Introduction

This chapter contains an overview of bulk and quantum confined semiconductor nanocrystals, their electronic structure, different optical properties and different reported high temperature injection colloidal synthesis protocols. In addition, introduction of different transition metal dopants and possible change of photo-physical properties of the host nanocrystals are described. Finally, motivation of our work has been discussed.
Chapter 1: Introduction

1.1 What is a nanomaterial?

A small word “nano” with a large potential has been introducing itself into the world’s consciousness over the past few decades. The prefix “nano” means one billionth; nanometer (nm) implies 1/1,000,000,000 meter. Thus the dimension is indeed small but nearly an order of magnitude larger than a typical atom or small molecule, for example, 10 hydrogen atoms in a line make up 1 nm. Owing to its extremely small size, preparation, characterization and measurements of different properties of such a nanostructure are extremely challenging tasks and require special efforts equipped with advanced techniques. However, in spite of numerous challenges and difficulties, the study of nanomaterials is one of the most active research fields today because of its extreme importance. Nanoscale is unique, since it is the length scale where common properties of bulk materials like conductivity, color, melting point etc. meet with the more exotic and fundamental properties of atomic and molecular world such as quantum confinement effect. Thus the understanding of nanomaterials is important if we want to understand the evolution of bulk materials starting from their atomic limits. From technological perspective, nanomaterials exhibit a plethora of new properties which are neither achievable in the bulk limits nor in the atomic limits; banking on such unique properties, a whole lot of applications have already been demonstrated, opening a new world of technology. The change in the properties in nanoscale is not simply a result of scaling factors but mainly depends on quantum confinement effects and large surface to volume ratios in nanomaterials and hence cannot be deduced through extrapolations of our existing knowledge in the bulk or atomic limits; thus, nanoscale does not merely signify a small dimension but it is a different kind of small with an unprecedented impact on the present and future science and technology.

Michael Faraday synthesized colloidal gold of different colors in 1850, which were nothing but gold nanoparticles. In fact, colloidal gold was used as a method of staining glass from the medieval era.\(^1\) However, the visionary talk of Richard Feynman at an American Physical Society meeting in 1959 suggesting “There’s Plenty of Room at the Bottom”, had conceptualized the terms “nanoscience” and “nanotechnology”. But the realization of these concepts started only in early 1980’s with the pioneering works of
Henglein et al. (1982), Efros et al. (1982), Brus (1983) and so on. Following these reports, tremendous efforts have already been made to understand and achieve different aspects of nanoscience, ranging from synthesis of high quality nanomaterials, gaining insights into the physics and chemistry of such nanomaterials, developing experimental and theoretical methodologies to probe such nanomaterials to manipulating and controlling them in the atomic level and many more. Of late, research in this field not only covers the synthesis and investigation of fundamental properties, but also has a profound focus on the potential applications of such materials covering optical, magnetic, electronic, and catalytic and many other applications.

1.2 Quantum confinement effect

Bulk semiconductors exhibit a characteristic fixed energy gap, known as bandgap, separating the valence band and conduction band. In a direct-gap semiconductor, where the valence band maximum and conduction band minimum correspond to the same electron momentum state, absorption of a photon can directly promote an electron from the valence band to the conduction band, thus generating an electron-hole pair as shown in figure 1. A valence-band hole is nothing but a missing electron and has a charge opposite to that of a valence-band electron. Because of the opposite charge, there is coulomb attraction between the electron and hole, which results in the formation of a bound pair, known as exciton. Single electron–hole pair problem is similar to the hydrogen atom, where the hole plays the role of the proton. However, the binding energy for an electron-hole pair is orders of magnitude smaller than that in the hydrogen atom. This reduction is mainly because of the effective electron and hole masses are substantially smaller than the free electron and proton masses. The background dielectric constant of the semiconductor also reduces the Coulomb attraction strength. Smaller exciton binding energy implies a larger spatial separation of electrons and holes and thus a larger excitonic Bohr radius. When the size of semiconductor becomes comparable to the excitonic Bohr radius, then the carriers are confined by the boundaries of the material. This phenomenon is known as quantum size effect and leads to atom like quantized states in nanocrystals (NCs), as shown in the right hand side of the of figure 1.1. Semiconductor nanocrystals in a nanometer scale which confines the electron-hole pair in all three dimensions are called as...
“Quantum Dot”. Therefore if the size of the crystallite is comparable to this length, the electron and hole are “quantum confined” by the crystallite boundary.

