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Colloidal quantum dots: synthesis, properties and applications

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Key recent results obtained in studies of a new class of luminophores, colloidal quantum dots, are analyzed. Modern methods for the synthesis and post-synthetic treatment of colloidal quantum dots that make it possible to achieve record high quantum yield of luminescence and to modify their characteristics for specific applications are considered. Currently important avenues of research on colloidal quantum dots and the problems in and prospects for their practical applications in various fields are discussed.
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I. Introduction

Quantum dots are semiconductor nanoparticles whose electronic properties are significantly different from those of a corresponding bulk substance. As the nanoparticle size decreases below 10 nm, the energy of an electronic transition can gradually increase by 1 – 2 eV relative to the value for the bulk sample. Correspondingly, the absorption and luminescence spectra of such nanoparticles undergo a continuous shift throughout the visible region and near-IR region depending on the particle size. The phenomenon called the quantum size effect was predicted theoretically long ago. An example of calculations of the dependence of the energy of electronic transition in a spherically symmetric 3D potential well on the size of the well can be found in a monograph.[1]

The quantum size effect was experimentally discovered in a study of CuCl nanocrystals whose size was varied from 2 to 31 nm.[2] The nanocrystals were grown in controlled manner in multicomponent silicate glasses in the course of thermally induced diffusive phase decomposition of a supersaturated solid solution containing copper and chlorine compounds. Theoretical substantiation[3] of the quantum size effect in semiconductors was recently followed by experimental observation of the phenomenon in ultradisperse semiconductor particles (CdS, CuBr, CdSe, PbS, ZnS, Zn_3P_2, Cd_3P_2) synthesized in silicate glasses[4] and in colloidal solutions.[5–8] An analysis of the experimental data and results of theoretical studies on the quantum size effect available at that time (see a review[9]) revealed the existence of a class of systems with unique properties that opened a new page in solid state physics.

The term 'quantum dot' dates back to 1988.[10] Since then, it has been applied to ultradisperse particles that exhibit the quantum size effect. Probably, even at that time researchers perceived that quantum dots are of interest from the standpoint of not only basic research, but also practical applications.

The early 1990s were marked by the development of a high-precision physical method for the preparation of quantum dots by molecular beam epitaxy.[11] It involves the deposition of a thin layer of a semiconductor material on an atomically smooth substrate. As the thickness of the deposited semiconductor layer reaches a critical value of the order of a few monolayers, the layer spontaneously breaks down with the formation of a regular structure representing rectangular-pyramid-shaped quantum dots on the substrate. However, the method is complicated and expensive.[12]

In 1993, Murray, Norris and Bawendi[13] proposed a simple and highly efficient chemical method of synthesis of quantum dots called high-temperature colloidal synthesis. The approach initially used to synthesize $A^{II}B^{VI}$ semicon-

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ductor quantum dots was extended to other types of semiconductor quantum dots ($A^{III}B^{V}$ and $A^{IV}B^{VI}$). Its main advantage consists in the possibility of large-scale chemical synthesis of structurally perfect colloidal quantum dots (CQDs) of specified average size (dispersion of the size distribution function is $\sim 5\%$).

This opened great opportunities for comprehensive studies on the properties of CQDs and cleared prospects for practical applications of these systems. The essence of high-temperature colloidal synthesis is to use high-boiling tri-n-octylphosphine oxide (TOPO), which simultaneously acts as solvent, metal precursor and anticoagulant forming the ligand shell of CQDs. Tri-n-octylphosphine (TOP), which is structurally isomorphic to TOPO, acts as nonmetal precursor and also participates in the formation of the ligand shell of CQDs.

Owing to the development of high-temperature colloidal synthesis there has been steadily growing interest in colloidal quantum dots since the early 1990s. The number of publications on these systems also rapidly increases (Fig. 1). Further progress in this approach, including the search for new precursors, ligands and methods for post-synthetic modification of CQDs made it possible to achieve high quantum yields of luminescence. At present, CQDs represent a new class of luminophores with narrow emission lines (linewidth is 20 – 30 nm) that can be tuned in a wide spectral range (from 300 to 1200 nm) by varying the average size of CQDs. Unlike molecular luminophores, CQDs are expected to have much higher thermal stability and photostability.

The quantum size effects in semiconductors were for the first time experimentally demonstrated in the 1970s for so-called quantum wells.[14] A quantum well is a structure comprising an epitaxially grown, narrow-band gap semiconductor thin film sandwiched between two wide-band gap semiconductor layers. If the motion of charge carriers along a certain direction in the semiconductor is spatially confined, one deals with quantization of momentum along this direction, namely, a given length scale should be a multiple of an integer number of the de Broglie half-waves. Correspondingly, various quantum size effects appear in spatially confined semiconductors. Eventually, they are related to the fundamental changes in the density of electronic states in the semiconductor. The quantum size structures can be classified with respect to the number of the dimensions of free motion of electrons and holes, namely, 2D structures (quantum wells), 1D structures (quantum wires) and 0D structures (quantum dots).

The experimentally observed manifestation of the quantum size effect in the 0D structures consists in the shift of the absorption band edge and the luminescence maximum as the average size of semiconductor nanoparticles varies. This is illustrated in Fig. 2 for CdSe colloidal quantum dots whose size varies from 3 to 5.5 nm.

The effect is explained as follows. In a bulk semiconductor, absorption of a photon whose energy exceeds the band gap is followed by the appearance of a quasi-free electron in the conduction band and a quasi-free hole in the valence band. Here, 'quasi-free' means that both electron and hole move in the crystal as quantum particles characterized by plane-wave wave functions. Therefore, they can have any energy within the conduction band for the electron and within the valence band for the hole. The only difference is that the masses of these particles are usually much smaller than the mass of an electron freely moving in vacuum. Correspondingly, the de Broglie wavelength should be much larger than that in vacuum at the same energies. As the nanoparticle size matches the de Broglie wavelength, the continuous energy spectrum becomes discrete. The allowed electron and hole energy levels can be determined by solving the Schrödinger equation [1]

$$E_{n_e l_e} = \frac{\hbar^2 \rho^2_{n_e l_e}}{2 m_e R^2} \quad (1)$$

$$E_{n_h l_h} = \frac{\hbar^2 \rho^2_{n_h l_h}}{2 m_h R^2} \quad (2)$$

where n_e, l_e, n_h, l_h are the principal and orbital quantum numbers of the corresponding electron and hole states; $\rho_{n_e l_e}$ and $\rho_{n_h l_h}$ are the sets of numbers specified by the roots of the

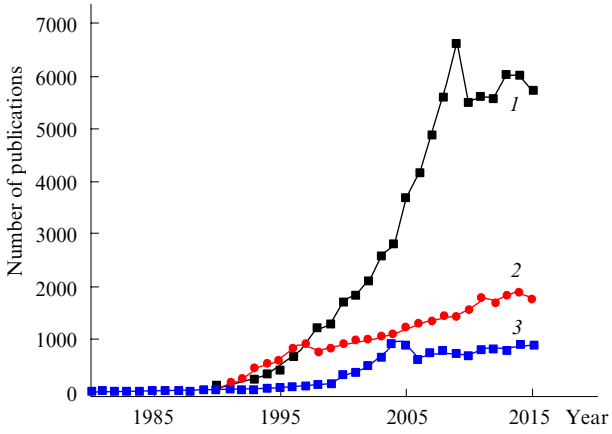


Figure 1. Number of publications indexed in the Scopus database. Subject: colloidal quantum dots (*1*), fullerenes (*2*) and quantum computing (*3*).
Plots (*2*) and (*3*) are shown for comparison.

