

Recent advances in magnetic ion-doped semiconductor quantum dots

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Dilute magnetic semiconductor (DMS) quantum dots (QDs) have potential to be used as basic working components of spin-based electronic devices. Therefore it is important to study these materials from fundamental and technological viewpoints. Quantum confinement effects are known to enhance exchange interactions and induce properties that were previously not observed in bulk materials. In fact, properties are known to alter dramatically when dimensions are reduced to nanometre size regime. In this review we briefly discuss the recent advances in chemical (synthetic) and physical (properties) aspects of DMS QDs. We first discuss the various issues involved in the synthesis of DMS QDs followed by a discussion of the solutions obtained so far. We then discuss the interesting properties of DMS QDs with emphasis on their magnetic, magneto-optical and magneto-electrical properties arising from the cooperative effects of spin-exchange interactions.

Keywords: Dilute magnetic semiconductors, quantum dots, magnetic circular dichroism, spintronics.

Introduction

DMS materials, wherein non-magnetic semiconductors and insulators were found to be ferromagnetic upon doping with a small percentage of magnetic metal cations like Cr, Mn, Fe, have galvanized the field of magnetism since their discovery several decades ago due to their potential as spin polarized carrier sources and ease with which they can be integrated into a semiconducting device. Simultaneous manipulation of charge and spin^{1,2} of electrons can enhance the performance and functionality of semiconductor devices as compared to only charge-based electronics. DMS materials are potential candidates for these spin-based electronic devices³. This counter-intuitive, surprising yet significant phenomena, has given rise to several interesting properties suitable for various applications such as non-volatile memory, quantum computing and communication in the solid state, magneto-optical communication devices, high density magnetic

data recording^{4,5}, and energy storage catalysis^{6–9} and have remained in the forefront of research for years. Specifically, early studies proving cooperative effects via spin exchange interactions in Mn-doped GaAs^{10–13}, both theoretically and experimentally have demonstrated the extensive potential of this field. Transition metal-doped bulk oxides^{14,15} with probable ferromagnetic transition temperature above room temperature¹⁶ have further enhanced the interest in this field. However, though the prospect of high temperature ferromagnetism in these materials for use in spintronics has been envisaged in a variety of research papers^{17–20}, lack of stability and reproducibility have prevented the establishment of definitive conclusions in this field. Nevertheless, interest in DMS materials is sustained by a variety of other interesting properties arising out of a strong interaction of the metal ion with electronic structure of the host material via *sp-d* exchange interaction between band electrons and localized magnetic moments leading to properties like giant Zeeman splitting^{21,22}, Faraday rotation, magnetic polarons²³, carrier-induced magnetic ordering²⁴, electrical spin polarization, magnetically tunable lasing and so on.

With the advent of nanomaterials, study of magnetism in the scale of quantum confinement has become interesting due to a number of fundamentally exciting^{25,26} and technologically^{27,28} important properties. For example, though all open shell atoms are magnetic in their ground state as described by Hund's rule, electronic state delocalization in the solid state quenches their magnetization and only Fe, Co, Ni exhibit ferromagnetism in their solid form²⁹. However, upon decreasing their sizes to quantum-confined regime, magnetic properties in this confined state are discernible and can be modulated by engineering their size and morphology. Furthermore, Frenkel and Dorfman in 1930 predicted that any ferromagnetic material below a critical size limit would result in large magnetization due to formation of a single domain wherein the magnetic moments of free electrons would be aligned with respect to the magnetic field³⁰. This prediction resulted in an enormous interest to study magnetism at quantum confined level. It is well known that, with decrease in size of ferromagnetic material, the number of domains decreases, eventually leading to the formation of single domain magnetic nanocrystals with enhancement

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in coercivity^{31,32} when the diameter is below critical diameter (D_c). This diameter is given by

$$D_c \approx \frac{36\sqrt{AK}}{\mu_0 M_s^2},$$

where A is the exchange constant, K the measure of energy per unit volume required to flip magnetization direction (effective anisotropy constant), μ_0 the vacuum permeability and M_s is the saturation magnetization. However, when the size of a ferromagnetic nanoparticle is below critical diameter, the spins of unpaired electrons are aligned in one direction due to ferromagnetic coupling. Single domain nanocrystals further observe an increase in coercivity due to the absence of domain wall contribution²⁵. Finally, upon further decrease in size, the thermal energy ($k_B T$) outweighs anisotropic energy and coercivity goes down to zero.

