

## Effect of transition metal dopants on the optical and magnetic properties of semiconductor nanocrystals

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**Abstract.** This review discusses the recent developments in doped semiconductor nanocrystals with a special emphasis on the effect of dopant on the electronic structure of the host nanocrystals. The review focusses on 3d transition metal dopants with unique electronic structure making them receptive for dramatic changes in magnetism, absorption and photoluminescence properties by the successful introduction of a small percentage of dopants into the nanocrystals. Many of these properties are shown to be qualitatively different from that of the bulk properties, leading to challenges in understanding the nature and effects of the confinement of the host. The optical and magnetic changes induced by Mn doping is first reviewed, followed by the use of Cu as a probe to understand the bulk and surface electronic structure of the host. The review concludes with a short section on photomagnetism induced by Cu on the host nanocrystal and a summary of the work with other transition metal ions.

**Keywords.** Quantum dots; doping; magnetic properties; optical properties.

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### 1. Introduction

Colloidal semiconductor nanocrystals (NCs) have dominated the research activity [1–3] for over three decades because of their size-dependent optical and magnetic properties [4]. The efforts have evolved from the initial focus on the chemistry of controlling the size and size distribution to the physics of their size-dependent detailed electronic structure [5] including the fine structure of the absorption spectra [6,7]. Theoretical works on various systems have since expanded our knowledge base on the size-dependent properties of the NCs [8–12]. These efforts have led to the delicate tailoring of NC properties by understanding and controlling parameters like shape [13,14], surface chemistry [15], composition etc., leading to real-world applications. NCs are now known to be promising

materials for a diverse set of applications ranging from bioimaging [16], photovoltaics [17–19], solid-state lighting [20–24] to quantum computing [25,26].

A very active area of research in this field involves chemical doping [22,27–37], the introduction of impurity elements (typically transition metal ions) into a host lattice to fine-tune optical and magnetic properties of the NCs [22,27–29,35,36]. Dopants are intentional impurities introduced to locally modify the electronic structure, leading to global changes in optical and magnetic properties of the host system. Doping in NCs is aimed at exploiting the enhanced spin [38], luminescence and electronic properties [39] and is inspired by the success of analogous doping in bulk and their triumph in the electronics industry. Owing to the potential applications as size-tunable phosphors [22,40] as well as interesting magnetic properties [38,41], considerable attention has been focussed on doping II–VI chalcogenide semiconductor nanocrystals with transition metal atoms.

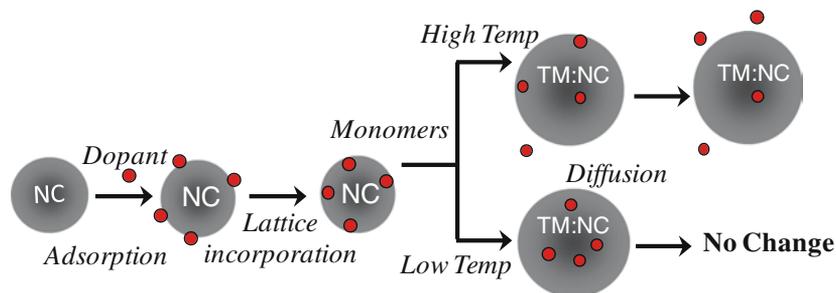
Nevertheless, nanostructure doping has not proven to be straightforward [32] and is hindered by the exclusion of impurities during growth [42]. Though doping in semiconductor NCs is extensively studied, incorporation of requisite percentage of dopants at the precise spatial location is still in its infancy [21,43]. Recent research has demonstrated the existence of interesting handles like the dopant distribution or the presence of defects in the host NC [44] to determine the efficiency of the dopant-introduced optical and magnetic properties. Till date, Mn-doped NCs have been the single-most studied semiconductor nanocrystals [22,28,35], thus giving rise to a host of new interesting properties, both at a fundamental level as well as at the technological level. Recently, Cu has also invoked a lot of interest in the research community [36,41,45,46] mainly because it could modify the electronic properties of many II–VI compounds giving rise to intragap luminescence in the visible spectral range. The other dopants of interest include Co, Ni and Fe [47–49] that have also been used to alter the optical as well as magnetic properties of the NCs.

