic procedures described above [32, 33, 38]. This includes the hydrothermal synthesis [69, 77], illumination [95], ultrasonic [106] or microwave irradiation [107, 108] treatment, the use of an inert atmosphere [109], variation of reagent concentrations [75–77, 80] and pH [76, 80], and the use of alternative capping agents like glutathione [110].

3. ZnSe nanocrystals

Currently, a lot of attention is paid to the safe handling of nanometer-sized materials [111], which demands among others the development of syntheses of colloidal semiconductor NCs from low-toxic materials and the use of environmentally friendly technologies [112–116]. ZnSe NCs [117] synthesized in water is one of the prominent examples of such kind of nanomaterials.

The synthetic procedure for ZnSe NCs is very similar to the synthesis of CdTe NCs [42, 118, 119]. In a typical synthesis $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in water in the

range of concentrations of 0.02 M or less, and an appropriate amount of the thiol stabilizer (1-thioglycerol, TGA or MPA) is added under stirring, followed by adjusting the pH by dropwise addition of 1 M solution of NaOH to 6.5 in the case of TGA or MPA capping, or to 11.2–11.8 in the case of TG. The mentioned pH values were experimentally found to be optimal for the synthesis of stable colloids. The solution is deaerated by N₂ bubbling for 1 h. Under stirring, H₂Se gas (generated by the reaction of Al₂Se₃ lumps with an excess amount of 1 N H₂SO₄ under N₂ atmosphere [42] or electrochemically [73]) is passed through the solution together with a slow nitrogen flow. ZnSe precursors are formed at this stage. The further nucleation and growth of the NCs proceed upon refluxing at 100°C under open-air conditions with a condenser attached.

A typical temporal evolution of the absorption of the ZnSe NCs is shown in Fig. 9. A growth of the NCs during reflux is indicated by a low-energy shift of the absorption. The PL efficiency of these solutions is negligible and shows mainly a broad trap-emission band (400–600 nm). An additional very weak band-edge emission appears only after long times of reflux. Among the capping agents used a relatively stronger trap-emission is found to be characteristic for TG-capped ZnSe NCs. The synthesis and characterization of this type of white-blue-emitting NCs was reported in details recently [118, 119]. Widely used ratio of the precursors Zn:Se:R-SH is near 1:0.5:2.5, which is similar to the traditional one for the CdTe NCs

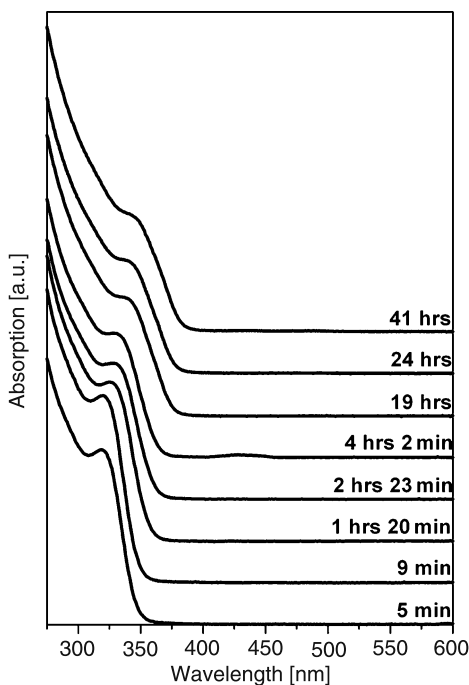


Fig. 9. Evolution of the absorption spectra of a crude solution of ZnSe NCs during the synthesis. Reproduced from [42], © 2004, with permission from American Chemical Society