The other parameters governed by size include, size enhanced spin canting effect³³, Neel relaxation time and magneto-crystalline anisotropy. Neel relaxation time describes the thermal fluctuation time scale of magnetization direction for nanoparticles and is given by

$$\tau_N = \tau_0 \exp \frac{KV}{k_B T},$$

where τ_0 is a constant. Materials with shorter relaxation time τ_N than the measurement time τ_m , typically about 100 s, exhibit superparamagnetic behaviour. On the other hand when relaxation time is longer than measurement time, the magnetization direction cannot be reversed within the duration of measurement and hence it does not come to zero. The temperature at which relaxation time is equal to measurement time is called the blocking temperature T_B and is given by

$$T_B = \frac{KV}{k_B \ln \frac{\tau_m}{\tau_0}},$$

while the superparamagnetic particles are known to be in blocked state. Magnetocrystalline anisotropy, also expressed as spin-orbit interaction of a material, is dependent on its crystal structure that in turn affects the coercivity of a material. Higher the anisotropy constant, higher is the coercivity. Shape-anisotropy also affects magnetic properties mainly in terms of its coercivity. Confinement in one direction leads to shape anisotropy and hence enhances coercivity. Magnetization as well as coercivity of nanoparticles can also be tuned by varying the composition of constituent materials.

Properties related to magnetism arising in nanoscale systems can be sub-divided into three categories: DMS

QDs, magnetism from non-magnetic clusters with sub-nanometer diameter and QD magnetic materials including metals, alloys and oxides of Fe, Co and Ni. Size-dependent and chemically induced nano-magnetism has been observed and reported in otherwise non-magnetic systems³⁴. For example, the strong binding of dodecanethiol with 1.4 nm Au clusters is shown to display ferromagnetism while weak binding of tetraoctylammonium ion shows diamagnetic behaviour³⁵. In addition, magnetic materials like metals, alloys and oxides of Fe, Co and Ni QDs also display size-specific magnetic behaviour. This has been extensively summarized in many comprehensive reviews^{26,36}. In this review, we give an overview of the recent advances in the field of nanoscale magnetism with emphasis on DMS QDs.

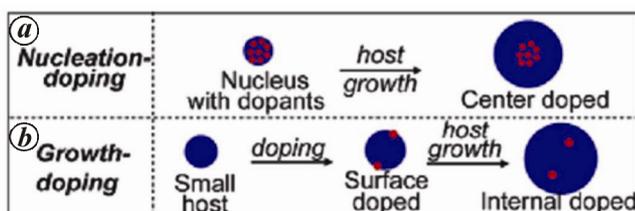
Dilute magnetic semiconductor quantum dots

With the advent of DMS QDs, wherein wave functions of the electrons and holes are confined within a limited volume leading to extended overlap of the dopant d electrons and host sp electrons, the possibility of manipulating their exchange coupling strength via quantum confinement has captured the interest of several researchers^{37,38}. Additionally, QDs lead to a decrease in the coordination number due to increased surface-to-volume ratio, and an increase in moment per atom is observed, as the extent of localization increases and valence bandwidth decreases²⁹. Further, it has been well-known in literature that quantum confinement can give rise to completely new and interesting properties that have not been observed in bulk materials. However, major bottleneck till date in the study of DMS QDs is the synthesis of uniformly doped QDs with controlled size, morphology and dopant concentration without formation of magnetic islands. So far, incorporation of a few atoms in a lattice of a few hundred atoms has proven to be energetically hostile and successful doping without the formation of clusters of dopant ions, either at the surface or in bulk of QDs, is challenging. In most of the early techniques used, while a few atoms were doped into the host lattice, a majority of the dopant atoms remained on the surface or formed magnetic clusters³⁹. In such cases, it is non-trivial to assign properties observed in these materials, e.g. magnetism, to $sp-d$ exchange interaction with the host rather than from magnetic islands. Apart from this, properties arising out of surface doping or magnetic clusters are plagued with problems of reproducibility and are, in general, not useful for applications. In fact, several reports in bulk as well as nanomaterials highlight the significance of dopant uniformity in host matrix on their properties^{40,41}. Hence, in order to study the properties associated with DMS QDs, effective synthetic methods are required to synthesize uniformly doped semiconductor nanocrystals.

