



Recent advances in quantum dot physics / Nouveaux développements dans la physique des boîtes  
quantiques  
**Colloidal quantum dots**

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**Abstract**

The applications and physical properties of colloidal quantum dots are briefly reviewed and contrasted with those of Stransky–Krastanov grown quantum dots. **To cite this article:** *P. Guyot-Sionnest, C. R. Physique 9 (2008).*

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**Résumé**

**Boîtes quantiques colloïdales.** Cet article est une revue brève des applications et propriétés des boîtes quantiques colloïdales, contrastant avec celles des boîtes quantiques obtenues par croissance Stransky–Krastanov. **Pour citer cet article :** *P. Guyot-Sionnest, C. R. Physique 9 (2008).*

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**1. Introduction**

Nowadays, one can purchase liquid solutions of Quantum Dots. These colorful fluorescent solutions make for good visual effect, and they show the workings of quantum mechanics in a very obvious way. Taking the same material but merely changing the size of the nanocrystals of this material gives a rainbow of colors progressing smoothly with size. Students can see reproductions of atomically resolved pictures of the nanoscale quantum dots taken by Transmission Electron Microscopy, and they can correlate the color and size, realizing that the smaller particles emit higher energy photons, in the same direction as the uncertainty principle predicts.

The simple demonstration of quantum mechanics using colloidal Quantum Dots is the result of advances in the understanding of material properties and of synthetic progresses in colloidal chemistry, that have been sustained by established and developing technological interest in the materials.

The topic of colloidal quantum dots has several excellent and detailed reviews to which the reader is referred [1,2]. This short review within this special issue aims to contrast the development and successes of the colloidal dots with the alternative surface grown quantum dots that will be referred to as Stransky–Krastanov grown quantum dots or SK-dots.

For both systems, the key concept is Quantum Confinement in semiconductors, an idea that surfaced in 1970 [3]. The quantum confinement concept was first investigated when the development of Molecular Beam Epitaxy (MBE)

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in the 1970s allowed one to make thin layers of various materials with atomic precision thickness. In these systems, quantum confinement is acting along the thickness of the layer, leading to Quantum Wells. The quantum confinement has dramatic consequences. The most obvious is that the material is now transparent at a photon energy where it strongly absorbs in the bulk. The new “band edge” is blue-shifted by the amount of the confinement energies, and the shift can be designed by choosing the layer thickness. Another feature of the spatial confinement is to increase the probability of recombination of an electron in the conduction band and a hole in the valence band. This makes Quantum Wells excellent electrically driven lasers with chosen wavelength. Today, the Quantum Wells are essential components of optical communications and optical data storage systems.

The Quantum Dots are the extension of the quantum confinement ideas to three dimensions. It is in the early 1980s that papers in the Russian literature, by Ekimov and Efros, gave the first experimental and theoretical description of 3D quantum confinement with semiconductor nanocrystals [4,5]. Shortly after, the discrete density of states of quantum dots were proposed to present advantages for lasers, compared to quantum wells [6]. The chemistry community then started exploring colloidal semiconductor nanocrystals [7,8], in fact well before the advent of the SK-dots [9,10]. In contrast to the rather high-tech interest in the SK-dots, two motivations from the chemical community to pursue the development of nanocrystals were large scale solar energy conversion and photocatalysis, as this was soon after the first oil crisis. These are again popular motivations today. Besides using quantum confinement to optimally tune the absorption wavelength to some redox potential, it was felt that the proximity of the carriers with the surface would improve collection efficiency or surface reaction yields [11].

Throughout the 1980s, colloidal synthesis provided some limited control over size and the materials had still rather poor optical definition and low fluorescence efficiency [12]. The most monodispersed colloidal quantum dots with the widest size range were those made in glasses by controlled precipitation of Cd, Zn S and Se impurities, and otherwise used as color filters [13]. While monodispersed colloidal growth was well known for amorphous sub- $\mu\text{m}$  sulfur or silica particles, as in the earlier works of La Mer [14] or Stauber [15], the growth of crystalline monodispersed nm-sized colloids in aqueous solutions was more difficult probably because the range of possible surfactants that can be used to temporally separate nucleation and growth was limited. Furthermore, the surface chemistry in aqueous environment is complicated because of competing acid-base equilibrium associated with the solvent, redox reactions and hydroxyl formations.