In this review, we discuss the properties of the host NCs modified by doping transition metal ions in NCs that has given rise to a rich field in the area of doping semiconductor NCs. A brief overview of the optical and magnetic properties of Mn and Cu will also be given. Though historically the motivation behind the investigation of manganese doping in NCs is the use of bright orange emission at 580 nm as luminescence-sensitized photoluminescence (PL) activators [50], gradually other interesting properties of Mn such as the coupling of the electrons and holes with the embedded magnetic ion spins via giant *sp*–*d* exchange coupling [51] and the interesting magneto-optical properties like spin-polarized bands and pronounced nonlinear band splitting have come to light. Additionally, it has also been shown that it is possible to polarize the energy and intensity of the Mn *d*–*d* transition in a Mn-doped II–VI NCs [38] unlike in the bulk [52]. The interest in Cu doping arises because of the ease of conversion of copper between  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  oxidation states that facilitate the down-conversion of luminescence with the aid of the intragap states [36]. Furthermore, of late, this intragap state luminescence arising from Cu doping has also been used to study the electronic structure of the host NCs [46]. An understanding of the mechanism of this emission has led to an understanding of the role of each ligand in II–VI semiconductors [46]. Additionally, copper doped in II–VI NCs has been recently shown to retain magnetic memory in the NCs [41]. After discussing this rich field, we will then conclude with a summary of other transition metal dopants.

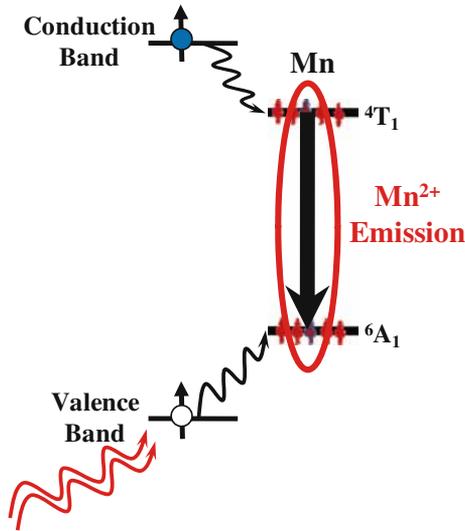
## 2. Mn-doped NCs

Despite several successes in the synthesis of doped NCs, efficient doping of nanocrystals by placing the dopants in the desired radial position have only been achieved in a very few cases [21,43]. One of the important strategies of doping that allows appropriate placement of the dopant ion has been the decoupling of doping from the growth of the host nanocrystal [40]. However, though this allows one to place the dopant in the desired radial position, it does not ensure that the dopants remain in that position during the growth of the host nanocrystals. It is well known that due to the small number of atoms in the NCs, even one or two dopant atoms contribute a substantial percentage of the host material, leading to stress in the host semiconductor lattices. This phenomenon propels the expulsion of the dopant from the host lattice even though it has been placed in the most suitable position [42]. Thus, the successful incorporation of the dopants in required quantities in the bulk of the host nanomaterial is a nontrivial equilibrium between the diffusion within the lattice and the increase in energy due to the lattice defects. A simple schematic of the same is shown in figure 1. In the case of Mn doping in some of the II–VI semiconductors, this phenomenon has now been extensively studied and ways were found to enhance high doping concentrations at the required radial positions in the NCs giving rise to several interesting properties and applications. The most notable among them is the tuning of the position of the Mn emission band through the entire visible spectrum by appropriate variation of strain on the host around the Mn ion [43]. In fact, this is in direct contrast to the expected prominent and defining feature of the incorporation of the Mn ion as a dopant atom, that is traditionally defined by the presence of the emission peak arising from the Mn  $d-d$  transition at about 580 nm or 2.15 eV. In fact, the same group has also shown earlier that the width of this 580 nm peak as observed from single molecule studies is actually a sum of much sharper peaks observed over a large range of wavelengths [53].