Synthesis of DMS QDs

Varied nanoscale synthetic strategies have made it possible to chemically synthesize these DMS QDs with high monodispersity which in turn can be used for various fundamental studies as well as technological applications. The most common magnetic dopants include Fe, Co, Ni and Mn and semiconductor hosts include alloys and heterostructures of II–VI semiconductors. They can be synthesized by various chemical routes of which colloidal synthesis is the most explored technique due to the ease of controlling size, shape and protecting them against uncontrolled oxidation.

The first step towards obtaining uniformly doped DMS QDs requires an understanding of the origin of clustering in these materials. Among several issues involved, the two key factors responsible for clustering and surface doping were found to be difference in reactivities of the host and dopant precursors and the concept of self-purification⁴², where, the dopant atoms are expelled from the host to reduce defect energy and obtain a thermodynamically favourable state. The first problem of differential reactivity was recognized by Pradhan *et al.*⁴³ and Peng *et al.*⁴⁴ and two possible solutions based on the decoupling of doping from nucleation/growth of the host QD, namely, nucleation doping and growth doping were proposed such that the dopant atoms were placed in the desired radial position as shown in the Scheme 1. Nucleation doping involved synthesis of a small cluster of



Scheme 1. Schematic for (a) nucleation doping and (b) growth doping (reproduced from ref. 43).

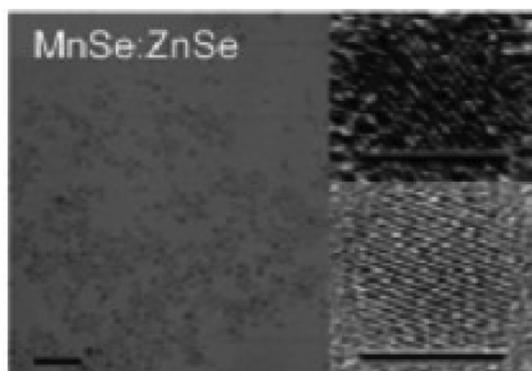


Figure 1. TEM image of MnSe:ZnSe nanocrystals. Scale bar = 50 nm (5 nm for inserts; reproduced from ref. 43).

dopant metal chalcogenide at high temperature followed by an overcoating of the host chalcogenide at a slightly lower temperature avoiding independent nucleation of the host chalcogenide (Scheme 1 a). In contrast, growth doping was achieved by surface incorporation of the dopant ion into small host clusters at low temperature for extended period of time followed by overcoating of the host matrix at slightly higher temperature (Scheme 1 b). Typical transmission electron microscopy (TEM) images of the particles obtained from this method are shown in Figure 1.

Though the separation of dopant incorporation and growth of the host received reasonable success, an in-depth study of dopant incorporation revealed the presence of several kinetic processes. Primarily, high temperature annealing increases entropy of the system and assists the defects to leach out to the surface^{42,45} as well as the expulsion of dopant from the QDs⁴⁶. This problem of dopant expulsion at high temperatures was termed self-purification (Scheme 2). For a long time, successful doping in semiconductor QDs was limited by competitive expulsion of dopants during the overgrowth of the host QDs at high temperature. Hence this process of self-purification was considered a deterrent for doping, and growth of QDs was limited to a few nanometers before the complete expulsion of dopant atoms.

Later Saha *et al.*⁴⁷ showed in 2016 that self-purification of dopants, previously considered a bane, could be used as a boon for synthesis of uniformly doped QDs of required size. In this process, a small magnetic core was