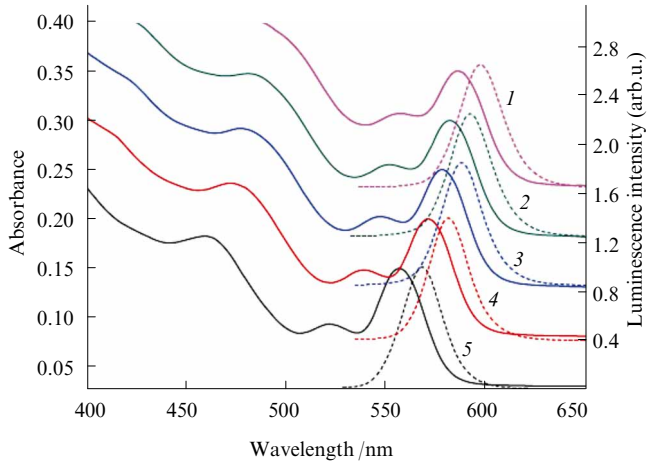


Figure 2. Positions of the absorption band edge and the maximum in the luminescence spectrum of CdSe quantum dots plotted *vs.* average particle size.[15]
Average CQD size /nm: 5.5 (*1*), 4.8 (*2*), 4.0 (*3*), 3.5 (*4*) and 3.0 (*5*).

Bessel spherical functions arising in solving the Schrödinger equation for spherically symmetric 3D quantum well of radius R; and m_e and m_h are the effective masses of electron and hole, respectively. The first three roots, $\rho_{10} = 3.142$, $\rho_{11} = 4.493$ and $\rho_{12} = 5.763$, respectively, correspond to the 1s, 1p and 1d quantum states (Fig. 3).

The selection rules specify the allowed transitions between these energy levels and thus the absorption and emission spectra of quantum dots (see Fig. 3). Expressions (1) and (2) lead to the Brus formula [9] for estimating the ΔE value which relates the shifts of the absorption and luminescence spectra of nanoparticles to the nanoparticle size,

$$\Delta E \approx E^{e}_{10} + E^{h}_{10} - E_g = \frac{\hbar^2\pi^2(m_e + m_h)}{2R^2 m_e m_h} - \frac{1.8e^2}{\varepsilon R} \qquad (3)$$

Here E_g is the band gap of a bulk semiconductor, R is the radius of the nanoparticle and ε is the dielectric constant. The second term includes the Coulomb interaction in the electron – hole pair in the CQDs.

Actually, the particle size dependences of the absorption spectra and luminescence spectra are not exactly described by the Brus formula. These dependences are determined in high-precision experimental studies involving independent measurements of the size of CQDs by various physical methods and subsequent comparison of the results obtained with exact spectroscopic data.

Unique properties of CQDs and simple synthetic procedure predetermine a broad range of potential applications of CQDs in the design of advanced functional nanomaterials including active media for light-emitting diodes, displays, solar batteries, optical amplifiers, lasers and other nanophotonics devices. More distant prospects are related to molecular electronics and quantum computing. Seemingly, CQDs are also highly promising for chemo- and biosensorics and biomedical diagnostics.

More than 50 000 publications on colloidal quantum dots appeared in the last decade. Among them, there are a large number of reviews on various aspects including applied ones. The most important of them will be cited below. A distinctive feature of this review is that general analysis of the state of the art in the title field is combined with detailed consideration of the most important recent studies on the methods of synthesis and post-synthetic treatment of CQDs aimed to achieve record high quantum yields of luminescence and to fabricate CQDs with specified properties for solving particular applied problems. We will also discuss the key avenues of research on CQDs, as well as problems in and prospects for their applications in photonics and biomedical diagnostics.

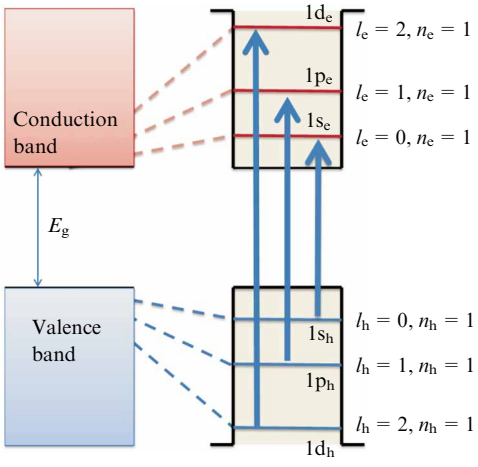


Figure 3. Electronic structure of a bulk semiconductor (on the left) and electronic transitions between the corresponding electron – hole states specified by expression (1) in a quantum dot (on the right).

II. Methods of synthesis and post-synthetic treatment of quantum dots

II.1. Physical methods for preparation of quantum dots

Methods for preparation of quantum dots can be conditionally divided into physical (no chemical transformation of matter occurs) and chemical ones (chemical reaction of formation of a substance as necessary step).

Physical methods usually involve nucleation and growth of particles in the vapour phase or in solutions. Theoretical prerequisites for fabrication of nanoparticles with specified size distribution have been analyzed.[16] However, the one and only practically valuable, pure physical method for preparation of semiconductor quantum dots is molecular beam epitaxy.[12] The approach involves deposition of atomic or molecular beams produced in some sources on crystalline substrates with atomically smooth surface in ultrahigh vacuum. Spontaneous formation of ordered quantum dot arrays on crystalline surfaces represents an example of self-organization of matter in the course of stress relaxation in thin epitaxial films; these stresses originate from the mismatch between the lattice constants of the film and substrate. The method provides a unique possibility to produce quantum dot arrays with ultrasmall dispersion of the size distribution function and to study the quantum size effects. For instance, PbSe quantum dots with record small dispersion of the size distribution function (only 2%) were prepared.[17] However, the method requires complex equipment and high-purity materials.

In the text below we will consider various chemical methods of synthesis. In essence, they represent liquid-phase condensation, that is, a chemical reaction creates a necessary supersaturation followed by nucleation and growth of nanoparticles. The emphasis is placed on the post-synthetic treatment of CQDs because the freshly prepared quantum dots are often characterized by very low quantum yield of luminescence, and nanoparticles with efficient luminescence cannot be obtained without additional treatment. Among the methods of post-synthetic treatment, various physical methods are of great importance.

II.2. Micellar synthesis of colloidal quantum dots

Colloidal synthesis of various nanoparticles including CQDs in 'water-in-oil' reverse microemulsions was proposed in the late 1980s – early 1990s. The method is based on a chemical reaction controlled by intermicellar exchange of reactants, which results in nucleation and growth of nanoparticles. The method was used to synthesize metal,[18 – 21] metal oxide,[22 – 24] silver halide [25 – 28] and many other semiconductor nanoparticles.[29, 30] The state of the art in micellar synthesis of nanoparticles was analyzed in a

review.[31] For long it was assumed that growth of nanoparticles in reverse microemulsions is confined by the reverse micelle shell. Since reverse micelles themselves can be considered as monodisperse, it was expected that nanoparticles obtained by reverse micellar synthesis should also be monodisperse. More over, in accordance with this logic, the size of the nanoparticles thus synthesized can be varied because the reverse micelle size can be controlled with ease by varying the water and surfactant concentrations. However, a recent study[32] revealed a much more complicated mechanism of nanoparticle stabilization. Other significant drawbacks of the approach include low concentration of resultant nanoparticles and a large variance of the size distribution function (at least 20%).

II.3. High-temperature colloidal synthesis

High-temperature colloidal synthesis was for the first time reported by Murray, Norris and Bawendi,[13] who fabricated CdS, CdSe and CdTe colloidal quantum dots with bright tunable luminescence using a simple one-step reaction, namely, pyrolysis of organometallic precursors at 300 °C. To this end, a cold (room-temperature) solution of a mixture of precursors (TOP-Se and dimethylcadmium) in tri-n-octylphosphine was injected into hot (300 °C) tri-n-octylphosphine oxide. This was accompanied by burst-like nucleation and the temperature of the mixture dropped to ~180 °C; no further nucleation was observed. The temperature of the reaction mixture was gradually raised to 230 – 260 °C and maintained in this range throughout the nanocrystallite growth process. High temperature of the synthesis facilitated annealing of particles and formation of almost defect-free crystal lattice;[33] therefore, the CQDs thus prepared demonstrated strong band-to-band fluorescence and no luminescence from deep traps was observed.