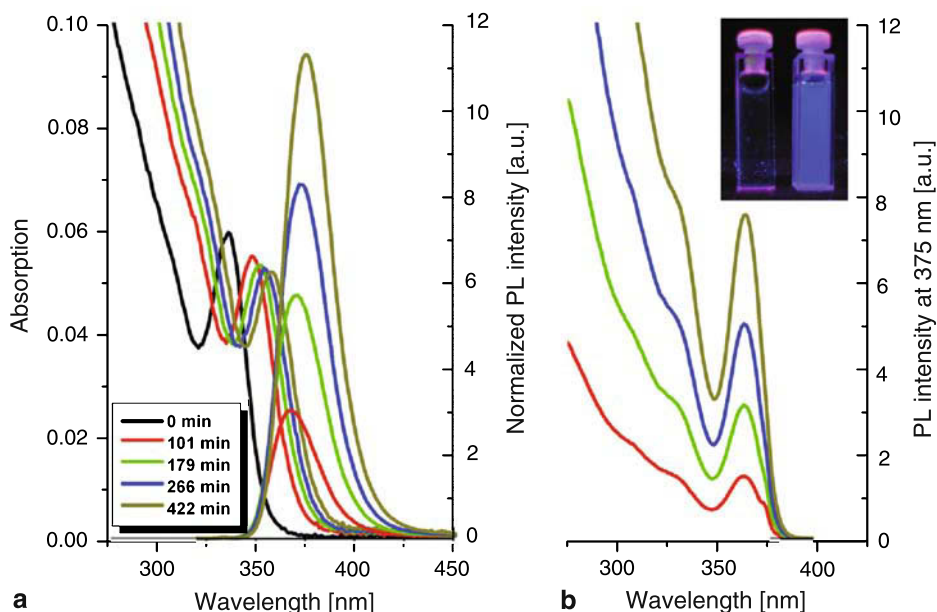


Fig. 10. Evolution of the absorption and PL (a) and of the PL excitation spectra ($\lambda_{\text{observation}}$ 375 nm) (b) of ZnSe NCs during illumination. Inset shows a true color fluorescence image (λ_{ex} 366 nm) of the ZnSe NCs before (left) and after (right) the photo-treatment. Reproduced from [121], © 2006, with permission from American Chemical Society

synthesis. The varying of this ratio towards lower amounts of the stabilizer allowed improvement of the photoluminescence in the case of 1-thioglycerol stabilizer resulting in strong whitish-blue trap-emission [119], but did not result in any considerable improvement in the cases of MPA and TGA.

In order to improve the PL properties of the ZnSe NCs (enhancement of the band-edge and suppression of the trap-emission), the colloidal solutions can be irradiated with a xenon lamp [42] or alternatively with a UV-lamp [120]. The presence of excess of Zn^{2+} ions and TGA molecules was found to be necessary. The dependence of the PL spectra on the duration of the irradiation is shown in Fig. 10. Under illumination, the PL QE increases from ca. 0.1% being characteristic for the as-prepared solutions up to 10–30% [42] and even 50% [120] if the pH during the treatment maintained to be 6.5 and 11, respectively.

The position of the PL maximum and the absorption edge shifted to the lower energy region during the irradiation. The PL emissions with maxima in the region 330–400 nm were achieved under the white-light irradiation and pH 6.5 [42], while larger NCs with PL maxima up to 435 nm may be prepared under UV light at pH 11 [120]. Since the ZnSe NCs studied are in the regime of size confinement, i.e. a low-energy band-edge corresponds to larger particles, we can assume, that the colloidal ZnSe particles grow under irradiation. Additionally, powder XRD and a HRTEM analysis show that the improvement of the PL QE is accompanied by the growth of the NCs. The XRD peaks shift to values which are characteristic for ZnSe/ZnS

alloys (the sulfur appears as a product of photodecomposition of the TGA in solution [82]). Electrochemical studies were performed to show that surface Se-related states in the photochemically treated ZnSe NCs are efficiently exchanged with S-related states [121]. The formation of such a shell from a larger band gap material (ZnS) should provide an additional stabilization of the core particles and hence leads to better PL properties. Solutions treated by this way show narrow PL bands being almost free from trap-associated emission (Fig. 10). Moreover, the observed evolution of the PL properties of the ZnSe(S) NCs is generally followed by a decrease of the Stokes shift. ZnSe NCs capped with TGA, MPA or TG showed a similar increase in PL efficiency after irradiation. However, for both MPA- and TG-capped ZnSe NCs a pronounced increase of the trap-emission band was observed as well. The resulting colloids show a reasonable stability: several months of storage in the dark under air result neither in coagulation nor in recognizable changes in the optical properties. In a very recent report [122] the possibility of direct (without photochemical treatment) synthesis of strongly emitting ZnSe NCs capped with glutathione has been demonstrated.

4. HgTe and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ nanocrystals

In a typical aqueous synthesis of HgTe NCs [41, 122] metal Hg^{2+} ions react under N_2 atmosphere in aqueous solution with H_2Te gas in the presence of a thiol stabilizer. Adjustment of the pH to an appropriate value (11–12), as well as the judicious choice of absolute and relative concentrations of the reaction components allows the reaction rate, the quality of the product and its PL QE to be efficiently controlled [41, 122]. 1-Thioglycerol was found to be the best for controlling the synthesis at the precursors ratio of Hg:Te:R–SH being 1:0.25:2.5. The HgTe NCs grow upon reaction of the precursors at room temperature; the reaction may be stopped by cooling the reaction solutions down in ice pad and keeping them later in a fridge. Reaction lasting for approx. 2 h produces highly concentrated solutions of HgTe NCs of approx. 4 nm in size, with a strong (40–50% PL QE) emission. The drawback of this reaction is the broad size distribution of the resulting samples, leading to a broad luminescence peak of the as-prepared NCs covering the spectral region from 800 to 1400 nm with a maximum located at 1080 nm. However, this broad spectral coverage is advantageous for telecommunication applications, as it coincides with the 1.3- μm telecommunications window. To obtain HgTe NC fractions with various mean sizes and narrower size distributions, a standard size-selective precipitation technique can be applied. Recently it was reported that size and emission maxima of the HgTe NCs may be varied by the controllable growth in presence of 2-mercaptoethanol or 1-thioglycerol in the region from 1200 to 3700 nm [68]. HgTe nanoparticles so prepared belong to the cubic (coloradoite) HgTe phase. Upon gentle (70°C) heating of the as-prepared HgTe NC solutions for progressively longer times, the NCs grow through the Ostwald ripening mechanism, which results in a shift of the PL band towards longer wavelengths with the PL intensity gradually declining to a value of $\sim 10\%$ quantum efficiency. A similar gradual red shift was observed during the storage of as-synthesized HgTe NC solutions at room temperature on the time scale of weeks, which was accompanied by a gradual decline of the emission intensity. To