Nearly three decades old, the field of colloidal quantum dots has matured so much that it can reach into physics issues or applications that were once considered the hallmark of SK-dots while still preserving its unique potential for material and biological applications.

## 2. Fabrication

In 1993, a key advance was the synthesis of semiconductor nanocrystals colloids in high temperature organic solvents. Using the rapid decomposition of pyrophoric metal-organic complexes and high boiling point, long chain ligands to slow down the growth [16], CdSe nanoparticles were produced that had much improved crystallinity, high monodispersivity and with a very wide range of quantum confinement. These new materials led to many advances in the characterization of the electronic properties of the colloidal dots. In particular, the strongly structured optical spectra as shown in Fig. 1 are now understood for the most part and the peaks are assigned to specific transitions between electron and hole states. Using this route, it was later demonstrated that other II-VI and III-VI materials could be synthesized as well. Size control is usually ascribed to a time-wise well separated homogeneous nucleation from slow and independent growth of the particles due to the excess of reagents. In practice the parameter space is vast, including concentrations, reagents, stoichiometry, ligands, solvent temperature and time. The development of a successful protocol for any material involves a low-cost and low-tech approach, rather Edisonian, rooted in chemical synthesis.

In these colloidal materials, the surface is always unknown due to the lack of appropriate characterization tools. One has only a rough idea of how the ligands bind to the surface, typically guided by previous inorganic chemistry studies of small molecule structures. As a result, the surface can often be blamed for many properties. This is the case for the fluorescence where it is assumed that unpassivated surface atoms lead to trapping and non-radiative recombination. The CdSe particles in particular had low quantum yield. In 1995, this was partially solved for CdSe by burying the surface under a thin ZnS shell which is a wider band gap material providing electron and hole barriers. This simple shelling procedure led to strong and sturdy photoluminescence [17]. Strongly fluorescent materials have generated

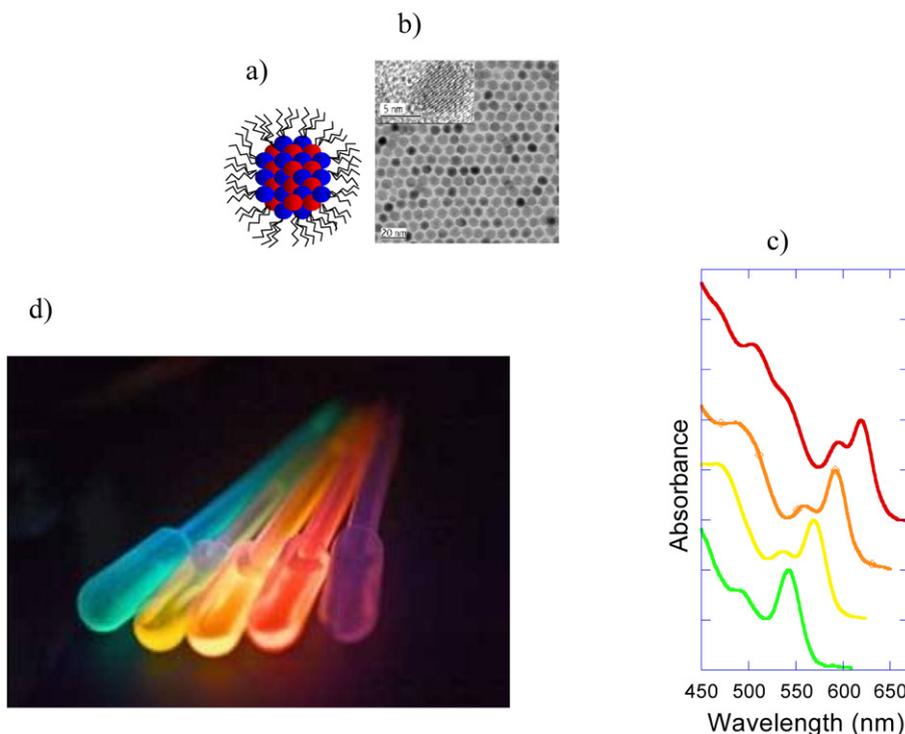


Fig. 1. (a) Cartoon showing the ligands surrounding a colloidal nanocrystal. (b) Organized array of PbSe nanocrystals of  $\sim 6$  nm diameter and high resolution image a single nanocrystal in the inset. (c) Absorption spectra of four sizes of CdSe colloidal quantum dots, from 3.5 nm to 5 nm diameter. (d) Fluorescence of CdSe/ZnS core/shell colloidal solutions

much further interest and the core/shell approach has been extended to many more heterostructures combinations, with epitaxial growth and monolayer precision achieved with some material combinations.