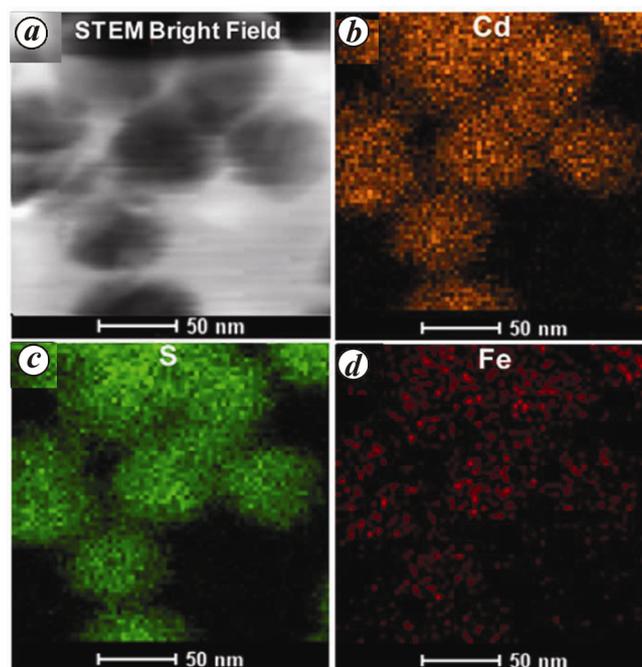
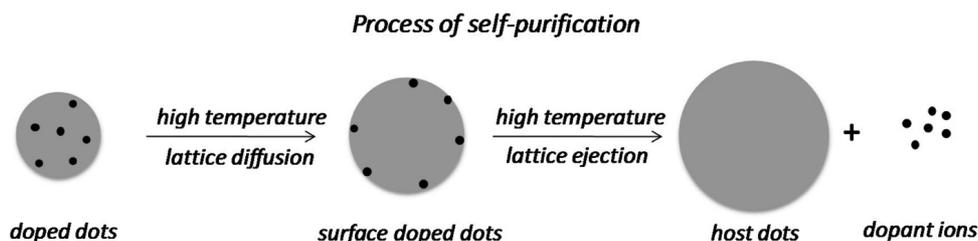
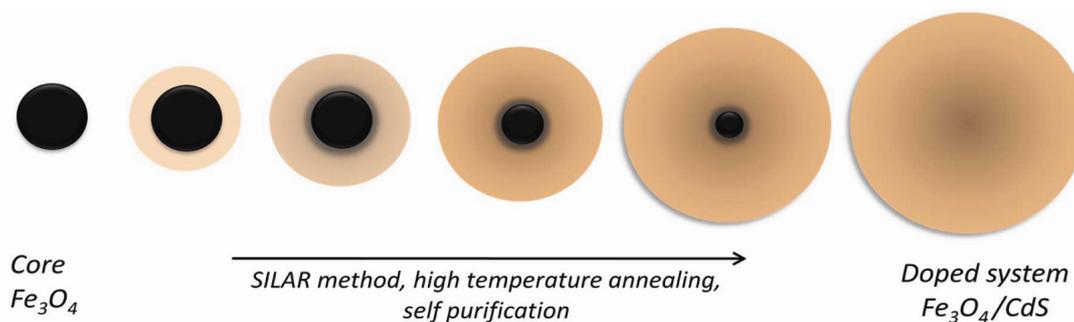


Figure 2. TEM elemental map of Fe-doped CdS showing STEM. a, bright field image; b, Cd map; c, S map; d, Fe map (reproduced from ref. 47).



Scheme 2. Schematic depiction of process of self-purification.



Scheme 3. Diffusion of dopants into the CdS matrix to get Fe-doped CdS QDs.

synthesized (demonstrated with the example of Fe_3O_4) and was overcoated with a thick semiconducting shell (CdS). The system was annealed at high temperature for a long time to diffuse the magnetic core into semiconducting shell before it eventually diffuses out of the matrix as shown in Scheme 3. Though FeO and CdS bonds are very stable, there exists a lattice mismatch of 4.4% between Fe_3O_4 and CdS. This lattice mismatch gives rise to a highly strained interface and high temperature annealing serves as a driving force to diffuse out Fe_3O_4 into the CdS matrix leading to Fe-doped CdS. It was observed that with high temperature annealing, the core diffuses into the shell with reduction in the size. All parameters were controlled such that the rate of diffusion was slower than the growth of semiconducting shell in order to have controlled diffusion of magnetic impurities in the host. Successive ionic layer adsorption reaction (SILAR) method was used to overcoat the magnetic core along with annealing and self-purification process in order to diffuse out dopant into the matrix and get Fe-doped CdS QDs, with excellent control over percentage of dopant, uniformity, distribution of dopants and size of dots. Oxides, sulphides and selenides are the most common choice for core materials. As reported earlier, this process provides both uniform doping as well as control over the size of nanoparticle and percentage of doping, depending upon annealing time and temperature. Along with X-ray diffraction (XRD) and TEM, distribution of Fe in CdS matrix was studied through X-ray absorption fine structure (XAFS) where, the local structure investigation of Fe in CdS was obtained along with element specific mapping of energy dispersive X-ray (EDX) as shown in Figure 2,

confirming the uniform distribution of Fe ions in CdS matrix with a complete absence of magnetic clusters.