The second noteworthy feature in the Mn emission is the origin of this 580 nm peak. Historically, it is understood to originate from internal ( ${}^4T_1-{}^6A_1$ ) transitions within the excited  $3d^5$  shells of the  $Mn^{2+}$  ions. The large absorption cross-sections of the semiconductor host lattices combined with rapid energy transfer to the dopants yield efficient PL emission [22] as shown in the schematic in figure 2. This is due to a substantial ensemble Stokes shift arising from the atomic-like emission states of Mn. This overcomes the self-quenching problem in applications like light emitting diodes and also gives thermal stability [40] as it arises out of atomic-like states that do not allow strong coupling with the lattice phonons. However, for a long time, the origin of this peak, specifically with



**Figure 1.** Schematic of insertion of the dopant into the host nanocrystal.



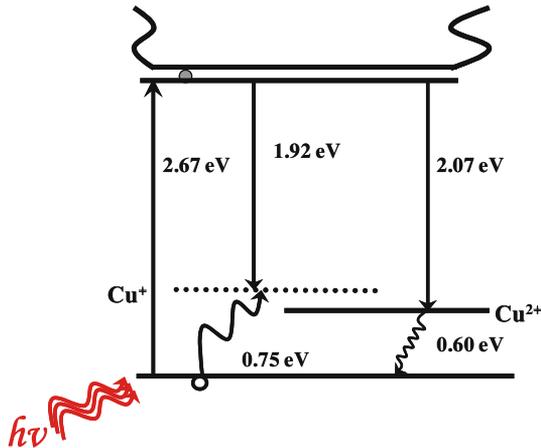
**Figure 2.** Schematic of the mechanism of Mn emission in the absence of magnetic field.

emission quantum yields as high as 50–70% has generated a lot of interest in the literature.  $\text{Mn}^{2+}$  ion with a  $3d^5$  configuration has a  ${}^6A_1$  ground state with five unpaired electrons. Hence, a Mn  $d-d$  transition with  $\Delta l \neq 1$  and failure to conserve spin during a transition from  ${}^4T_1$  state or any other higher-lying state to the  ${}^6A_1$  ground state would be both orbital as well as spin forbidden transition. Hence the mechanism of excitation through the host NC as well as the emission has led to extensive research [52].

Recently, it has been observed that the NCs provide a unique playground in terms of understanding the nature of this forbidden transition [38]. For instance, in the case of bulk semiconductors, 2D and 1D materials, it was observed that this emission quickly decayed with increasing magnetic field at the cost of band-gap emission [52]. In earlier literature, this was understood to arise as a consequence of spin-forbidden Auger-like recombination in the presence of magnetic field. However, surprisingly, the band-gap emission is completely absent in the 3D confined NCs and we observe that the Mn emission is polarized in intensity and energy splitting is a function of increasing magnetic field. The study of the Mn emission as a function of temperature and magnetic field in NCs surprisingly reveals that the circular polarization of the  $\text{Mn}^{2+}$  PL follows the paramagnetic (Brillouin-like) magnetization of the spin-5/2  $\text{Mn}^{2+}$  ions. Essentially these studies reveal that the processes of both  $\text{Mn}^{2+}$  excitation and  $\text{Mn}^{2+}$  emission are essentially different in colloidal dilute magnetic semiconductor (DMS) NCs as compared to conventional DMS materials. Thus the magneto-optical properties of Mn in semiconducting NCs provide interesting challenges both in understanding the basic mechanisms as well as in applications.

### 3. Cu-doped NCs

Though doping in NCs came to the forefront with the introduction of Mn, recently Cu doping has invoked similar interest because of its unique electronic structure [46]. It is



**Figure 3.** Origin of Cu emission in bulk CuZnSe [68,69].

now common knowledge that impurities like Cu, similar to Mn, introduce atomic-like states within the band gap of the host semiconductor. These states may facilitate either radiative or nonradiative decay through these channels. In the case of Cu, a characteristic long-lived intragap Cu-related radiative photoluminescence (PL) band is observed along with the suppression of the intrinsic BE emission [36]. This band is understood to arise from the CB of the host to the Cu  $d$  level transition similar to that of the bulk shown in figure 3. Hence the ability of the dopant to provide information about the host NC through its optical interaction with the host has offered researchers with a new avenue to investigate the electronic structure of the host. Atomic-like states of Cu is expected to be independent of size and hence the position of the PL peak provides an internal standard to measure the shift in the CB of the host as a function of size [46,54]. In addition, permanent incorporation of charges into NCs can be achieved by the placement of active impurities into the lattice. Doping Cu into the NCs, with its ability to exhibit variable valence is a promising strategy to achieve this goal. This has provoked interest in the study of Cu-doped NCs.