In 2000, the introduction of synthetic protocols using air-stable ionic precursors [18] instead of the pyrophoric organometallics reduced drastically the psychological barrier and some of the potential hazards of the synthesis of II-VI nanoparticles. This was achieved without losing any of the quality of the earlier synthetic results. This approach, since then demonstrated for many systems, covering II-VI and IV-VI, but also beyond semiconductors, has led to an explosion in the number of groups synthesizing and investigating semiconductor nanocrystals by the colloidal approach.

Nowadays, highly luminescent and photostable quantum dot colloids, covering the near UV to near IR, typically based on combinations of Cd and Zn as well as Se and S, can be made in laboratories without a glove-box and they are available from a growing number of companies around the world. The field has so far focused mostly on Cadmium, Zinc and Lead chalcogenides and these are the materials with the best optical properties to date, as compared to InP or InAs. One reason why the III-Vs are lagging is their more covalent nature as well as the sensitivity to oxidation of the reagents and products. The more dangerous sources of reactive arsenic or phosphorous have also been limiting the number of groups willing to invest in these materials. Nevertheless, if there is a strong motivation to develop III-V materials, it is very likely that successful protocols by colloidal synthesis will be developed.

Besides the high monodispersivity provided by colloidal synthesis, that typically exceeds that of SK-dots, colloidal chemistry offer exciting potential for shape and composition control which is inconceivable in SK-dots. The new ease of synthesis of nanoscale colloids coupled with imaging with Transmission Electron Microscopy (TEM) is providing rapid discoveries, most of which have been of materials with novel shapes, and potentially interesting functions. The former has been demonstrated with rod [19], disk or multipodal [20] structures. The latter includes core/shells with controlled shell growth at the monolayer level [21], of materials with up to 12% lattice mismatch, such as for CdSe and ZnS, with smaller thicknesses for larger mismatches. Recently it has been shown possible to incorporate dopants and to vary the position of impurity with monolayer precision in the materials, as for CdS/ZnS:Mn [22]. This is possible because, at the growth conditions used, the diffusion of atoms, once incorporated into a lattice site, is less

than one atomic distance over the time of the synthesis, while at room temperature, diffusion over atomic distances is effectively eliminated.

We are thus in the middle of a decade of tremendous progress in the quality of the synthesis of nanostructures by colloidal methods. The last five years alone have produced about 5 times more scientific publications on colloidal quantum dots than the previous twenty years combined. To date, shape control and impurity doping are still restricted to a few materials, but there seems to be no end to the level of complexity and organization that colloidal chemistry will achieve.

### 3. Applications

Besides the low technological entry barrier compared to SK-dots, the potential of colloidal materials for improving existing technologies or developing novel applications is highly motivating. Some of the potential application niches are listed below.

#### 3.1. Biological fluorescent tags

One commercial application has been the use of colloidal dots as biological tags [23], a strategy first demonstrated in 1998 [24,25]. It turns out that core/shell colloidal dots can be made to be more photostable than existing molecular dyes while they exhibit narrower luminescence and provide a broader and continuous absorption spectrum. Colloidal dots offer also opportunities in the near-infrared, where the blood is most transparent but where organic molecules are weakly fluorescent. These nice properties are the result of the weaker extension of the photoexcited electrons and holes into the liquid, hence less photochemistry, as well as generically weaker electron–phonon coupling in the semiconductors compared to organic materials. For all these excellent reasons, there is a considerable activity to modify the surface of the colloidal dots, rendering them soluble in water and specific to particular biological targets for imaging. Colloidal dots are now commercially offered as biological tags, along with modified dye molecules, and fluorescent proteins.