It was also observed that the oxidation state of Fe was reduced from 2.44 to 2 through the reducing agents present in the reaction and was replaced in Cd site through substitutional doping. With this method it was shown that a large range of sizes could be achieved along with monodispersity of size, uniform and controlled concentration of dopant ion distribution by controlling the reaction conditions. Having control over the synthetic process by tuning the core size, reaction time and temperature, the authors were able to get 5% Fe-doped CdS nanocrystals with size around 60 nm as shown by TEM in Figure 3. Thus, with the evolution of various synthesis techniques, DMS QDs of different sizes and dopant concentrations have been prepared over past several years and have been studied for various interesting properties of these materials.

Properties of DMS QDs

Properties specific to DMS QDs can be broadly divided into magnetic and magneto-optical as well as magneto-electrical properties. Here we provide an overview of the recent advances in DMS QDs in both these sections and compare them with their bulk counterparts wherever appropriate.

Magnetism in DMS materials is expected to arise from the *sp-d* exchange interaction of dopant ion with the host semiconductor. However, the exact origin and the factors governing this ferromagnetism are unknown in these DMS materials. Despite this, the research into understanding

the magnetism in DMS QDs is powered by the potential of using spins of small size magnetic materials that can be manipulated by an external magnetic field to serve as extremely small sized memory storage bits for future technology.

One of the first impediments arose from the absence of a method to quantify magnetism arising from DMS QDs. Most of the early reports expressed magnetic moments in emu per gram of the material rather than the well-known moment per magnetic ion. This is due to the presence of quantitatively unknown weight of ligands on the surface of QDs that makes conversion to moment per magnetic ion impossible. Early reports on magnetism in DMS QDs showed the presence of small moments arising due to magnetic ion doping in the order of a few memu/g (ref. 48). However, it was observed around the same time that, even non-magnetic QDs like CeO₂ show ferromagnetic behaviour with similar moments attributed to oxide vacancies at the surface of QD⁴⁹ making it difficult to separate the contribution arising out of the magnetic dopant. More recent papers have not shown substantial improvement in magnetic moment⁵⁰⁻⁵² despite improved synthesis methods, possibly due to clustering of magnetic dopants and/or due to inherent nature of *sp-d* exchange interaction. Further, the absence of quantitative magnetic moment per ion has also hindered the comparison of absolute magnetic moment with bulk materials.

One of the notable breakthroughs was obtained by co-doping of ZnO with Fe and Cu⁵³. Interestingly, individually doped Fe-ZnO and Cu-ZnO are antiferromagnetic with no evidence of ferromagnetic order. This work demonstrates the presence of anti-ferromagnetically ordered Cu doped ZnO from *M* versus *H* plot and the antiferromagnetic interactions in Fe-doped QDs using inverse susceptibility plots as a function of temperature that exhibits a negative intercept. However, it is worth noting that the Fe, Cu co-doped system shows clear signatures of ferromagnetism in these dots with magnetic moments as high as 600 memu/g. This anomalous ferromagnetism in these QDs was explained by a direct correlation between electronic structure changes and ferromagnetic coupling. It was demonstrated using X-ray absorption spectroscopy

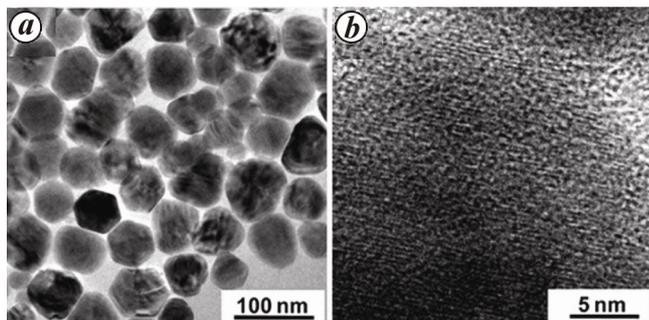


Figure 3. (a) TEM and (b) HRTEM images for ~60 nm Fe-doped CdS nanocrystals (reproduced from ref. 47).

(XAS) that both Fe²⁺ and Fe³⁺ species were present and the relative percentage of the species was dependent on the presence of Cu as a dopant. More recently, it was observed that upon synthesis of DMS QDs using the inside-out method⁴⁷, it was possible to obtain much higher magnetic moment compared to earlier counterparts. In this work, it was shown that smaller QDs showed a moment of 80 memu/g at room temperature and the surface-only magnetism on undoped CdS also shown in the same scale was negligible. Recent reports^{47,54} have used thermogravimetric analysis in these high quality uniformly doped QDs to realize the quantitative percentage of ligand weight and hence obtain the moment per magnetic ion. From these measurements, it can be observed that the magnetic moment per magnetic ion was found to be about 0.45 μ_B/ion for smaller particles which increased to 1.6 μ_B/ion for larger particles suggesting comparable values with that of the bulk Fe.