This synthetic approach meets the conditions for production of high-quality CQDs, that is, (i) nucleation and growth are separated in time and (ii) annealing of nanoparticles is possible. The high-temperature method allows one to obtain defect-free CQDs with relatively high quantum yield of fluorescence and narrower size distribution of particles compared with other liquid-phase methods. In some cases, the variance of the size distribution function of CQDs was $<5\%$.[34, 35] Further progress in high-temperature colloidal synthesis is associated with the search for new high-temperature solvents, precursors and ligands and with the possibility to extend the method to other types of semiconductors.

II.4. High-temperature colloidal synthesis of $A^{III}B^{V}$ semiconductor quantum dots

Cadmium selenide quantum dots characterized by impressive parameters are of limited use because of high toxicity of cadmium, which is a carcinogen.[36] Coating the CdSe quantum dots with different-type shells, *e.g.*, silicon dioxide[37 – 40] or amphiphilic polymer,[41] makes the situation somewhat better (the amount of Cd^{2+} ions that escape from the nanoparticle cores decreases); however, the problem still persists because cadmium-based CQDs remain unsafe. The least toxic cadmium-free compounds ($A^{III}B^{V}$ semiconductors) include GaAs, InP, InAs and InSb. Indium phosphide is similar in physicochemical properties to cadmium selenide, thus being the best candidate for replacing CdSe.[42, 43]

Indium phosphide is a direct band-gap semiconductor with a band gap of 1.27 eV (*cf.* $E_g = 1.74$ eV for CdSe)[44] and a tetrahedral structure of the wurtzite or sphalerite type. Its crystals are in a state with predominantly covalent bonding, the contribution of ionic component being nearly 15%.[45] Owing to high covalency the exciton Bohr radius of InP (10.6 nm) is much larger than that of CdSe (5.2 nm);[44] therefore, the size effect is more pronounced for InP than for CdSe.[46] Besides, stronger covalent bonding improves the photostability of the InP quantum dots, which can be used instead of the CdSe quantum dots in various, especially biomedical applications.

However, attempts to produce InP quantum dots by high-temperature colloidal synthesis using the conditions, solvents, ligands and precursors that proved themselves in the fabrication of CdSe quantum dots gave unsatisfactory results. Nucleation and crystal growth in this system occur very slowly and the growth of nanoparticles of a specified size requires very long periods of time (hundreds of hours).[47] Besides, high strength of the bond in InP complicates the synthesis of monodisperse CQDs because it is difficult to separate the nucleation and growth of nanoparticles. Therefore, one gets a broader nanoparticle size distribution and, consequently, broader bands in the luminescence spectrum, namely, the full width at half maximum (FWHM) is usually 60 nm (and more)[48, 49] *versus* ≈30 nm for CdSe.[44] The duration of synthesis was significantly decreased using octadecene as solvent and a fatty acid (palmitic acid or myristic acid) as indium-coordinating ligand. In particular, nearly 3-nm InP nanoparticles characterized by a variance of the size distribution function of 4.7% were grown within a few hours.[50]

Utilizing indium carboxylates (lauratre, myristate, stearate) as indium precursors extends the possibilities of synthesis of InP quantum dots.[51] By appropriately choosing a precursor one can prepare different-size CQDs with the luminescence bands characterized by FWHM ~60 – 70 nm. To enhance the reactivity of indium carboxylates and to accelerate the synthesis, fatty amines were used as activators.[42] This makes it possible to fabricate different-size InP quantum dots with tunable spectrum in the range from 390 to 720 nm within ~60 min.

The choice of phosphorus source is of great importance for the synthesis of InP quantum dots. Tris(trimethylsilyl)-phosphine widely used to this end is far from being the best source. When introduced into the reaction medium, this highly reactive compound is very rapidly and almost completely consumed within a short period of time, providing no resources for the prolonged growth of nanoparticles. Nucleation and growth of nanoparticles occur almost simultaneously and thus preclude the formation of monodisperse CQDs.[52] Besides, tris(trimethylsilyl)phosphine is not only expensive, but also a hazardous, spontaneously inflammable compound. Its use in large-scale syntheses of InP quantum dots seems to be problematic.

Other sources of phosphorus include yellow phosphorus,[53] gaseous phosphine (PH_3) formed in the reaction of calcium phosphide (Ca_3P_2)[54] or zinc phosphide (Zn_3P_2)[55] with hydrochloric acid. Although these precursors offer some advantages, they were unnoticed by researchers who paid much more attention to the cheaper and safe tris(dimethylamino)phosphine. This compound was for the first time used as phosphorus source by Matsumoto, Maenosono and Yamaguchi[56] and as reactant for high-temperature colloidal synthesis by Song *et al.*[48] Colloidal quantum dots synthesized in the latter study were characterized by rather

narrow size distribution functions and the position of the luminescence band maximum could be smoothly tuned in the range from 500 to 600 nm by varying the synthesis duration provided identical synthesis conditions.

Thus, by appropriately choosing the reactants and reaction conditions one can synthesize InP quantum dots with narrow size distribution within reasonable periods of time and vary the nanoparticle size over a relatively wide range. However, the quantum yield of luminescence of InP quantum dots in all the studies mentioned above was very low (at most 1%).

This is due to the high strength of covalent bonds, which leads to formation of numerous deep surface traps (unsaturated bonds and packing defects) on the InP quantum dots; the activation barriers to escape from the traps are higher than in the case of the $A^{II}B^{VI}$ semiconductors.[45] The quantum yield of photoluminescence can be increased by chemical modification of the nanoparticle surface or by epitaxial growth of shells using semiconductors with wider band gaps. An example of surface modification is provided by treatment of CQDs with HF or NH_4F solutions (chemical annealing).[57, 58] The resultant CQDs are characterized by intense band-to-band luminescence, and the quantum yield of luminescence increases by more than an order of magnitude up to 30%. Indium phosphide CQDs dispersed in tetrahydrofuran exhibit stable bright luminescence over a period of at least two weeks. It is believed that in the course of chemical annealing fluoride anions fill the phosphorus vacancies on the InP surface and replace oxygen in the oxide layer.[57]

Yet another method is to combine chemical annealing and photochemical annealing; in this case, an additional UV irradiation for 8 h causes the quantum yield of luminescence to nearly double.[59] Back in 2001 it was found that the growth of a wide-band gap semiconductor shell is an efficient method for increasing the quantum yield of luminescence of InP quantum dots.[60] The formation of InP@ZnS quantum dots with the core@shell structure caused the luminescence efficiency to increase by a factor of 73. Then, the technique was essentially modified and found wide application.

Analogously,[42] experiments on the growth of ZnS shells on InP cores revealed an increase in the quantum yield of luminescence from less than 1% for the initial InP cores to more than 40% for the product, *viz.*, InP@ZnS quantum dots with the core@shell structure, and a significant improvement of air stability of the quantum dots. Various semiconductor shells can be grown, such as CdSe, CdS, ZnSe, ZnSe/ZnS or $ZnCdSe_2$; however, most publications and the best results were obtained for the structures with the ZnS shells.[61 – 63] The semiconductor shell can be formed not only after, but also in the course of the synthesis of the InP quantum dots like, *e.g.*, in a study [64] where all components for the synthesis of the InP cores and for the shell growth were placed in the reaction vessel simultaneously and heated to 300 °C. The synthesis was accompanied by a considerable increase in the fluorescence efficiency to 70%. This was associated with the formation of the core@shell CQDs due to the different reactivities of the InP and ZnS precursors.