#### 3.2. Light emitting display

Another proposed application has been to use colloidal dots as emitters in Light Emitting Diodes (LED) [26]. After many years, recent progress indicates that it is actually possible to obtain efficiencies of commercial interest [27]. To date, these colloidal dot LEDs must however use hole and electron transport organic layers which are similar to those for organic LEDs. This is because the mechanism for light emission is most likely an energy transfer from an electron–hole pair recombining in an organic fluorophore to the quantum dots. The quantum dot thus acts as a phosphor rather than being directly involved in the carrier transport and capture. As a result, the quantum dot active layer must be very thin, at most a couple monolayers, and situated as close as possible to the recombination layer of the organic LED [27]. An advantage is that the devices bypass the need for electron and hole injections in the quantum dots. This is fortunate as electrical hole injection is a priori difficult, and so far unverified in the visible light emitting CdSe based quantum dots. On the other hand, achieving direct electron and hole injection, as in the inorganic LEDs, without having to rely on the organic LED structure, will be needed to achieve higher currents and luminosity. So far, direct electron and hole injection followed by radiative recombination has only been successful in electrochemical cells and has been used to generate electrochemiluminescence [28]. With lower current requirements, colloidal dots are electrochromic material [29], where absorption or fluorescence can be reversibly switched off with addition of a small number of electrons in the dots, which is an effect rather specific of the smaller sizes of the colloidal dots. This may lead to applications in displays as well.

#### 3.3. Photovoltaics

With high energy cost and global warming worries, there is significant funding in photovoltaics, and the possible application of colloidal dots in solar energy conversion, one of the early motivations for these materials, is again actively researched by many groups [30]. It is clear that a semiconductor colloid is a valid starting point to print thin-film solar cells. As discussed later, it is a possibility that the “Quantum Dot” nature of the colloidal material will be of relevance [31]. However, the solar cell application requires overcoming many traditional challenges, such

as mobility, trapping and charge separation, in order to take advantage of the quantum dot nature rather than simply having the properties of a disordered semiconductor structure. To date, there is no evidence that quantum dot films lead to improvements over their bulk semiconductors for photovoltaic applications, but the topic is actively pursued.

### 3.4. Lasers

Quantum dots have long been proposed to be the best semiconductor form for highly efficient laser [6], and electrically driven SK-dot lasers have been made for more than a decade. However, the SK-dot packing density achieved so far in these devices is too low to provide a net advantage over existing Quantum Wells. With dried films of close-packed colloidal dots, the packing density could increase by two orders of magnitude over that achievable by SK-dots. This could promise improved lasers. However, although photo-pumped lasing has been demonstrated with colloidal dots [32], a big challenge is to achieve high injection currents. This rests on achieving high mobility in colloidal dot films, which is in itself an interesting but difficult topic with ongoing progress.

### 3.5. Infrared phosphors

Colloidal dots have a particular niche as optical materials in the mid-infrared. Indeed, in the visible and UV spectral range, organic dye molecules can have near 100% photoluminescence efficiency and the quantum dots struggle to compete. However in the near-IR the quantum dots win easily. This is because organic dye molecules have high frequency vibrations that couple strongly with electronic transitions leading to fast intramolecular relaxation. Thus the quantum yield of dye molecules falls below 1% around 1  $\mu\text{m}$  and organic dyes provide no detectable photoluminescence beyond 2  $\mu\text{m}$ . The inorganic colloidal dots made with heavy atoms have very low vibrational frequencies and they can be excellent emitters in the near infrared with 80% efficiency at 1.5 microns, or about  $1000\times$  better than the best organic dye [33]. Colloidal dots could be strong emitters in the mid-infrared as well with potential applications for atmospheric optical communications, and the main limitations in that spectral range will be the ligands molecular vibrations and their physical proximity [34].

## 4. Physics of colloidal dots

From a physics perspective, colloidal dots have evolved on parallel paths with the SK-dots but they differ in several interesting ways.

### 4.1. Strong confinement

The confinement potential depth provided by the organic surfactants or matrix can be much larger than anything yet achieved with SK-dots. Furthermore, because they are not limited by strain requirements, colloidal dots can be made much smaller than the SK-dots with diameters of 2 nm being common. Colloidal dots can thus be well into the limit of strong confinement with confinement energies, up to 1 eV or more and with separation between electronic states an order of magnitude larger than phonon energy. Thus the fluorescence of CdSe colloidal solutions covers the whole visible spectrum [1], while PbSe nanocrystals cover the near and mid-IR from 1 micron to 3 microns [35]. The absorption spectra of colloidal dots unobstructed by a barrier material, are very rich. They have allowed the identification of many transitions, and they largely deserve to be called “artificial atoms”. Early on, k.p. calculations using the 8- or  $2 + 6$ -band Luttinger model applied to a spherical box have led to a good agreement [13,36,35]. That the models based on a parametrized description of the center of the Brillouin zone lead to such satisfying description up to excess energies of 1 eV is rather surprising. At energies where significant anisotropy or other band extrema contribute, these k.p. calculations should fail and one is left with atomistic models [37].