### 3.1 Synthesis of Cu-doped NCs

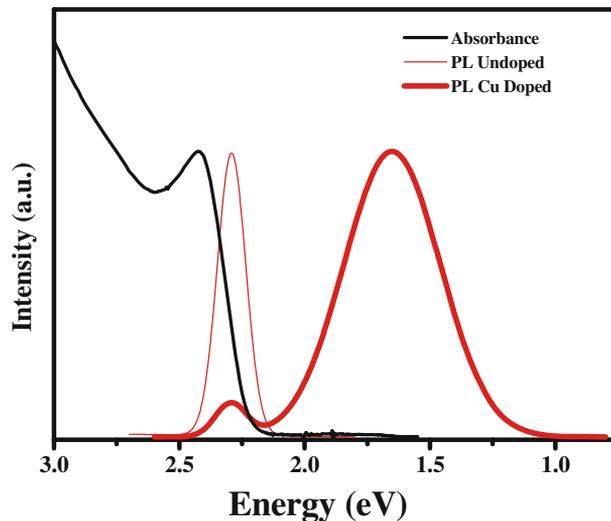
Cu doping into NCs was a challenge mainly due to the differential reactivity of the Cu precursors compared to the Zn or Cd precursors [55]. Cu precursors, being much more reactive than its  $d^{10}$  counterparts, would invariably form CuSe or CuS and precipitate out of the reaction mixture. However, Pradhan *et al* [55] overcame this challenge by separating the growth of the host from the doping of the Cu using variable temperatures. Since then, extensive research has led to the successful synthesis of Cu doped in various II–VI semiconductors like CdS, CdSe, CdTe, ZnS and ZnSe [46] and alloys like ZnSe/CdSe [36]. It is interesting to note that during these syntheses, care has been taken to keep the dopant level at substantially low ( $\sim 1\%$  or lower) percentages so that the electronic levels of the dopant remain atomic-like and do not affect the electronic structure of the host. This is important because Cu doping is carried out not only to exploit the red-shifted size

tunable luminescence efficiency in the visible and IR regions but also for its capability to associate the atomic state of Cu with the CB of the host semiconductor.

### 3.2 Luminescence of Cu-doped NCs

Intragap luminescence centres associated with Cu dopants in bulk II–VI semiconductors have been known since the early 1960s [56]. More recently, the development of characteristic intragap Cu-related emission feature in II–VI semiconductor NCs have also been demonstrated. However, the oxidation state of Cu and the luminescence mechanism in these NCs are subjects of debate [57,58]. The accurate determination of the oxidation state of the Cu ion is important to understand the mechanism of Cu-related emission. While  $\text{Cu}^{2+}$  is an optically active ion with an optically active hole present at all times, irrespective of the photogenerated electron–hole pair, the  $\text{Cu}^+$  is an optically passive ion. In fact,  $\text{Cu}^+$  ion is a  $d^{10}$  system and hence cannot participate in emission without first capturing the photogenerated hole. The presence of electron paramagnetic resonance (EPR) spectra for the Cu ion would have concluded the presence of  $\text{Cu}^{2+}$  species. However, somewhat surprisingly,  $\text{Cu}^{2+}$  ions substituted into a II–VI lattice do not give rise to any detectable EPR signature, possibly due to the line broadening [59]. This was initially hypothesized incorrectly as the signature of  $\text{Cu}^+$  ion. However, later studies showed that Cu ions indeed show exchange with the host materials as observed from magnetic circular dichroism spectrum, that is characteristic of a  $d^9$  ion. Hence it was later concluded to be a  $\text{Cu}^{2+}$  ion.