Combining chemical annealing and subsequent growth of a wide-band gap semiconductor shell seems to be very attractive. However, preliminary chemical annealing of InP cores may lead to formation of a defect structure of the ZnS shells because HF blocks the surface of CQDs.[65] As mentioned above, the formation of a ZnS shell causes a considerable increase in the quantum yield of luminescence. Also, the synthesis of InP quantum dots in the presence of zinc ions can reduce the concentration of surface defects and facilitate the formation of the ZnS shell.[48] Besides, zinc ions may contribute to stabilization of the surface of CQDs and to the decrease in the critical nucleus size and thus to narrowing of the particle size distribution function.[66]

Summing up, the approach involving the use of new components, optimization of the synthesis conditions, chemical and photochemical annealing and new procedures for the formation of semiconductor shells allows one to prepare high-quality InP quantum dots whose properties are comparable with those of cadmium CQDs.[67] One can expect this may help to synthesize other $A^{III}B^{V}$ semiconductor CQDs.

II.5. Hydrophilic semiconductor quantum dots

High-quality CQDs prepared by high-temperature colloidal synthesis and stabilized with hydrophobic ligands bearing long organic 'tails' are well soluble in nonpolar solvents. However, many practical applications including biomedicine [68] as well as electroluminescence and photovoltaic systems [69, 70] require water-soluble CQDs or CQDs stabilized with small molecules.

There are three main synthetic routes to hydrophilic CQDs:[71]

— synthesis in aqueous solutions;

— replacement of hydrophobic ligands in the particle-stabilizing shells by hydrophilic ones; and

— formation of the secondary (water-soluble) shell surrounding hydrophobic particles.

Colloidal quantum dots can be synthesized in aqueous solutions using various polymeric binders,[72 – 74] reverse micelles [29, 30, 75 – 78] or stabilizers, such as carboxylic acids or amines.[79] In most cases, various thiol-substituted compounds are used, *e.g.*, mercaptoacetic acid,[80, 81] mercaptopropionic acid,[82] dihydrolipoic acid,[83] cysteine,[84] 2-mercaptoethanol, 1-thioglycerol, *etc.*[85, 86]

Colloidal quantum dots synthesized in aqueous solutions are usually characterized by a broad size distribution [87] and very low luminescence efficiency of the freshly prepared CQDs; therefore, additional procedures are required in order to improve their properties.[88, 89]

II.6. Refluxing

Refluxing is a widely used procedure for not only growing CQDs to a specified size, but also increasing the quantum yield of luminescence.[84, 90 – 92] A clear demonstration of significant increase in the luminescence efficiency in the course of refluxing of CdTe quantum dots stabilized with 3-mercaptopropionic acid is available.[93] Prior to refluxing, the absorption spectrum of (even small) nanoparticles exhibited a well-resolved band of the first excitonic transition, but the nanoparticles did not luminesce. Refluxing for 5 – 6 min at 100 °C caused the colloids to become rich in colour and weak luminescence was observed. Prolonged refluxing makes it possible to produce CQDs of different size; in this case, the peak position in the luminescence spectrum can vary from 487 to 590 nm.

The quantum yield of luminescence of CQDs depends strongly on the pH value of the medium and on the precursor concentrations; it considerably increases in the course of refluxing and reaches a value of 67% after treat-

ment for 10 h under the optimal conditions. The luminescence bandwidh (more exactly, FWHM) varies with increasing the duration of refluxing from 30 nm in the early stage of the process to 60 nm in the final stage. Cadmium telluride quantum dots thus prepared showed very high stability, namely, the CQDs with the quantum yield of luminescence equal to 67% exhibited neither decrease in the luminescence efficiency nor changes in position and shape of the luminescence band after storage for a period of 50 days. Probably, this is a record high result for the CdTe quantum dots produced by refluxing in the aqueous phase.

This heat treatment procedure was also used to prepare water-soluble CQDs with the core@shell structure[94] and very high quantum yield of luminescence (up to 81%). Refluxing is an efficient tool for controlling the nanoparticle size in the course of the synthesis of CQDs; however, the quantum yield of luminescence can decrease.[95] This was associated with the development of mechanical stress and the appearance of defects at the core/shell interface due to the mismatch of the lattice constants between the core and shell materials.

II.7. Hydrothermal method

Water-soluble CQDs with efficient luminescence are often synthesized by the hydrothermal method, which involves heating of freshly prepared CQDs in an autoclave at temperatures up to 200 °C (this much exceeds conventional refluxing parameters) over a period of a few hours.[94] The technique was used to prepare ZnS,[96] CdS,[97] CdSe[98] and CdTe quantum dots.[99]

Although the quantum yields of luminescence of CdTe quantum dots stabilized with glutathione (GSH) and thioglycolic acid (TGA) were not reported, the efficiency of their luminescence follows a non-monotonic dependence on the experimental conditions (pH value, duration and temperature of synthesis, GSH/TGA mole ratio, and the amount of ligands and cadmium ions).[100] Hydrothermal method was used to prepare water-soluble CdTe@CdSe quantum dots with tunable luminescence in the near-IR region (from 620 to 740 nm).[101] The quantum yield of luminescence was as high as 44.2% with no post-synthetic treatment. The method allows one to control the thickness of the growing CdSe shell and the final luminescence properties of the CQDs that exhibited high photostability.

II.8. Microwave-assisted synthesis

At present, microwave-assisted synthesis of CQDs has been increasingly used to prepare small high-purity CQDs with narrow size distribution within rather short periods of time. These features are due to the fact that microwave-assisted synthesis ensures uniform and very rapid heating of the whole bulk of the reaction mixture.[102] It can be used to prepare water-soluble individual CQDs (CdS,[103] CdSe,[104] CdTe,[105] ZnSe,[106] alloyed CQDs,[82, 107] core@shell CQDs[108 – 110] as well as water-soluble CQDs doped with copper or manganese.[111]

The microwave-assisted method is suitable for producing hydrophobic CQDs in nonpolar solvents[112 – 117] and even for solvent-free synthesis of ZnSe quantum dots.[118]

By varying the experimental conditions (temperature, pH, reactant ratio and concentrations, as well as the duration of microwave treatment) one can control the average nanoparticle size and vary their spectroscopic characteristics in a wide interval (of the order of 100 nm and more). Usually, the quantum yield of luminescence of water-soluble CQDs lies in the range from 10% to 30%, being as high as 60% for the CdTe[105] and 90% for the $Zn_{1-x}Cd_xTe$ CQDs;[107] the last-mentioned value seems to be record high for water-soluble nanoparticles. A severe drawback of microwave-assisted synthesis is a rather wide size distribution of CQDs ; a FWHM value of 33 nm[105] is a very good result.

II.9. Replacement of hydrophobic ligands by hydrophilic ones

Water-soluble CQDs are most often synthesized using ligand exchange reactions. This approach allows one to produce not only water-soluble, but also biocompatible CQDs.[119] Usually, the stabilizing shells of the CQDs synthesized in organic solvents contain hydrophobic ligands, such as TOPO, TOP, dodecylamine, tetradecylphosphonic acid and oleic acid (OA). These ligands can be replaced by water-soluble bifunctional molecules which are hydrophobic on one end anchored on the surface atoms of CQDs and hydrophilic on the other end.[120] Examples of thiol-containing molecules are provided by oligomeric phosphines, dendrons, peptides,[121] mercaptocarboxylic acids; the most often used short hydrophilic thiols include mercaptopropionic acid,[122, 123] 2-aminoethanethiol, dithiothreitol, dihydrolipoic acid and cysteine.[87, 124]

In particular, CdSe@ZnS quantum dots stabilized with oleic acid were hydrophilized by replacing the molecules of the stabilizing ligand with various thiol molecules (L-cysteine, mercaptoacetic, mercaptopropionic, mercaptosuccinic and mercaptoundecanoic acids).[125] Almost all hydrophilic CQDs thus produced were characterized by weaker luminescence compared to the initial hydrophobic nanoparticles. However, the CdSe@ZnS quantum dots capped with mercaptoacetic acid showed the most efficient luminescence among the thiols tested, which was as efficient as that of the initial nanoparticles. This was explained by the fact that the sulfanylacetic acid molecules are the smallest among the thiol molecules studied and, probably, form a dense shell, thus providing better passivation of the nanoparticle surface.