Traditionally, magnetic fields were used to address individual storage elements in magnetic storage materials. However, flexibility and storage density of these devices can be improved if magnetic properties are addressed via electrical or optical means other than the use of magnetic field alone. DMS materials have proven themselves as ideal materials with classic signature response to optical and electrical excitations. When an external magnetic field is passed through a non-magnetic substance, a small internal magnetic field is generated due to splitting of the exciton given by $g_{e,h}\mu_B B$, where $g_{e,h}$ is the excitonic Zeeman splitting which is of the order of 2 and B is the external magnetic field. This is typically around 100 μeV/T. However, in the presence of a few magnetic ions, a strong internal magnetic field is generated in a small external magnetic field due to the alignment of magnetic ions in the direction of the magnetic field. This splitting is given by $J_{sp-d}S_{Mn}\cdot\sigma_{e,h}$, where J_{sp-d} is the exchange interaction between magnetic ion and the

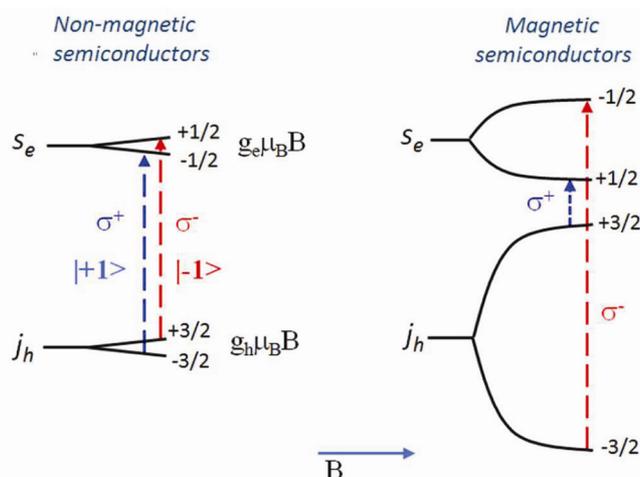


Figure 4. Exciton Zeeman spin splitting for non-magnetic and magnetic semiconductors in presence of external magnetic field.

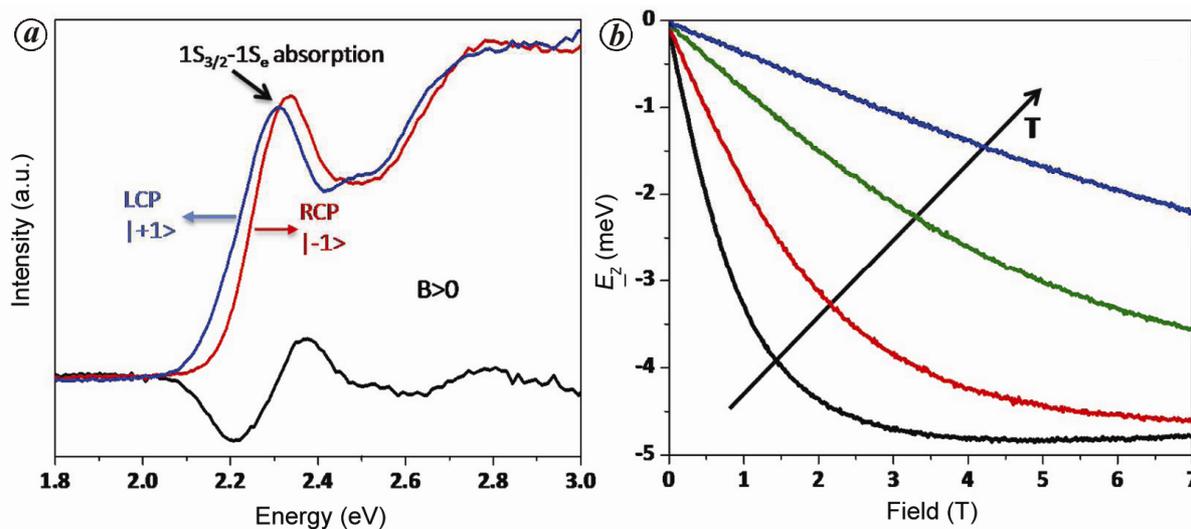


Figure 5. MCD spectra showing (a) host absorption in presence of external magnetic field using left and right circularly polarized light, (b) intensity of the difference spectrum versus applied field as a function of temperature.

host and S_{Mn} , the effective spin given by paramagnetic Brillouin function. This exchange field is typically of the order of about 1 eV and the effective spin is sensitively dependent on temperature. Further from these expressions, it is evident that while the non-magnetic splitting is linearly proportional to the applied magnetic field, the magnetically doped QDs with strong exchange interaction is highly non-linear with applied magnetic field as shown in Figure 4.