A typical spectrum for Cu-doped CdSe is shown in figure 4 which usually shows the presence of two distinct features, one corresponding to the band edge emission with a lifetime of about 20 ns and the other corresponding to Cu-related emission with a lifetime of about 50–1500 ns depending on the host. However, it is evident that the lifetime of the Cu-related emission is much longer than that of the band edge emission. Given that

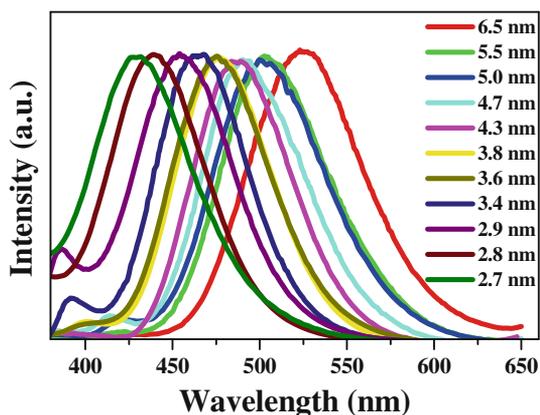


**Figure 4.** Typical absorption and PL of spectra of undoped and Cu-doped CdSe nanocrystals.

the photoexcited electron competes with the photoexcited hole in the valence band and the optically active hole at the Cu site, the recombination through the Cu site should be highly unlikely owing to the long lifetime of the Cu-related emission. However, if the photoexcited hole is scavenged through the hole traps of the NC, then we observe the Cu-related emission [36]. This has been explicitly verified by the addition of known hole traps like thiols in CdSe NCs to see an increase in the copper emission at the cost of band edge emission. Thus, while the position of the Cu emission provides signatures of the shift in the conduction band edge, the intensity of the Cu emission is indicative of the percentage of hole traps on the surface of the NC contributing to the decay of the band-edge emission [46]. Similarly, as the Cu-related emission involves only the photoexcited electron, the nonradiative component of the lifetime curve arises only due to the presence of electron traps on the surface of the NC. Hence, the mechanism of emission of the Cu-related band provides a unique method to study the efficiency of surface passivation on the NCs.

### 3.3 *Electronic structure of the host NCs*

In this section, we briefly discuss the electronic structure of some of the host semiconductors as well as the role of a few ligands. For example, with the model system of ZnSe, we note that the Cu peak shifts to higher wavelength with increasing size of ZnSe as shown in figure 5. This shift can be attributed to the shift in the conduction band and hence can be used as a probe to study the shift in the conduction band. These results are in excellent agreement with the available photoelectron spectroscopy data [60–63] as well as the theoretical data [64] providing us with a less time-consuming and straightforward method to accurately map the CB and VB positions in the nanocrystals [46,54]. In addition, this method is also useful for determining the relative band offsets in semiconductor nanocrystals providing a useful tool to design quantum dots-based solar cells that rely on charge transfer at the interface. Moreover, Cu can also be used to study the role of the ligand in the passivation of the nanocrystal surfaces [46]. To name a few, oleic acid in CdS and CdTe is shown to act as electron trap passivator while it does not affect the CdSe nanocrystals [46]. Similarly, trioctyl phosphine has been shown to passivate hole traps in CdSe



**Figure 5.** Variation of Cu peak as a function of size in Cu-doped ZnSe nanocrystals.

nanocrystals [46]. Thus, Cu as a dopant has opened up a new novel probe to study the bulk and surface electronic structures of the host.

In addition to all this, Cu doping has also shown the presence of a strong exchange interaction leading to the presence of magnetism in semiconductor nanocrystals [57]. A rather surprising consequence of magnetism in Cu-doped nanocrystals is the pronounced and long-lived photoinduced enhancement of their paramagnetic properties. While the exact mechanism of photomagnetism is yet to be understood, technologically this property can have far reaching consequences in potential applications for magneto-optical storage and optically controlled magnetism.