### 4.2. Large excitonic exchange interaction

One interesting consequence of the small colloidal dot size is the stronger exchange interaction between electron and hole [38,39]. Of course singlet-triplet splittings are very large in molecules, typically on 1 eV scale, but they are very small in SK-dots. Colloidal dots are in the intermediate regime. For small CdSe colloidal dots, exchange

interaction leads to singlet-triplet splitting exceeding 10 meV which shows up as a Stokes shift between band edge absorption and luminescence [40,41]. The lower energy triplet also leads to recombination at low-temperature with very long lifetimes. For CdSe colloidal dots, low temperature PL lifetimes can exceed 1 microsecond [40], again a feature that is quite different from the SK-dots.

#### 4.3. Slow radiative lifetimes

It is to be noted that, even at room temperature, the fluorescence radiative lifetimes in colloidal dots remain rather slow, ranging from  $\sim 20$  ns for CdSe [42] to  $\sim 1$   $\mu$ s for PbSe [33]. This is much slower than for SK-dots, where radiative lifetimes are typically sub-ns. Part of the differences could arise from differing electron and hole overlaps, however, one clear contribution to the slow room temperature lifetimes is the thermal occupation of triplet (dark) and singlet (bright) states. However, in some systems, such as PbSe, the weaker exchange interaction is not the main contributor to the slow lifetime [43]. Instead, slow radiative recombination is also partly arising from the typically large dielectric mismatch with the matrix which screens out the external electromagnetic field and this is a generic effect for colloidal dots. This classical effect already leads from 4 (CdSe) to 20 (PbSe) fold increase in the expected lifetimes [33].

#### 4.4. Fast multicarrier relaxation

The smaller size of colloidal dots can also lead to much stronger carrier–carrier interactions as compared to the larger SK-dots. For example, colloidal dots can be charged by electron transfer and have their fluorescence quenched. Similarly, multiple excitons can be optically pumped into a dot, leading to fast non-radiative Auger-like relaxation [44] on time scale of 100 ps for a biexciton, effectively quenching the photoluminescence from biexcitons [45]. That such fast biexciton non-radiative lifetime is not seen in SK-dots is primarily related to the smaller volume of the colloidal dots. An Auger-like model would predict size scaling as  $R^6$  while experiments show a lower scaling more as  $R^3$  [46]. This lower scaling has been justified by the reduced density of state in smaller dots [47]. The strong size scaling already explains why multicarrier recombination is of lesser importance in SK-dots especially given that radiative relaxation is also much faster in these systems. For the small colloidal dots the much faster multicarrier recombination time scale compared to the radiative recombination time has been identified as a major difficulty to achieve efficient lasing. One solution is to increase the exciton–biexciton energy spacing, thus reverting to a situation similar to dye molecules. This has led to efforts to build type II heterostructures which can separate electrons and holes such that the biexciton repulsion becomes larger [48].

The reverse process of multicarrier recombination is multicarrier or multiexciton generation. It is hoped that the reduced requirement for momentum conservation along with the expected slow intraband relaxation in quantum dots [49], will lead to efficient carrier multiplication in small quantum dots [31]. Notwithstanding the expectation of slow cooling in the dots, excitonic relaxation has repeatedly been shown to be extremely fast [50] likely because the excitonic density of states is still not sparse enough [51]. Yet, there have been reports of extremely efficient multicarrier generation from transient absorption measurements [52], with up to 700% in PbSe [53], meaning that seven excitons are generated from one high energy exciton. Several groups have at least partially reproduced the observations. Others have attempted to monitor the effect with alternative techniques with varying results [54]. At the moment, the most non-committal statement that can be made in this review is that the magnitude of the observed carrier multiplication effect is uncertain, ranging down to no enhancement compared to the bulk, and that this state of uncertainty should be cleared up soon [55].