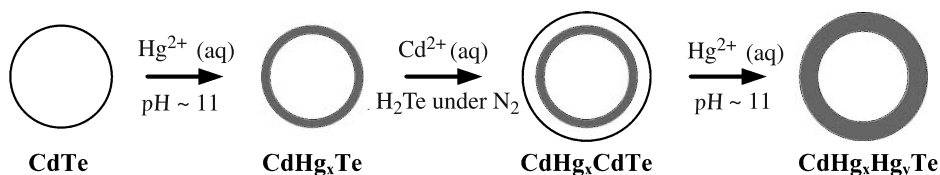


Fig. 11. Schematic diagram of the idealized synthetic routes to achieve mixed-phase $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ nanoparticles

prevent this undesirable effect, capping of HgTe NCs with a shell of a wider-band gap material CdS can be undertaken [123], resulting in positive improvements both for the long-term storage and for the stability of the samples during high-temperature treatments involved in device fabrication.

HgTe NCs synthesized in water can easily be transferred into non-polar organic solvents, such as toluene, styrene, chloroform, chlorobenzene etc., by exchange of the stabilizer with long-chain thiols [68, 83]. Once the NCs have been transferred to non-polar solvents they can be easily processed by traditional spin-coating or casting techniques and are also suitable for the preparation of blends with optically transparent and/or conjugated polymers [124].

Alloyed $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs emitting in the spectral region between 800 and 1100 nm have been synthesized in water through the chemical modification of pre-synthesized thiol-capped CdTe NCs by Hg^{2+} ions [40, 125]. Due to the lower solubility of HgTe in comparison to CdTe in water, the Hg^{2+} ions substitute Cd^{2+} ions at the surface of the nanoparticles forming a $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloy in the near-surface region, as schematically depicted in Fig. 11. A layer of CdTe can then be grown on the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs by addition of more Cd^{2+} ions reacting with H_2Te gas, and the substitution process can be repeated further leading to an increase in both the NC size and the relative Hg content in the alloyed particles (Fig. 11). The substitution reaction occurs with a finite rate and starts at some thermodynamically preferred site. Alloying in bulk $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ systems (MCT) is well-known and is in fact the basis of long-wavelength infrared photodetectors, such that with time Hg^{2+} ions first incorporate on a surface and then into the volume of the particles. The near-surface region of the NCs can therefore be described as a solid solution, alloy or mixed crystal of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, possibly with a concentration gradient decreasing towards the particle interior. The greater the amount of Hg^{2+} ions added and the longer the time period allowed, the greater the concentration of mercury in the interior of the particles until a real $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloy results. The band gap of bulk $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloy varies approximately linearly with the composition from +1.6 eV at $x = 1$ (pure CdTe) to -0.3 eV for $x = 0$ (pure HgTe) [126]. This has been observed experimentally for the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs as a red shift in both the absorption and luminescence spectra with increasing Hg content resulting in emission wavelengths ranging from 700 to 1350 nm depending on the composition. PL quantum efficiencies as high as 50% have been measured for the alloy $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs which is similar to that of HgTe NCs.