**Figure 1.1** Left panel shows a schematic representation of a bulk semiconductor that has continuous conduction and valence energy bands separated by a fixed bandgap $E_g$, whereas, a quantum dot (middle panel) is characterized by discrete atomic-like states with $E_g$ determined by its size where the nanocrystals belongs its three dimensional quantum confinement (right panel).

For example, for a different size of CdSe nanocrystals, the absorption spectrum (Figure 1.2 (a)) shows sharp features which arises as a direct consequence of quantum size effect and are very different from that of a bulk CdSe; typical absorption spectrum from a bulk is continuum above the bandgap. Because of the sharp atom like energy states, these NCs are also termed as artificial atoms, but they are large enough to hold crystallinity. Furthermore, the absorption spectrum of CdSe NCs is substantially blue shifted compared to the bandgap of bulk CdSe, which is indicated by an arrow in the figure. This is one of the most important aspect of semiconductor NCs resulting from quantum confinement effect. To understand this, we consider the simple model of particle-in-a-box. The series...
of CdSe nanocrystals shown in Figure 1.2 (b) is a powerful visual demonstration of the particle in a box.

Figure 1.2 (a) Typical optical absorption spectra from an ensemble of CdSe quantum dots with different size of CdSe nanocrystals mention inside the figure. (b) Digital images of tunable CdSe nanocrystal dispersed in chloroform under 365 nm UV irradiation.
Energy of the $n^{th}$ state of the particle of mass $m$ in a one dimensional box of length $L$ is given by

$$E_n = \frac{n^2 h^2}{8m L^2}$$

(1.1)

where, $h$ is the planks constant. Important point to note is that the energy is inversely proportional to $L^2$ and so is the separation between two energy levels ($E_n - E_m$). For a spherical NC, one can start with particle in a sphere model and a similar energy expression was obtained with energy in this case is inversely proportional to the square of the radius of the sphere. Thus, the above mentioned simplistic model allows us to make qualitative statement that when the particle radius is comparable to Bohr excitonic radius, bandgap of semiconductor increases with decreasing the particle size. However, more rigorous studies have been reported to obtain quantitative calibration of bandgap with nanocrystals size.

1.3 Band-edge optical transition

Absorption of a photon by a semiconductor NC generates an electron-hole pair, which is known as exciton. When the electron resides in the bottom of the conduction band and the hole on the top of the valence band, the exciton is known as band-edge exciton and is the lowest excited state. This band-edge electron-hole pair then can recombine via emission of light that is known as band-edge emission. CdSe is one of the most studied II-VI semiconductor NCs and has been discussed here as a representative case study. Figure 1.3 (a) shows the tunable band edge emission spectra of different size CdSe nanocrystals. Bottom of the conduction band, also termed as lowest unoccupied molecular orbital (LUMO), is composed of Cd 5s orbital; whereas, top of the valence band, highest occupied molecular orbital (HOMO) formed from Se 4p orbitals is more complex due to 3-fold spatial degeneracy (Figure 1.3 (b)).
Figure 1.3 (a) Tunable photoluminescence spectra of different size CdSe nanocrystals dispersed in chloroform where the excitation wavelength is 365 nm. (b) (left) the molecular orbitals of the hole (bottom) in the Se\(^{2-}\) electronic system and the electron (top) in the Cd\(^{2+}\) electronic system in a CdSe semiconductor nanoparticle; (right) the band gap (interband or HOMO to LUMO) transition (separating the electron and hole) and the different intraband transitions of the electron (top) and hole (bottom) in a semiconductor nanoparticle. The interband transition is a charge transfer type of transition from the Se\(^{2-}\) molecular orbital (MO) to the Cd\(^{2+}\) MOs to form a delocalized Cd\(^{+}\) and Se\(^{-}\) electronic system in the band gap state. This figure is adapted from reference 17.

In a semiconductor nanoparticle like CdSe, the occupied MOs are made of a linear combination of atomic orbitals on the negatively charged anions (e.g., Se\(^{2-}\)), while the unoccupied MOs are made of atomic orbital on the metallic cations (e.g., Cd\(^{2+}\)) (see Figure 1.3 (b)). Hence, the band gap excitation involves a charge transfer of an electron from the HOMO in the Se\(^{2-}\) electronic system to the vacant LUMO of the Cd\(^{2+}\) (the bottom of the conduction band in the bulk). This creates a hole in the HOMO (which is top of the...
valence band in the bulk). Thus, the holes always occupy the anion MOs, while the excited electrons occupy the cation MOs.\textsuperscript{16,17} Because of this and the high dielectric constant of the semiconductor material, the charge carriers in a semiconductor nanoparticle are weakly coupled and thus are not strongly correlated. Thus, it can be excited, be trapped, and relax nonradiatively almost independently of one another. Furthermore, excitation of the excited electron formed in band gap absorption takes place between different MOs of the metal cation. The holes formed in the band gap absorption can be excited to other higher energy anion MOs. The excitation of either charge carrier formed in the band gap absorption is called the intraband excitation, while the band gap excitation itself is termed the interband excitation. In II-VI semiconductors, the different MOs made from the $n$-$p$ atomic orbitals of the negatively charged anion are much closer to one another in energy than those formed from the five $s$ atomic orbitals on the positively charged cations. For this reason, the electron intraband absorption occurs at higher energy than the hole intraband absorption, which is observed in the infrared region.