#### 4. Other dopants

While a great deal of attention has been paid to Mn and Cu, mainly due to their interesting luminescent properties, the other dopants that have received some attention include Fe, Co and Ni. Fe-doped oxide nanocrystals [49,65] have been shown to have ferromagnetic behaviour at room temperatures while Co and Ni have also shown interesting magnetic behaviour [49,66]. But, due to the absence of readily observable luminescence in these materials they have received less attention than Mn and Cu. However, dopants like Co and Ni hold a promising future as they can be used as multifunctional materials with their capability to show luminescence as well as magnetism when they are internally doped within the nanocrystals [67].

#### 5. Conclusion

In this review, the dopant-induced optical and magnetic properties in nanomaterials have been reviewed. The study of the origin of strong dopant emission due to Mn and Cu has been discussed. Further, the anomalous increase of Mn emission intensity in nanomaterials has also been explored. The electronic structure correlations of host nanomaterials using Cu as a probe has been introduced. The study has been extended to other dopants as well.

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#### References

- [1] A P Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996)
- [2] W S Song and H Yang, *Chem. Mater.* **24**, 1961 (2012)
- [3] F Wang *et al*, *Nat. Mater.* **10**, 968 (2011)
- [4] B P Khanal *et al*, *ACS Nano* **6**, 3832 (2012)
- [5] M A El-Sayed, *Acc. Chem. Res.* **37**, 326 (2004)
- [6] J Nanda, B A Kuruvilla and D D Sarma, *Phys. Rev. B* **59**, 7473 (1999)
- [7] M E Schmidt *et al*, *Phys. Rev. B* **53**, 12629 (1996)
- [8] G Allan, Y Niquet and C Delerue, *Appl. Phys. Lett.* **77**, 639 (2000)