A study[126] on the influence of the alkyl chain length in various oligo(ethylene glycols) on the luminescence of TOPO-stabilized CdSe@ZnS quantum dots revealed an increase in the luminescence efficiency of hydrophilic CQDs with increasing the thiol chain length, although all water-soluble CQDs prepared by replacement of ligands exhibited lower quantum yields of luminescence compared with the initial hydrophobic nanoparticles. This was associated with more efficient displacement of water molecules from the CQD surface.

To avoid the decrease in the quantum yield of luminescence due to replacement of hydrophobic ligands by hydrophilic ones, one uses di-, tri- or polythiols that form stronger bonds with the CQD surface. For instance, TOPO-capped CdSe quantum dots were hydrophilized by exchange of ligand molecules by hydrophilic dithiocarbamate molecules.[127] The quantum yield of luminescence of these CQDs was higher than that of the initial particles (2.4% *vs.* 15%, respectively); this was explained by efficient passivation of the CQD surface by dithiocarbamate. The use of bidentate ligands with other nature of terminal groups is not a universal route to success. In particular, an attempt[128] to hydrophilize hydrophobic CdSe@ZnS quantum dots stabilized with TOPO and n-hexadecylamine by replacing these ligands by bidentate pyrocatechol-contain-

ing water-soluble ligands was successful. However, the water-soluble nanoparticles thus produced were characterized by very weak luminescence (the quantum yield of luminescence decreased to 0.5% *vs.* 24% for the initial hydrophobic CQDs).

An analysis of published data revealed that ligand exchange can lead to significant changes in the chemical and physical state of atoms on the CQD surface; therefore, in most cases the efficiency of photoluminescence of the water-soluble CQDs prepared by this method appreciably decreases, being at most 40% – 45%.[129] It follows that even ideal surface passivation in organic solvent may be violated after hydrophilization of particles. Also, despite the fact that thio group readily interacts with metal atoms on the nanoparticle surface, thiol-based stabilizers do not make them highly stable in water because they can leave the CQD surface after some time and be involved in irreversible formation of disulfides and subsequent aggregation and precipitation of the CQDs.[87, 130]

II.10. Formation of secondary water-soluble shell

Yet another important method for hydrophilization of CQDs is the formation of secondary hydrophilic shell surrounding the primary hydrophobic shell. In this case, the structure of surface defects formed in the course of synthesis of hydrophobic particles can remain unchanged. The secondary hydrophilic shell can be fabricated in different manner, namely, through formation of a micelle-like structure surrounding the organic layer of CQDs, encapsulation into an additional inorganic (*e.g.*, SiO_2) shell or formation of a water-soluble polymeric coating.

Colloidal quantum dots hydrophilized using these methods usually retain high quantum yield of luminescence. However, encapsulation into a silicate or polymer-phospholipid shell leads to a considerable increase in the quantum dot size, although ensures stability in a wide range of pH values. For nstance, the diameter of CdSe@ZnS quantum dots encapsulated into phospholipid and block copolymer shells increases from 4 – 8 to 20 – 30 nm.[131, 132] Phase transfer of CQDs between aqueous solution and an organic solvent of high polarity can be achieved by coating them with amphiphilic molecules through electrostatic, hydrophobic or specific (host – guest) interactions.[119] Hydrophobic fragments of amphiphilic molecules can anchor on the primary hydrophobic layer and thus form the second ligand layer surrounding CQDs, thus providing solubility in water at the expense of outer hydrophilic groups.[133] Hydrophobic CdSe@CdS/ZnS quantum nanorods with primary TOPO/OA shells were hydrophilized by encapsulation into the phospholipids/poly(ethylene glycol) secondary shell.[134] This made it possible to retain the absorption and luminescence spectra and the quantum yield of luminescence in a broad range of pH values (3 – 10) and temperatures (25 – 70 °C). Electron microscopy studies confirmed that no aggregation and 'ripening' of nanoparticles occurred in the course of encapsulation into the phospholipid micelles.

Inert and nontoxic organosilicates seem to be convenient for coating the CQD surface.[135] This kind of encapsulation imparts not only hydrophilic properties, but also biocompatibility to the CQDs owing to the presence of NH_2 or SH groups as constituents of the organosilicate coatings.[87]

Various types of cyclodextrins (CDs) were tested as agents for hydrophilization of hydrophobic CQDs. The best results in hydrophilization of oleylamine-stabilized CdS quantum dots were obtained using β-CD because it has no effect on the particle size or particle size distribution.[136]

A sonochemical method [137] for the preparation of water-soluble CdSe@ZnS quantum dots with intense luminescence using α-, β- and γ-CD as surface-coating agents is based on the formation of host – guest complexes between the surface ligand in the primary TOPO shell and CD through hydrophobic interactions. The bandwidths and positions of maxima in the absorption and luminescence spectra of the hydrophilic CQDs thus produced exactly matched those in the spectra of the initial hydrophobic nanoparticles. The quantum yields of luminescence of α-CD-CQDs, β-CD-CQDs and γ-CD-CQDs in water were 45%, 39% and 27%, respectively. Transmission electron microscopy studies showed that the sizes of the hydrophobic CQDs and CD-CQDs were almost the same, thus indicating that the modified particles are monodisperse and uniform in water. Hydrophilized CD-CQDs are stable in water over a period of a few days and the intensity of their luminescence is independent of pH in the pH range from 6.0 to 9.0.[137]

A very interesting and relatively simple method for hydrophilization of nanoparticles was proposed by Fan *et al.*[138, 139] A solution of hydrophobic Au nanoparticles was added to an aqueous solution of a surfactant (cetyltrimethylammonium bromide or hexadecyltrimethylammonium bromide) under vigorous stirring to form an oil-in-water microemulsion. Then, the organic solvent was removed from the mixture using a a rotary evaporator and the nanoparticles transferred to the aqueous phase. Hydrophilization was driven by hydrophobic interactions between alkane chains of the stabilizing ligand from the first shell and alkane chains in the secondary shell and resulted in an interpenetrating bilayer micelle-like structure with hydrophilic cetyltrimethylammonium bromide surface groups responsible for the stability of the nanoparticles in water. Spectroscopic and electron microscopy studies confirmed that nanoparticles thus produced remained monodisperse, demonstrated no aggregation in water and that the peak positions and widths in the absorption spectra of the nanoparticles remained unchanged. Aqueous solutions of nanoparticles in these micelle-like structures are stable in a wide range of pH values. The method initially developed for hydrophilization of gold nanoparticles was successfully extended to CdSe quantum dots.[140, 141]

Compared to replacement of ligands, methods involving the formation of secondary hydrophilic shells give much better results. Indeed, since there are no direct interactions with the surface atoms of CQDs, the initial luminescence efficiency is retained, while the side chains of the new ligands enhance hydrophobic interactions and thus improve the stability of the water-soluble CQDs.

II.11. Microreactor synthesis

A flow microreactor synthesis of CQDs was proposed quite recently.[142] In brief, appropriately chosen CQD precursors are delivered through microchannels to a micromixer and then the mixture passes through a number of zones with a specified temperature gradient. Nucleation proceeds in the hot zone while subsequent growth of CQDs occurs at much lower temperatures. Emphasize that the microreactor method enables efficient separation of the nucleation and

growth of CQDs.[143] Conducting the process under optimum conditions allows one to prepare CQDs with very narrow size distribution.