In organic molecules, both spin and orbital angular momentum are good quantum numbers but strong spin-orbit coupling ($\Delta = 0.42$ eV) in CdSe lifts the valence band degeneracy, where $J = L + S$ is a good quantum number for hole. Thus, Se $p$ HOMO yields $j = 3/2, 1/2$ subbands. Using the usual notations, the band-edge excitonic state is represented as the $1S(e) - 1S_{3/2}(h)$, where $1S(e)$ and $1S_{3/2}(h)$ represent the electron (e) and hole (h) states, respectively, for a hypothetical spherical nanocrystals with the ZB crystal structure. In reality, generally for wurtzite CdSe nanocrystals are not exactly spherical. Such asymmetry in the crystal field and/or NC shape splits the $1S_{3/2}$ (h) state into $j = \pm 3/2, \pm 1/2$ states, as shown in figure 1.4. On the other hand, bulk semiconductors exhibit a negligible electron-hole exchange splitting in the order of $10^4$ eV, due to extreme delocalization of the electron and hole wavefunctions but in NCs, such exchange interaction can not be neglected because of the stronger overlap of electron and hole wavefunctions as a result of quantum confinement. Electron-hole exchange interaction mixes the electron and hole angular momenta, yielding five excitonic states: $F = \pm 2, \pm 1^L, 0^U$, $\pm 1^U$ and $0^U$, as shown in figure 1.4 (where U and L correspond to the upper ("+" in energy scale) and lower ("-" in energy scale) respectively; F is the total exciton angular momentum projection.\textsuperscript{18,19}
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Figure 1.4 Energy level diagram shows the band-edge exciton fine structure. Asymmetry in crystal field (as in wurtzite structure) and particle shape along with the electron-hole exchange coupling raise the 8-fold degeneracy of $1S(e)-1S_{3/2}(h)$ excitonic state. Five excitonic states are labeled according to the total angular momentum projection along the wurtzite hexagonal axis. $E_{\text{elec}}$, $E_{\text{hole}}$, and $E_{\text{ex}}$ are referred to the energies of the electron, hole and the exciton, respectively. Adapted from reference 18.

This establishment of excitonic fine structure has allowed the understanding of many important fundamental photophysics. Excitonic fine structure shows that $F = \pm 2$ is the ground state with energy only a few meV (0.13 meV for bulk and 13 meV for dots) below the $F = \pm 1^L$. $F = \pm 2$ and $0^L$ are dipole forbidden for optical transitions and are known as "dark" states; while, $\pm 1^L$ excitons have a larger oscillator strength compared to $\pm 1^L$. Thus, $F = \pm 1^L$ excitons correspond to the first band in the linear absorption. After excitation, the excitons reach to the lowest excitonic state, $F = \pm 2$, via fast (~1 ps) nonradiative energy transfer. Optical emission takes place from $F = \pm 2$ state, which has lower energy the absorption state, $F = \pm 1^L$, can explain the stokes shift between absorption and emission spectra. In spite of the fact that exchange coupling in CdSe NCs increases up to 2 orders of magnitude with decreasing particle size, the splitting remains small compared to kT at room temperature. Thus, the dark exciton effects are not seen at room temperature, where the thermalization with the optically active $F = \pm 1^L$ ("bright") excitonic state is rapid and steady-state emission is due to the $\pm 2$ as well as the $\pm 1^L$ excitons.19,21

Excited electron and hole, residing in the HOMO and LUMO, respectively, can recombine by emitting light, known as radiative recombination or by releasing heat, via
nonradiative recombination. Quantum confinement effect results in a stronger overlap between the electron and hole wavefunctions in NCs, increasing the optical transition probability and NCs exhibit higher fluorescence quantum efficiency compared to their bulk counterpart. However, large surface to volume ratio of the sub-10-nm particles give rise to significant amount of surface-defect related electronic states that lie within the band gap. Excited electrons and holes can relax into those states involving nonradiative energy transfer, whereupon they typically undergo either nonradiative or radiative (surface-state emission, characterized by broad FWHM and significantly red shifted from absorption spectrum, generally producing very low quantum efficiency) decay to the ground state.\textsuperscript{22}