Hence, the most direct measurement of DMS materials is the measurement of magnetic circular dichroism wherein, the host absorption is probed in presence of external magnetic field using left (LCP) and right circularly polarized (RCP) light as shown in Figure 5a. The intensity of difference spectrum is plotted as a function of applied field for varying temperatures as shown in a typical curve in Figure 5b to obtain DMS signature of the magnetically doped QDs. The solid lines are the Brillouin function which fit to the experimental data. These data have been studied in a variety of host semiconductors, largely for Mn doping but also for Cu⁵⁵ and Co⁵⁶ doping and effective g -factors as high as 1000 have been demonstrated in DMS QDs. Further use of hetero-structures of semiconductor QDs are shown to assist in tuning the magnitude as well as the sign of exchange correlations³⁷. In fact, theoretical modelling of electronic and magneto-optical properties of core-shell nanoparticles doped with magnetic impurity, i.e. Mn-doped CdS–ZnS, predicts that, by controlling the position of magnetic impurities, the g factor in these nanocrystals can be attuned over wide range and forge them as potential candidates for spintronic applications⁵⁷. Spectral fingerprints of spin–spin interaction between the dopant and excitons of the host are also revealed by single-particle spectroscopy with discrete spin projections of individual Mn²⁺ ions as

obtained from spectrally well-resolved emission peaks. These QDs show enhancement in exchange splitting by an order of magnitude compared to their epitaxial counterparts paving the path for solotronics applications at elevated temperatures.

The other interesting and classic signature of DMS materials is the study of circularly polarized photoluminescence in the presence of magnetic field, also known as MCPL. MCPL has largely been studied for Mn-doped materials due to the presence of band edge emission and a strong Mn emission at 580 nm or 2.15 eV in many materials. Typically, bulk DMS materials have shown a strong polarization of band edge emission due to splitting of the band as discussed in Figure 4. However, the Mn emission which is basically a spin and orbital forbidden emission does not demonstrate any polarization⁵⁸ as expected and is shown in Figure 6a and b. Surprisingly, it was observed that in three dimensionally confined QDs, Mn emission was observed to be polarized in the presence of magnetic field⁵⁹ as shown in Figure 6c and d. Though, a complete understanding of the polarization of Mn emission is not yet achieved, it can be expected that due to confinement, we observe stronger overlap of wave functions leading to unexpected results.

A fascinating example of magneto-optical response displayed in DMS QDs is the magnetism induced due to photoexcitation in Cu-doped chalcogenide QDs due to strong spin-exchange interaction between paramagnetic Cu dopants and conduction and valence bands of the host semiconductor⁵⁵. In these Cu-doped ZnSe/CdSe QDs, it has been shown that the paramagnetic response is enhanced up to 100% upon illumination with UV light as revealed by magnetic circular dichroism (MCD) studies. In dark, these materials are shown to retain a photomagnetization memory for timescales of hours. Another