- [9] A L Efros and M Rosen, *Ann. Rev. Mater. Sci.* **30**, 475 (2000)
- [10] S Sapra *et al*, *Nano Lett.* **2**, 605 (2002)
- [11] S Sapra, N Shanthi and D D Sarma, *Phys. Rev. B* **66**, 205202 (2002)
- [12] R Viswanatha *et al*, *Phys. Rev. B* **72**, 45333 (2005)
- [13] C Burda *et al*, *Chem. Rev.* **105**, 1025 (2005)
- [14] X Peng *et al*, *Nature* **404**, 59 (2000)
- [15] H J Choi, J K Yang and H H Park, *Thin Solid Films* **494**, 207 (2006)
- [16] G Ruan and J O Winter, *Nano Lett.* **11**, 941 (2011)
- [17] R J Ellingson *et al*, *Nano Lett.* **5**, 865 (2005)
- [18] P V Kamat, *J. Phys. Chem. C* **112**, 18737 (2008)
- [19] A Kongkanand *et al*, *J. Am. Chem. Soc.* **130**, 4007 (2008)
- [20] M Nirmal and L Brus, *Acc. Chem. Res.* **32**, 407 (1999)
- [21] Y Yang *et al*, *J. Am. Chem. Soc.* **128**, 12428 (2006)
- [22] N Pradhan and D D Sarma, *J. Phys. Chem. Lett.* **2**, 2818 (2011)
- [23] D D Sarma *et al*, *J. Phys. Chem. Lett.* **1**, 2149 (2010)
- [24] Ranjani Viswanatha, J M Piertyga, V I Klimov and S A Crooker, *Phys. Rev. Lett.* **107**, 067402 (2011)
- [25] T D Ladd *et al*, *Nature* **464**, 45 (2010)
- [26] S Hughes *et al*, *Phys. Rev. B* **83**, 165313 (2010)
- [27] S Acharya *et al*, *J. Phys. Chem. Lett.* **1**, 485 (2010)
- [28] R Beaulac *et al*, *Adv. Funct. Mat.* **18**, 3873 (2008)
- [29] A K Bhattacharjee and J Pérez-Conde, *Phys. Rev. B* **68**, 45303 (2003)
- [30] S Brovelli *et al*, *Nano Lett.* **12**, 4372 (2012)
- [31] J D Bryan and D R Gamelin, *Prog. Inorg. Chem.* **54**, 47 (2005)
- [32] D Chen *et al*, *J. Am. Chem. Soc.* **131**, 9333 (2009)
- [33] M-H Du, S C Erwin and A L Efros, *Nano Lett.* DOI:10.1021/nl8016169 (2008)
- [34] N S Karan *et al*, *J. Phys. Chem. Lett.* **1**, 2863 (2010)
- [35] A Nag, S Chakraborty and D D Sarma, *J. Am. Chem. Soc.* **130**, 10605 (2008)
- [36] R Viswanatha *et al*, *Nano Lett.* **11**, 4753 (2011)
- [37] R Viswanatha *et al*, *J. Phys. Chem. B* **108**, 6303 (2004)
- [38] R Viswanatha *et al*, *Phys. Rev. Lett.* **107**, 067402 (2011)
- [39] N Pradhan *et al*, *Nano Lett.* **7**, 312 (2007)
- [40] N Pradhan and X Peng, *J. Am. Chem. Soc.* **129**, 3339 (2007)
- [41] A Pandey *et al*, *Nat. Nanotechnol.* **7**, 792 (2012)
- [42] G M Dalpian and J R Chelikowsky, *Phys. Rev. Lett.* **96**, 226802/1 (2006)
- [43] A Hazarika, A Pandey and D D Sarma, *J. Phys. Chem. Lett.* **5**, 2208 (2014)
- [44] A Saha *et al*, *J. Phys. Chem. Lett.* **4**, 3544 (2013)
- [45] R Viswanatha *et al*, *J. Phys. Chem. B* **110**, 22310 (2006)
- [46] G K Grandhi and R Viswanatha, *J. Phys. Chem. Lett.* **4**, 409 (2013)
- [47] P V Radovanovic and D R Gamelin, *J. Am. Chem. Soc.* **123**, 12207 (2001)
- [48] D A Schwartz *et al*, *J. Am. Chem. Soc.* **125**, 13205 (2003)
- [49] P V Radovanovic *et al*, *J. Am. Chem. Soc.* **124**, 15192 (2002)
- [50] R N Bhargava *et al*, *Phys. Rev. Lett.* **72**, 416 (1994)
- [51] D A Bussian *et al*, *Nat. Mater.* **8**, 35 (2008)
- [52] S Lee, M Dobrowolska and J K Furdyna, *Phys. Rev. B* **72**, 75320 (2005)
- [53] A Hazarika *et al*, *Phys. Rev. Lett.* **110**, 267401 (2013)
- [54] Z Zhang *et al*, *Chem. Mater.*, ASAP DOI:10.1021/cm5047269 (2015)
- [55] N Pradhan *et al*, *J. Am. Chem. Soc.* **127**, 17586 (2005)
- [56] H J Queisser and C S Fuller, *J. Appl. Phys.* **37**, 4895 (1966)
- [57] A Pandey *et al*, *Nat. Nanotechnol.* (2012) (in press)
- [58] A H Khan *et al*, *Angew. Chem. Int. Ed.*, Early View (2015)

- [59] B Clerjaud and A Gelineau, *Phys. Rev. B* **16**, 82 (1977)
- [60] J R I Lee *et al*, *Phys. Rev. Lett.* **98**, 146803 (2007)
- [61] Ph.D. Thesis of S Sapra, Solid state and structural chemistry unit, Indian Institute of Science, Bangalore, 2003
- [62] J Luning *et al*, *Solid-State Commun.* **112**, 5 (1999)
- [63] V L Colvin, A P Alivisatos and J G Tobin, *Phys. Rev. Lett.* **66**, 2786 (1991)
- [64] R Viswanatha and D D Sarma, *Chem. Asian J.* **4**, 904 (2009)
- [65] R Viswanatha *et al*, *J. Phys. Chem. Lett.* **3**, 2009 (2012)
- [66] R Beaulac, S T Ochsenein and D R Gamelin, in: *Nanocrystal quantum dots* edited by V I Klimov (CRC Press, 2004) p. 397
- [67] S Jana *et al*, *J. Phys. Chem. Lett.* **3**, 2535 (2012)
- [68] H G Grimmeiss *et al*, *J. Appl. Phys.* **48**, 5122 (1977)
- [69] G B Stringfellow and R H Bube, *Phys. Rev.* **171**, 903 (1968)