Ensemble of NCs exhibit multiexponential decay. Three possible explanations for such a behavior are: (i) each NC has its own unique single-exponential decay, different from other NCs present in the ensemble, (ii) the fluorescence decay of an individual NC is complex multiexponential or (iii) each NC has a single-exponential decay at any given moment but it fluctuates in time, so that the time-averaged fluorescence decay of an individual NC is multiexponential. Figure 1.5a shows the schematic of the corresponding lifetime distribution. After excitation of a NC from ground state $|g\rangle$, to the excited state $|ex\rangle$, both the radiative and nonradiative channels are available for relaxation. The observed decay $k_{\text{obs}}$, is nothing but the sum of radiative ($k_{\text{r}}$) and nonradiative ($k_{\text{nr}}$) decay. Additional acceptor levels $|tr\rangle$, arises mainly from the surface related defect states opens up new nonradiative decay channels reducing the fluorescence intensity and at the same time decreases the excited state lifetime. Instability of acceptor levels on the surface of the NC and/or in the surrounding matrix fluctuate the nonradiative decay channels, $k_{\text{nr}}$, changing the overall fluorescence decay with time.\textsuperscript{23}

Naturally, fluctuation of the fluorescence decay dynamics will lead to the fluctuation in the fluorescence quantum efficiency of the same NC with time. Another important mechanism for nonradiative energy loss in NCs is multiparticle auger recombination, which dominates when more than one exciton per NC is generated. Figure 1.5b schematically explains the auger process. In this process, the electron-hole recombination energy is transferred to a third particle (charge carrier), an electron or a hole, further re-exciting it to a higher energy level within the NC or even outside the NC. The latter case is known as auger ionization. Auger recombination is relatively less significant in bulk
semiconductors because of restrictions imposed by energy and momentum conservation. But in NCs, translation symmetry is broken since the charge carriers feel the NC boundary. Therefore, conservation of translational momentum does not hold good for NCs resulting in an increase in the auger recombination efficiency with a decrease in particle size. Auger recombination time (~ 10 – 400 ps) is much faster than the radiative recombination time (a few ns).^24

![Figure 1.5](image)

**Figure 1.5** (a) Schematic representation of energy levels and transitions in a NC. Adapted from reference 22. (b) Schematic representation of the multiparticle auger recombination. Adapted from reference 23.

Just to mention here that for any lasing action population inversion is essential, which means in a two-state HOMO-LUMO system more than one electron has to be promoted to LUMO. Auger assisted ionization of NCs leads to a very striking phenomenon known as fluorescence blinking. A charged NC already contain an odd electron or hole, on the other hand, upon absorption of photon a new electron-hole pair is generated. In such a situation with a total of three charge carriers in the NC, faster nonradiative auger process dominates instead of emitting light. Thus, the charged NC is termed as “off” state. Fluorescence is recovered when the NC regain neutrality and is known as “on” state. This on-off behavior is known as quantum dot blinking.\(^{25}\)
1.4 Bandgap engineering and heterostructure of semiconductor nanocrystals

The band gap energy, $E_g$, determines many of the semiconductor's properties, and because of this a great deal of interest has been given to band gap engineering as a powerful technique in the development of new semiconductor materials, particularly at the nanoscale. NCs having compositional inhomogeneities across the radius can be termed as heterostructured NCs. One of the most studied NC in this category is core/shell NC. These core/shell materials can be classified into three different categories based on the electronic structure of the material: (a) Type-I, (b) Inverted Type-I and (c) Type-II (Figure 1.6 (a), (b), (c) respectively).