Cadmium sulfide quantum dots with tunable luminescence in the 391–463 nm range, a moderate quantum yield of luminescence of 14.5% and FWHM values between 11.6 and 14 nm in the luminescence spectrum have been synthesized.[144] Microreactor synthesis was used to prepare CQDs of different composition including CdS, CdSe, CdSe@CdS and CdSeS.[145] Core–shell CdS@ZnS and CdSe@ZnS quantum dots were characterized by FWHM values in the 25–33 nm range and the following quantum yields: 41% for blue, 58% for cyan, 70% for green, 78% for yellow, 76% for orange and 61% for red.[146] Successful microreactor synthesis of Mn-doped water-soluble ZnS quantum dots stabilized with 1-thioglycerol suggested[147] that the approach is suitable for the preparation of various types of doped nanoparticles.

The advantages of microreactor synthesis over traditional methods of fabrication of CQDs are as follows: very small amounts of precursors, short synthesis time and small-size experimental setup. At present, this approach can be used solely for research purposes. However, it also seems to be promising for large-scale production of CQDs, although this requires not only scaling up the experimental equipment, but also comprehensive heat and mass transfer studies and the development of methods for efficient mixing of large volumes of solutions.

III. Spectral-luminescent properties of quantum dots

III.1. Luminescence blinking

High quantum yield of luminescence, the possibility of tuning the luminescence spectrum in a wide range by varying the chemical composition, size, shape and structure of particles, as well as high photostability of CQDs make them very promising for the design of advanced materials and devices for various applications. Noteworthy is a feature of single CQDs called luminescence blinking. The essence of the effect is that a single nanoparticle can undergo a spontaneous reversible transition from the radiative state ('on' state) to the nonradiative state ('off' state). The residence time of CQDs in 'on' or 'off' state varies from a few milliseconds to a few minutes. This feature of CQDs makes them 'single nanoparticles of limited use', reduces the luminescence efficiency and deteriorates the stability of the properties of the entire ensemble of CQDs.

An analysis of the state of the art in this field showed that the blinking intensity depends on various factors, such as the synthesis conditions, chemical composition, structure and (especially) thickness of the secondary semiconductor shell, ligand environment, location of nanoparticles on various conductive surfaces or near other nanoparticles (TiO_2, Ag), UV irradiation, pH, *etc*. The first observation of luminescence blinking[148] was followed by publication of hundreds of scientific papers including a number of reviews[149–153] devoted to various aspects of the effect in hand. Most publications concern investigation of the mechanism of the effect in single particles using modern equipment for single nanoparticle spectroscopy.[150, 154]

The mechanism of luminescence blinking in CQDs was for the first time proposed by Efros and Rosen.[155] It was assumed that the excitation light causes the quantum dot to charge, the process being accompanied by highly efficient nonradiative Auger recombination corresponding to the 'off' state. After spontaneous discharge the 'on' state of the quantum dot is recovered (Fig. 4).

At present, this mechanism continues to be relevant, although it does not describe all experimentally observed features of blinking. Therefore, it was modified[156–160] (mainly the character of the charged state, methods of

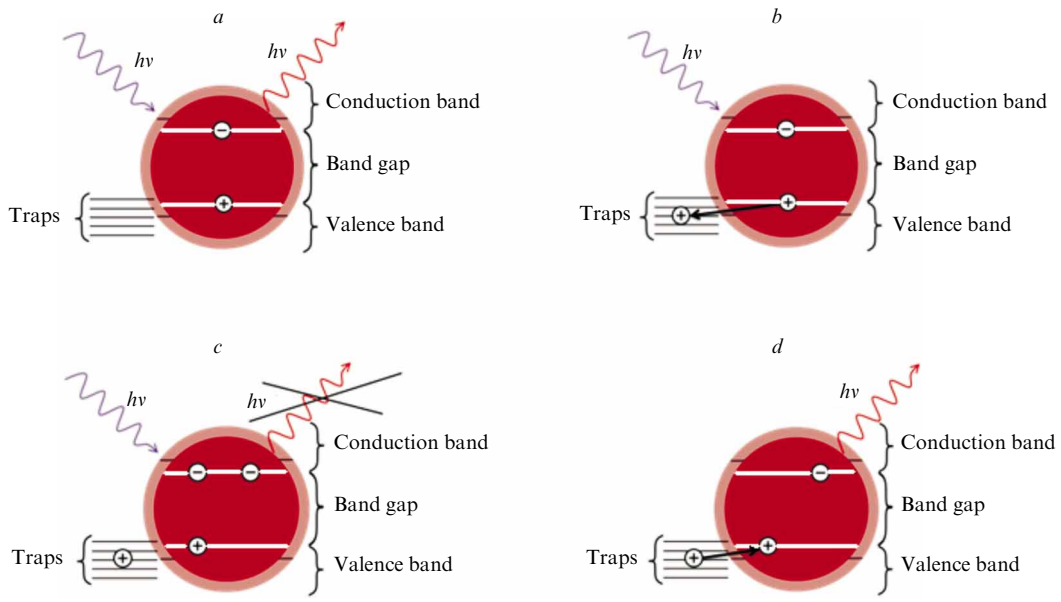


Figure 4. Mechanism of luminescence blinking in CQDs: a schematic.
'On' state: emission upon absorption of a photon (*a*); transition to 'off' state: trapping a hole upon absorption of a photon (*b*); 'off' state: nonradiative deactivation through Auger recombination upon absorption of a photon (*c*); and recovery of radiative 'on' state upon spontaneous transition of a hole from the trap to the valence band (*d*).

transition to that state and how to discharge was discussed) and new mechanisms were put forward.[154, 161, 162]

In spite of considerable body of information on the phenomenon, opinions are different as to the blinking mechanism. This is due to both complexity of the process and significant differences in obtaining and interpreting experimental data. However, all the mechanisms proposed emphasize a key role of the surface states of nanoparticles. The quantum yield of luminescence of an ensemble of CQDs is always less than unity. This means that the excitation energy transferred to CQDs is partially lost in nonradiative processes.[150] Consequently, a question rises as to whether all CQDs in a given ensemble are characterized by the same quantum yield. The situation was clarified, namely, it was shown that some single CQDs in an ensemble are characterized by quantum yields of luminescence of nearly 100%.[163, 164]

Thus, blinking is an efficient nonradiative process leading to significant luminescence degradation for some CQDs in a large ensemble of nanoparticles. Elimination or partial suppression of blinking would allow one to additionally increase the quantum yield of luminescence and to stabilize the luminescence properties of CQDs. Therefore, research of specific features of luminescence blinking is carried out in line with active search for methods for suppression of this (generally, negative) effect.

One of the key investigation lines is to encapsulate CQD cores into additional wide-band gap semiconductor shells. This approach is aimed to cut the charge carrier wave function beyond the CQD core. A peculiar feature is that suppression of luminescence blinking requires the formation of rather thick shells, a perfect match between the lattice constants of the core and shell materials and exact thickness control to avoid defect formation at the interface between two semiconductors. Giant CQDs with thick shell were prepared.[165] The shell fabricated in that study was as thick as 19 semiconductor monolayers. In the ensemble of such CQDs, the fraction of blinking particles is $\sim$20% *vs.* 70% in conventional CQDs. Besides, the giant CQDs are insensitive to the type of the surface organic ligands and to variations of the ligand concentrations and are more chemically stable than the CQD cores and conventional core@shell CQDs. Almost no luminescence degradation of the giant CQDs was observed upon multiple washing, deposition and dispersion, as well as replacement of ligands and hydrophilization. However, the quantum yield of luminescence in these systems requires optimization. Namely, it is 40% for the thick shell CQDs and 80% – 90% for thinner shell CQDs. Luminescence degradation was explained by the occurrence of nonradiative processes involving defect states (*e.g.*, dislocations) formed within the thick, structurally imperfect shell.