Figure 12 shows a series of normalized PL spectra of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe NC fractions (the latter were measured in D_2O) which cover the spectral region between

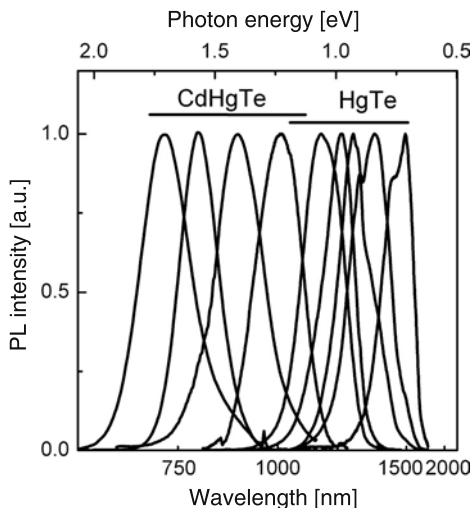


Fig. 12. Typical photoluminescence spectra of the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe NCs. Reprinted with permission from [130], © 2007 Wiley VCH

700 and 1900 nm. Both $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and HgTe NCs are near-infrared-emitting materials whose recognition has grown rapidly all over the world in the last few years. A potentially very significant application of these NCs is their deployment as optical amplifier media for telecommunications systems based on silica fibre technology which has optimal transmission windows around 1.3 and 1.55 μm , as discussed in several topical reviews [127, 128]. Another evolving fields with a great potential are applications of near-infrared-emitting NCs as fluorescent contrast agents for biomedical imaging in living tissue, electroluminescent devices, photodetectors and photovoltaics for solar energy conversion [129, 130]. It was found that $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs possess exceptionally high stability against photooxidation and degradation in typical biological buffer media like phosphate buffered saline [131]. This fact, together with the strong emission in the biological spectral window (both haemoglobin and water show minimum absorption of light between 800 and 1100 nm) makes this kind of NCs especially attractive for bio-imaging and bio-labelling. Recently, $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ NCs additionally protected by CdS shell were successfully used for the *in vivo* imaging [132].

5. Summary and outlook

Sufficient progress has been made during last decade in the preparation and the design of the surface properties of thiol-capped water-soluble NCs whose luminescence covers broad spectral range depending on the material and the particle size. Among the advantages of the aqueous synthesis its simplicity and high reproducibility should be mentioned. Keeping in mind the potential importance of highly luminescent NCs for large-scale applications, it should be mentioned that the aqueous synthesis of thiol-capped NCs can be carried out equally effective on a

vast scale, yielding up to 10 g of NCs per synthesis. These NCs can be precipitated, washed and kept in the dry state under ambient conditions for years, being stable and re-soluble in water.

NCs synthesized by the aqueous approach do not possess the degree of crystallinity of the NCs prepared in organic solvents by the hot-injection technique, where high annealing temperatures (200–360°C) are used during the synthesis [22, 133, 134]. A very effective separation of nucleation and growth stages achieved in the hot-injection technique allows to reach narrower size distributions of the NCs in comparison with those prepared in aqueous solutions. However, the aqueous approach generally allows the synthesis of smaller NCs, both CdS, CdSe and CdTe, and is the only existing reliable method nowadays allowing to produce mercury chalcogenide NCs. The post-preparative size-selective precipitation procedure works more reliable in case of aqueous colloids in terms of retaining the luminescence properties, than for their organically synthesized counterparts. The possibility to control the surface charge and other surface properties of thiol-capped NCs simply by choice of stabilizing thiol molecules with appropriate free functional groups used in the synthesis is extremely important, especially when water-soluble NCs are to be used for fluorescence tagging applications. The possibility to vary surface functional groups is also important when specific binding of NCs to other nanoparticles or to the surfaces is foreseen.

Semiconductor NCs prepared in aqueous solution have found several applications in material science and nanotechnology. Among others is the fabrication of polymer-NC [35, 42, 90, 124, 135–138] and glass-NC [120, 139] light-emitting composites which are robust and easily processable. Applications in optoelectronics cover the LEDs [34, 35, 124, 140], microarrays of multicolored light-emitting pixels [141] and photosensitive films [142, 143]. This is closely connected to photonic applications in which NCs play a role of subwavelength emitters [144], tunable light-sources coupled to optical modes of photonic crystals [145–147] and heterocrystals [148], spherical microresonators [149, 150] photonic molecules [151], and waveguides [152]. The ability of NCs to interact with neighboring nanoparticles or molecules gives rise to the fabrication of FRET-based [101, 153] and nanoplasmonic [103] devices as well as sensors [154–156]. The demands in light emitters which are compatible with water and the most common biological buffers [157] open for thiol-capped NCs such fields as bio-labelling [36, 131, 158–160] and bio-imaging [105, 110, 161]. They have been used as building blocks for self-organizing superstructures like luminescent nanowires [162–168], nanotubes [169] or nanosheets [92], for chemiluminescence generation [170], for fabrication of temperature-sensitive nanoassemblies [171], as luminescent components of multifunctional microbeads [144, 172–177] and polymer microcapsules [104, 131, 177–180]. Brightly emitting water-soluble NCs with a flexible surface chemistry determined by easy choice of capping ligands have already secured and will secure in future a wide field of applications, ranging from life sciences to photonics and optoelectronics. In the field of biological imaging of cellular processes, the ability to fabricate NCs with well-defined surface passivation is important in studying transport processes within living cells [181].

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