#### 4.5. Blinking

Size monodispersivity in colloidal dots can be excellent, down to 5% in several cases and superior to the best SK-dot systems. This nevertheless leads to emission linewidths still dominated by inhomogeneous broadening. Attempts to observe homogenous linewidths by fluorescence microscopy of single colloidal dots [56] started at about the same time as for SK-dots [57]. However, for colloidal dots, the time average linewidth remains broad because of significant spectral wandering [58,59]. Furthermore, the fluorescence intensity of a single dot blinks wildly between high and low emission states [60]. These effects, which are not seen in buried SK-dots, are typically attributed to

some role played by the surface. The strong Stark effects shown for the colloidal dots suggested the role of a localized but mobile surface charge [61] while the large fluorescence intensity fluctuations seen in blinking suggested the role of an interior charge leading to an Auger-like fast recombination [62]. The narrowest fluorescence linewidth measurements for a single colloidal dot have been recently obtained by an interferometry method [63] to circumvent the effect of PL wandering and blinking. The intrinsic linewidths compare well with hole-burning measurements on the absorption lines [64] and they do not differ much from the SK-dots, being limited by low temperature phonon dephasing.

The blinking shows a robust  $1/f$  statistics [65] that is still actively investigated. Blinking, first reported for the CdSe colloidal dots, is now seen in a wide variety of quantum systems, dots and molecules, coupled to a disordered environment, surface, glass, etc and there is not yet a consensus on the specific mechanisms [66].

#### 4.6. Conductivity in nanocrystal solids

Colloidal dots can be cast as films, with very high degree of order, leading to crystals of nanocrystals [1]. Such nice self-organization leads to hopes of engineering the band structure of the new solids made of the artificial atoms. The beautiful solids rely on the soft, of order  $kT$ , interactions mediated by the long surfactants and the drying solvent. However large disorder remains, even if not obviously visible in the TEM image or small angle X-ray scattering. Indeed the disorder associated with one trapped charge could lead to a 100 meV local potential fluctuation, which could be larger than the inhomogeneous energy bandwidth of the levels. Disorder in the tunneling properties can be very large as well, since a small ( $\sim 1 \text{ \AA}$ ) increase of an alkane chain length distance between nanocrystals would lead to an order of magnitude decrease in coupling strength. In spite of such odds, ohmic conductivity has been observed in films of monodispersed quantum dots [67]. This has been achieved by filling traps using electrochemistry or field effect [68], and by chemical processing to increase the coupling between the particles, for example by reducing the interparticle separation following a ligand exchange procedure [69]. However to date, there is no evidence for mini-bands in the solids. Most likely, the strength of the electronic coupling that has been achieved is still too weak to have band-like conductivity given the disorder still present. So far, the conductivity in colloidal dot solids is of a hopping nature, quenched at low temperatures [70] and thus similar to most organic conductors. Ensemble average mobilities in CdSe [71] and PbSe [72] colloidal dot films charged by electrochemistry have been observed in the range of  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with about one order of magnitude effect of the energy of the level in which the electron is placed in the dots. Mobilities measured in field-effect geometry are two orders of magnitude higher, of the order of  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for PbSe [68]. These materials' mobilities are competitive with the best organic materials, even though they are orders of magnitude worse than bulk crystalline semiconductors. The largest mobilities reported so far have been in laser spectroscopy measurement where local mobilities of  $\sim 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  were accessed by transient THz measurements [73]. Besides light emission or harvesting, one promising area of transport in quantum dot assemblies is in the development of improved thermoelectric materials [74]. Already, it has been shown that films of colloidal PbSe nanocrystals may provide enhanced thermopower over bulk PbSe [75].

In all transport measurements of colloidal dot films, one difficulty is the possibility of sintering. It is indeed possible that one could be measuring the response of a disordered semiconductor, which maybe interesting, but that has little to do with that of a true quantum dot solid. Especially if the transport data do not show effects clearly associated with the dots, it is important to have other characterization methods, such as the optical determination of the charging level. Electrochemistry on moderately thick films ( $\sim 100 \text{ nm}$ ) coupled with optical measurements allows for a uniform Fermi level while still allowing for an unambiguous optical characterization of the quantum dot levels being charged [67]. The drawback is the need to include a liquid and counterions in the voids between the quantum dots. In principle, an all-solid system would be best and well adapted to the field-effect transistor geometry. The drawback of the field-effect geometry [68] is that the Fermi level is modified only in the first monolayer of dots and uncontrolled elsewhere. Even for that first monolayer, charging is limited to typically less than one electron/dot, and simultaneous optical measurements are difficult. With much progress on the horizon, the current situation with transport studies in solid films of colloidal quantum dots is that such films can be made conductive, switched on and off by charging, and that, in some cases, they exhibit transport properties which are specific of quantum dots. Continuing such studies is essential to reach the level of mobilities that will be required for all applications requiring currents. Furthermore, although both n and p-type conductivity have been achieved by charging, whether by electrochemistry or FET, neither has yet been achieved by impurity doping and this remains an open area of research.