Taking InP@CdS quantum dots as examples, it was shown that an increase in the thickness of the CdS shell from 1 to 11 monolayers leads to suppression of blinking and Auger recombination and improves the photostability of both single CQDs and their ensembles.[166] Suppression of luminescence blinking with increasing shell thickness was also observed in another study.[167] Contrary to this, the preparation and properties of high-quality CdSe@CdS quantum dots with relatively thin CdS shell (2.4 nm, a total of seven monolayers) and strongly suppressed blinking (fraction of CQDs in the 'on' state was 0.94) were reported.[35] It was suggested that the degree of structural imperfection of the shell has strong effect on luminescence blinking.

Taking CdSe@$Cd_xZn_{1-x}S$ quantum dots with alloyed-type shell as examples, it was shown that the Zn concentration, which was varied in the radial direction, significantly influences the 'on'/'off' period ratio.[168] The highest degree of blinking suppression was achieved on CdSe@CdS/ZnS quantum dots with complex shell composition, which are characterized by the longest 'on' states.[169]

Among other factors that favour suppression of luminescence blinking, an important role is played by the ligand environment. In particular, a study[170] of water-soluble CdTeS quantum dots revealed high efficiency of thiol ligands. Luminescence blinking suppression was related to removal of surface traps owing to efficient coordination of thiol ligands to vacant cadmium atoms and formation of the CdS layer. The CQDs with suppressed blinking had high quantum yields of luminescence and were stable and water-soluble. However, thiols can also enhance blinking in CQDs.[169] This was also observed in Mn-doped ZnSe quantum dots.

It should be noted that luminescence blinking in CQDs depends on various factors including the synthesis conditions and UV irradiation,[171] nearest neghbours[172] and the pH of the medium.[173] It can be suppressed near the surface of a silver film[174] or ITO,[175] near silver nanoparticles[176] or TiO_2 nanoparticles.[177] The fact that the effect depends on a wealth of different-type parameters is not surprising because all of them influence the structure of surface traps in CQDs, which undoubtedly play an important role in manifestation of the blinking effect.

III.2. Multiple exciton generation in colloidal quantum dots

Yet another unique property of CQDs is an amazing effect called multiple exciton generation (MEG), which manifests itself as production of more than one exciton upon absorption of a single photon whose energy much exceeds the band gap. The effect was for the first time observed in PbSe quantum dots[178] and more recently in the PbS, PbTe,[179] PbS_xSe_{1-x},[180] CdSe,[181] CdTe,[182] InAs,[183] InP[184] and Si quantum dots.[185] The average number of excitons generated in CQDs upon absorption of a photon is first of all determined by the difference between the photon energy and the band gap. For instance, a total of seven excitons were generated in PbSe quantum dots upon absorption of a photon with an energy of $7.8\,E_g$.[186] This corresponds to only 10% conversion of the photon energy to heat. The high yield of charge carriers is of great importance for enhancement of light-to-power conversion in photovoltaic devices.

The mechanism of MEG was explained in 2001,[187] three years before the experimental observation of the phenomenon. In brief, a unique feature of CQDs is that the quantum size effect leads to creation of discrete energy levels in the conduction and valence bands instead of a continuum of energy states. The separation between these energy levels much exceeds the characteristic phonon energies. Therefore, 'cooling' of 'hot' charge carriers in CQDs should occur through simultaneous energy transfer to multiple phonons. Since the probability of this process is low, it was assumed that cooling of hot charge carriers in CQDs is essentially slowed. This leads to efficient competition between cooling of hot charge carriers and ionization through collisions, where a hot exciton created upon absorption of a high-energy photon transfers the excess

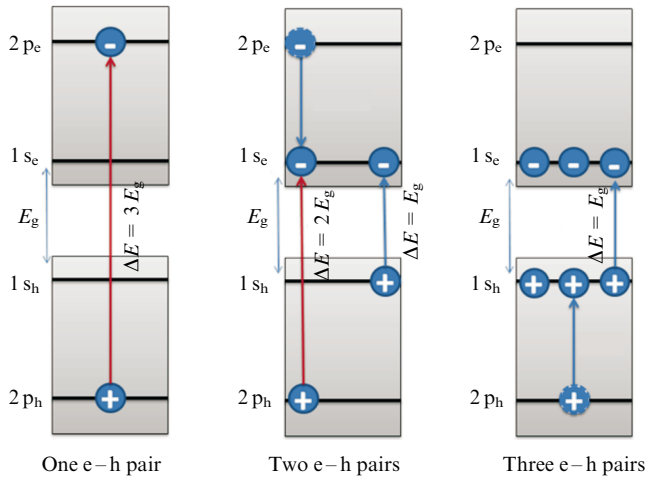


Figure 5. Multiple exciton generation upon absorption of a photon with $E > 3E_g$.

energy to one or more valence electrons that can thus move through the band gap (Fig. 5).

The effect was termed a 'phonon bottleneck'. However, numerous experimental studies showed that this mechanism is not always appropriate for correct description of the observed phenomena. For instance, it was found that the relaxation rate does not decrease with decreasing CQD size, although the separation between the energy levels increases.[188] In this connection, other MEG mechanisms were proposed.[189] In particular, it was assumed that a biexciton is generated directly through a virtual mono- or biexcitonic state. This mechanism was initially proposed [190] as a companion to the impact ionization mechanism. Yet another MEG model assumes an initial photo-excitation of a superposition of quantum states corresponding to all allowed states including multiple-excitonic ones.[191]

The existence of a number of models for the description of the MEG mechanism is indicative of its complexity. It cannot be ruled out that different models can explain the effect in CQDs of different composition and different state of the surface in different manner.

Up to now information on MEG was mainly obtained using pulsed induced absorption spectroscopy, which allows one to determine the amount of generated excitons. A few attempts to detect the MEG effect in realistic photovoltaic cells confirmed improvement of certain properties at photon energies above the band gap; however, the effect was weak for various reasons. In particular, a study [192] using a Grätzel cell revealed an increase in electron current, but the energy conversion efficiency was very low owing to weak light absorption by the CQD monolayer. Also, an external quantum efficiency of 114% was achieved [193] for photons with energies above $3E_g$ at a total light conversion efficiency of 4.5% under AM1.5 simulated sunlight. It was concluded that the operating properties of the cell can be improved under optimized conditions.

Thus, practical use of the MEG efffect requires that corresponding MEG charges be efficiently separated prior to their recombination. This complicated problem can be solved using, *e.g.*, charge transfer to an electron or hole acceptor attached to the CQD surface. However, treatment of the CQD surface can lead to suppression of MEG and should be done with great care.[194] Probably, the one and only study [195] carried out using PbS/Methylene Blue quantum dots as a model system revealed that MEG-assisted efficiency of exciton dissociation can be as high as ~112%.

IV. Prospects for practical applications of colloidal quantum dots

Unique properties of CQDs make them very attractive for various practical applications including photonics, optoelectronics and biomedicine.