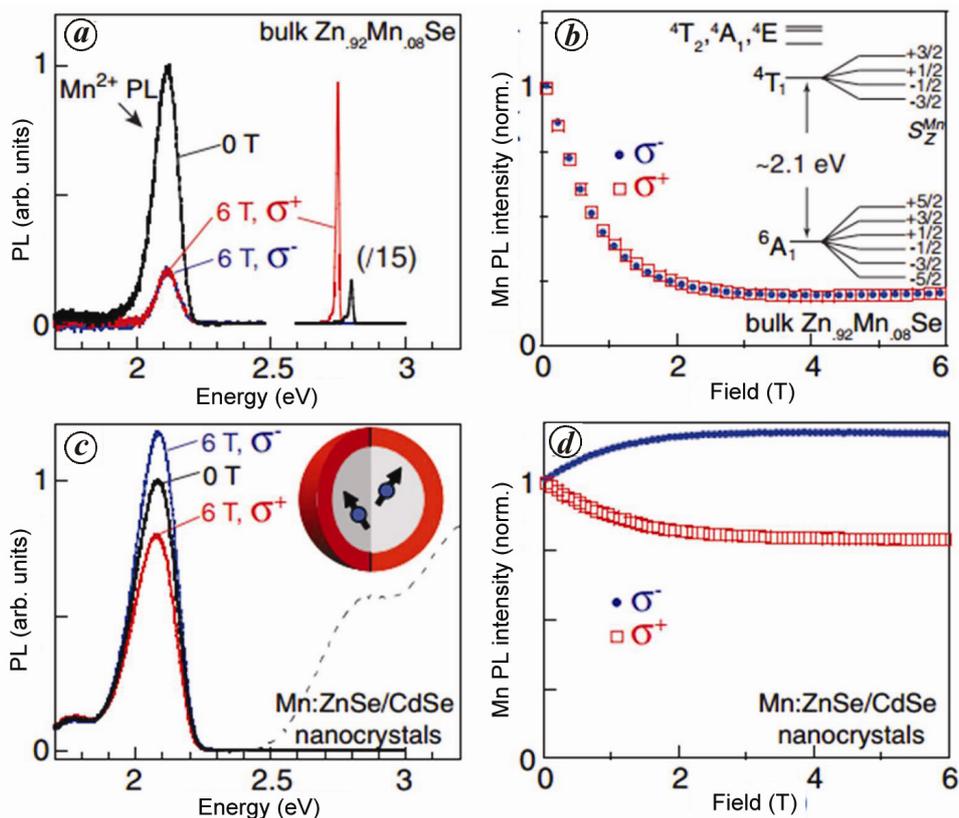


Figure 6. *a, b*, Magneto-PL from bulk ZnMnSe at 4 K, showing conventional DMS behaviour. 4T_1 to 6A_1 Mn^{2+} PL at 2.1 eV is suppressed by magnetic fields and remains unpolarized, while 2.8 eV exciton PL (scaled down 15*) increases. *c, d*, The contrasting magneto-PL from Mn:ZnSe/CdSe nanocrystals. The dashed line shows the QD absorption (reproduced from ref. 59).

example of light-induced spontaneous magnetization is Mn-doped CdSe QDs where spin effects are controlled in semiconductor nanostructures to generate, manipulate and read out spins³⁸. Here in the absence of applied magnetic field large dopant-carrier exchange fields are generated in strong spatial confinement giving rise to giant Zeeman splitting as a result of photoexcitation. These magnetic effects present due to photoexcitation are observed all the way up to room temperature. These materials have prospective applications for magneto-optical storage and optically controlled magnetism.

DMS QDs are not only known to respond to optical cues but also to charged carriers. For example, Zheng and Strouse⁶⁰ have shown carrier-mediated ferromagnetic interaction in Mn-doped CdSe QDs arising from photoexcited carriers from surface defect states of ultra small (<3 nm) QDs. Similarly, conduction band electron generated during photoexcitation is also shown to exhibit ferromagnetic exchange interactions in Mn-doped ZnO QDs under anaerobic conditions⁶¹ as well as in air-stable Fe-Sn co-doped In_2O_3 (ref. 24) and Mn-Sn co-doped In_2O_3 (ref. 54). In fact, despite the intrinsic antiferromagnetic super exchange coupling between next nearest neighbour magnetic cations such as $Mn^{2+}-O^{2-}-Mn^{2+}$ (ref.

61), Mn-Sn co-doped In_2O_3 was found to exhibit nearly ideal ($\sim 4.8 \mu_B/Mn^{2+}$ ion) magnetic moment at 2 K and 70 kOe, thus overcoming the antiferromagnetic super exchange interaction completely⁵⁴. These results confirm conduction band electron-dopant ferromagnetic exchange interaction, which can lead to magneto-electric and magneto-plasmonic properties.

Conclusion

As a search for a viable DMS material for incorporation into spintronic device progresses, the fundamental understanding of dopant incorporation and its behaviour into the semiconductor matrix needs to be explored. Presently, synthesis of DMS QDs has been the major bottleneck in the study of this class of compounds. Various techniques used to obtain these materials have been discussed here and the current state-of-the-art technique to synthesize these QD systems are highlighted. Fundamental insights can be gained from Faraday rotation, Kerr rotation, magnetic circular dichroism, magnetic circularly polarized photoluminescence spectroscopies, magnetism induced through optical excitation, magneto-electric and magneto-plasmonic

excitations. This can be used to reinforce cognizance related to spin dynamics and magnetic exchange interactions in DMS QDs with potential upshot for spin-based information technologies as discussed in this article.

Note: The authors declare no competing financial interest.

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