#### 4.7. Magnetically doped colloidal dots

At present, impurity doping in colloidal dots has been successfully achieved for paramagnetic transition metals. Manganese has long been used as a dopant in ZnS nanocrystalline films and nanoparticles, and observed by its characteristic orange phosphorescence. However, novel effects have been clearly observed first for the CdS:Mn system [76]. Although the result of an aqueous synthesis with rather polydispersed products, this system was the first to show the order of magnitude larger g-factors that can be obtained in a quantum dot due to the strong overlap between the confined electronic wavefunctions and the impurity spin wavefunction. The effect was then confirmed with the much more monodispersed organometallic synthesis of ZnSe:Mn [77]. Synthesizing highly monodispersed Mn doped colloidal dots remains a challenge. There has been some discussion as to why ZnS and ZnSe are so easily doped while CdS and CdSe are still a struggle. For ZnSe, it has been proposed that the doping proceeds by a surface insertion in Se dimer bonds which are present only on a specific reconstructed surface that exists for zinc-blend systems but not for wurtzite [78]. However doping in zinc-blende CdSe has not been particularly successful. Instead, the most successful CdSe:Mn synthesis has so far been achieved by a growth protocol that starts from small cluster precursors with a final wurtzite structure [79]. With this procedure, magnetically induced strongly circular polarized fluorescence has been detected with the colloidal CdSe:Mn [80]. Progress in the last few years in both the controlled charging of colloidal dots and the controlled doping of magnetic impurity will lead to novel studies investigating the coupling between electronic states and magnetic impurities, with the possibility of interesting magnetotransport effects [81].

#### 4.8. Surface

A key variable in the differences between the colloidal dots and the SK-dots is the proximity of the surface. This surface also marks a boundary between the chemistry and physics of the dots. The surface of the colloidal dots is a structurally uncharacterized region where dangling bonds are only partially passivated by floppy molecules and with likely but unknown reconstructions. This surface is dynamic, chemically accessible, and the surface atoms are more mobile or reactive which leads to reduced temperature and chemical stability. The poor knowledge of the surface has typically been a wedge between the communities of SK-dots and of colloidal dots. It is clear that many properties of the colloidal dots are influenced by the surface, such as the time average fluorescence quantum yields, blinking, carrier trapping and energy relaxation. While SK-dots can easily be buried under arbitrarily thick epitaxial layers, increasing the thickness and quality of epitaxial shells on colloidal dots is still an area in progress. With the ongoing improvement in the synthesis of better core/shell systems, the outer molecular surface becomes more remote and is also getting under better control. This will have significant consequences. For example, it has been shown that blinking was significantly reduced with increasing CdS shell thickness for CdSe/CdS [82]. While surface control is a much needed development for the colloidal dots, this varied and accessible surface is what allows for the control of shape, composition and assembly and the extremely versatile properties of the colloidal dots.

### 5. Conclusion

Since their discovery in the early 1980s, the quality of the semiconductor nanocrystal quantum dot has improved steadily, by improved control of the growth conditions and surface chemistry. The colloidal dots exhibit many physical phenomena shared with the SK-dots, with specific differences that have been highlighted in this brief review. Key physical differences are the generally smaller sizes and stronger confinement accessible with the colloidal dots which lead to stronger exchange interaction, and carrier–carrier interactions. The flexibility and lower production cost afforded by the solution chemistry is promising a wider range of applications. Already, fluorescent colloidal dot solutions are commercialized as specialty optical materials with applications as fluorescent markers in biology or as phosphors for organic light emitting diodes. They are one example of a general trend for rational design with Nanomaterials, where physical phenomena at the nm scale are used to establish design goals. The colloidal chemical synthesis provides the means to make such small objects and it is evolving towards the combination of colloidal materials with separately optimized properties and shapes, to assemble them as molecules, wires or crystals of nanocrystals with targeted physical, chemical, or biological properties.

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