IV.1. Colloidal quantum dot solar cells

Application of CQDs in photovoltaic systems is one of the most important and promising avenues of research. This is confirmed by numerous publications including reviews (see, *e.g.*, Refs 196–203) on the state-of-the-art and features of various types of CQD solar cells. There has been very rapid progress in the field. Indeed, the record high conversion efficiency reported in a review [203] published in 2013 was 6%.[204] One year later, a certified conversion efficiency of 8.55% was achieved for PbS quantum dots, the best samples being characterized by efficiencies up to 9.2%.[205] The authors of a review [206] devoted to recent advances in photovoltaic systems left Ref. 205 unmentioned but reported a record high solar cell efficiency of 9.2%, which was independently achieved using the same system (PbS quantum dots).[207]

IV.2. Colloidal quantum dot light-emitting diodes

Colloidal quantum dots are successfully used in the design of light-emitting diodes where nanoparticles act as both active (light-emitting) [208–211] and passive (converters of short-wavelength to longer-wavelength radiation) elements with unique colour-tuning properties.[212]

Light-emitting diodes prepared by the liquid-phase method using CdSe@ZnS quantum dots had a luminance of 28.76 cd m^{-2} and a current efficiency of 4.9 cd A^{-1}, both being twice as high as those of the reference structure.[213] The luminance can be additionally enhanced by introducing gold nanoparticles into the electron transport layer.[214] The emission efficiency of these light-emitting diodes is increased due to resonant exciton–plasmon interaction between CQDs and gold nanoparticles. Besides, quantum dot white light-emitting systems [215, 216] are of considerable interest for general lighting.[217]

IV.3. Biomedical applications of colloidal quantum dots

Unique luminescent properties of CQDs make them an ideal material for various biomedical applications including multispectral visualization of tissues and organs,[218, 219] detection of necrotizing damage regions or malignant cells,[220] and construction of trajectories of various cell targets.[221] A 'smart' CQD *via* aptamer conjugate with a fluorescent drug molecule was prepared and tested.[222] Initially, the system does not fluoresce due to nonradiative Förster energy transfer. The aptamer is needed to detect particular malignant cells and to deliver CQDs to a specified site. Having released the drug molecule, CQDs and the drug molecule luminesce because no Förster energy transfer occurs in the system. Fluorescence indicates that the drug was delivered to the target and released. This example demonstrates a modern trend towards significant complication of biomed-

ical probes in order to combine diagnostics and therapy. This investigation line was called 'theranostics'.[223]

Intensive attempts to use CQDs for biomedical applications, especially *in vivo*, require a detailed analysis of toxicity of the nanoparticles.[224] A partial solution to the problem is provided by encapsulation of 'cadmium' CQDs into safe shells. However, cadmium ions gradually penetrate the shell, so the 'cadmium' CQDs cannot be treated safe. Yet another method is to use cadmium-free CQDs.[219] A promising semiconductor to replace cadmium as CQD material is InP (see Section II.4).[44] The synthesis, physicochemical and spectral properties of InP nanoparticles were analyzed in a review.[67] An analysis of published data gave convincing proofs that InP@ZnS quantum dots provide an alternative to the CdSe@ZnS quantum dots in biological applications because the former demonstrate much lower toxicity in cell culture tests and laboratory animals.[36] A number of reviews on the state of the art in biomedical applications of CQDs are available.[68, 225, 226]

IV.4. Colloidal quantum dot lasers

Semiconductor quantum dot lasers have been designed since the emergence of molecular beam epitaxy. Quantum dots for these lasers are epitaxially grown on single-crystalline substrates under thorough control of exact match between the lattice constants of the substrate and quantum dots.

Colloidal quantum dots have started to be used as active laser media quite recently. They are also promising as elements of lasing systems.[227, 228] An undoubtful advantage of CQDs is the possibility of being deposited on any types of substrates. A laser based on a glassy capillary dipped in a suspension of PdS quantum dots in hexane was constructed.[229] Drying the capillary was followed by the formation of a thin film acting as a waveguide of high optical quality. Quantum dots were coated with short-chain ligands, so nanoparticles in the layer were arranged close to one another to provide energy transfer from smaller CQDs to larger ones. The laser operated at 1.55 μm and the laser emission wavelength was temperature-independent between 80 and 250 K.

Colloidal quantum dots are successfully used in the design of tunable semiconductor lasers. A laser based on CQDs on thin glassy substrate[230] was characterized by an average threshold fluence of 450 mJ cm^{-2} at $\lambda = 607$ nm. The laser emission wavelength could be tuned from 600 to 618 nm by mechanically bending the glassy substrate. Red, green and blue emission from a CdSe@ZnCdS quantum dot laser was demonstrated.[231] The spontaneous emission threshold was reached at a very low optical pump energy density of 90 mJ cm^{-2}.

A tunable single-mode, single-exciton laser on CdSe@CdS nanorods coated on silicon microbeads was designed.[232] A nanosecond laser based on poly(methyl methacrylate) films containing CdSe@ZnS quantum dots is characterized by a very low threshold fluence (0.5 mJ cm^{-2}), a narrow band (0.3 nm) and the possibility to tune the laser emisison wavelength from 605 to 616 nm.[233]

Blinking in CQDs used for lasing action is an undesired effect. Its mechanism is immediately related to Auger recombination (see Section III.1). Therefore, suppression of Auger recombination in CQDs is a topical task. A possible method to solve it is to use CQDs with a specific structure[234, 235] where blinking is fully suppressed.

IV.5. Sensors based on colloidal quantum dots

Colloidal quantum dots are very promising for applications in sensorics (environmental monitoring, clinical analyses, food quality control[236 – 238]). To this end, nanoparticles of different composition are used.[236] An NO_2 gas sensor on PbS quantum dots operating at room temperature is highly sensitive, has a short response time and is completely recovered upon removal of analyte.[239] An H_2S gas sensor on PbS quantum dots is characterized by high sensitiviy and selectivity and short response time.[240] A sensor based on PbS quantum dots with photoelectrochemical detection of DNA was reported.[241] Under optimum conditions, the biosensor detects analytes in a dynamic concentration range from 0.2 pmol $litre^{-1}$ to 1.0 nmol $litre^{-1}$, the limit of detection being equal to 0.08 pmol $litre^{-1}$.

Harmful bacteria are the most common cause of food poisoning and various waterborne diseases. A biosensor based on Mn^{2+}-doped ZnS quantum dots stabilized with chitosan was designed.[242] Quantum dots are attached to pathogenic bacteria and the photoluminescence spectrum of CQDs experiences a bathochromic shift, which is used to confirm the attachment of bacteria. Hence CQDs act as biosensor detecting bacteria present in water, food or in contaminated samples. The process takes a few hours *vs.* a few weeks for analyses by conventional biochemical methods.

Most often, sensors are based on 'cadmium' or InP CQDs. However, the design of oxide-based sensors is also promising.[243] In particular, oxide-based sensors for detection of acetone,[244] ethanol,[245] formaldehyde vapours[246] and chlorine dissolved in water[247] are available. A gas sensor based on nanocrystalline ZnO sensitized with CdSe quantum dots is suitable for detecting NO_2 under green light illumination at room temperature without additional heating.[248]

V. Conclusion

Tens of thousands of recent publications on colloidal quantum dots are available at the moment. A single review cannot cover all aspects of the problem. Therefore, we restricted ourselves to a key avenue of research in this field, *viz.*, methods for the synthesis and post-synthetic treatment of CQDs aimed at achieving record high quantum yields of luminescence. The emphasis was placed on the so-called cadmium-free CQDs. To provide a way for the reader to gain a deeper insight into other aspects of basic research on CQDs and specific applications of these systems, mention may be made of some recent reviews. These include a comprehensive review[249] on the formation and properties of core@shell CQDs as well as studies on photo-activated luminescence,[250] MEG[198, 251] and blinking mechanism.[149, 252, 253] Applied studies of CQDs are also well documented, especially, utilization of these systems in photovoltaic devices,[196, 199, 202, 203, 206, 254] biomedicine,[255 – 258] chemosensors and biosensors.[259 – 265] Other reviewed aspects include applications in photonics, in particular, light-emitting diodes,[199] photodetectors[202] and optoelectronic devices.[199] Mention should also be made of recent studies[31, 71, 266 – 272] carried out by researchers from the Russian Federation, who work hard in the field. In this review we tried to outline prospects for and potential of practical applications of CQDs rather than to give a comprehensive picture of the state of the art in the field.

Summing up, our analysis of the modern literature devoted to CQDs revealed a great potential of these systems. Further improvement of methods for preparation and post-synthetic treatment of CQDs aimed at increasing the quantum yield of luminescence, stability and narrowing the size distribution functions of nanoparticles will improve the properties of the systems and materials based on CQDs and extend the fields of their practical applications.

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