In Type-I structure, the shell has a higher band gap than that of the core material. Very often, a core NC such as CdSe is coated with a higher bandgap inorganic shell material such as ZnS or CdS to form a type-I core/shell NC, where both the electron and hole are confined in the core material, as shown schematically in figure 1.6 (a). Type-I core/shell NCs are mainly prepared to achieve higher photoluminescence (PL) efficiency, compared to organically capped core only NCs. Dangling bonds on the NC surface give rise surface related defect states in the bandgap region. These surface states reduce the PL quantum efficiency by providing additional decay channels for the excited electrons and holes. Shell of higher bandgap inorganic material on top of the core NC removes these surface-related states from the bandgap region and thus improves the PL efficiency. A small red-shift in the absorption and emission spectra is observed for type-I core/shell NCs compared to corresponding core only NCs. Such a red-shift occurs because of the small leakage of electron and hole wavefunctions to shell material and extent of such a red-shift depends upon the band offsets of both electron and hole. Lattice mismatch between the core and shell materials give rise to strain in the core-shell interface and eventually generates misfit dislocations with the growth of shell thickness. Such misfit dislocations can again open up channels for nonradiative recombination of excited electrons and holes, reducing the PL efficiency. It has been observed in the case of CdSe/ZnS NCs, quantum yield initially increases with an increase in shell thickness because of the better passivation of dangling bonds on the core surface and reaches maximum when 1.3 monolayers of ZnS
is grown but further growth of the shell thickness introduces misfit dislocations, reducing quantum yield, as shown in figure 1.7.32

Figure 1.6 Bandedge alignment at the core/shell interface (indicated by dotted vertical lines) for (a) Type-I, (b) Inverted Type-I and (c) Type-II core/shell NCs. VB1 and CB1 correspond to the top of the valence band and bottom of the conduction band of the core, respectively; while, VB2 and CB2 correspond to shell material. EPL is the energy corresponding to the observed photoluminescence.

In inverted type-I systems, a material with smaller bandgap is overgrown onto the core with larger bandgap (Figure 1.6 (b)). Exciton is at least partially delocalized in the shell and the emission wavelength can be tuned by the shell’s thickness. An example of this category ZnSe/CdSe core/shell NCs, where a wide-gap ZnSe core is overcoated with narrow-gap CdSe shell. Here, both the electron and hole will reside in the shell material.33,34 The advantage of Inverted Type-I structure is that its optical property can be tuned from Type-I to Type-II by changing the size of the core or the shell thickness.
Figure 1.7 (a) Absorption and emission spectra of CdSe nanocrystals before and after shelling with ZnS of different thicknesses (in monolayers, ML). Adapted from reference 32 (b) PL quantum yield is plotted as a function of ZnS shelling. Adapted from reference 29.

Unlike Type-I, in Type-II heterostructure the valence and conduction band edges of the core are lower (or higher) than that of the shell material. This leads to a situation where one carrier is mostly confined within the core, and other is confined within the shell (Figure 1.6 (c)). In addition the band gap of the Type-II nanocrystals can effectively be controlled by the band offsets of core and shell, and thus fundamentally one should expect that these nanocrystals may show novel properties which, otherwise, can not be achieved by either single core or shell. Spatial separation between electrons and holes is an essential requirement in photovoltaic cell and hence, type-II semiconductor NCs find easy application in photovoltaic technologies. Since the bandedge transition energy in the type-II structure is smaller ($E_{12} < E_{core}$ and $E_{shell}$, in figure 1.6c) than the energy gap of both the core and shell material, these NCs can be used to obtain infrared emission using combinations of well studied wide-gap semiconductors. Finally, Klimov et al. made a landmark development in the NC lasing by using type-II heterostructures, which uniquely allowed them to obtain optical gain in the single-exciton regime that eliminates the
problem of Auger decay. On the other hand, the slow recombination dynamics leads to very low photoluminescence quantum yield (QY), which is the drawback of these materials.

Alloyed nanocrystals are another good example of band gap engineering in solution. These nanocrystals have the advantages that their band gap can be tailored by changing both particle size, and also by changing the particle composition via control of constituent stoichiometries. Thus in this case it is possible to get different photoluminescence color just by changing the composition of the nanocrystals keeping the size unchanged. Alloyed semiconductor nanocrystals can be classified as having (i) a uniform structure (i.e., homogenous) or (ii) a gradient internal structure where the composition changes at the different region of the nanocrystal.

1.5 Preparation of nanocrystals

One of the largest activities in this field over the past a few decades and till date remained the synthesis of high quality NCs of desired size. High quality nanocrystals generally refers to better monodispersity of particles size, good crystallinity, electronically and chemically passivated NC surface etc. There are two different approaches to synthesize nanocrystals: “top-down” approach and “bottom-up” approach. Top-down approach generally uses physical methods, producing a larger quantity of NCs, whereas the synthesis of uniform-sized nanocrystals and their size control is very difficult to achieve. But for, bottom-up approach employs solution-phase colloidal chemistry to synthesize uniform nanocrystals with controlled particle size, but generally less quantities are produced. Furthermore, NCs of various shape, composition and heterostructures, can be controlled easily using the colloidal route. Semiconductor NCs have been prepared via a variety of physical methods like molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), vapor liquid solid (VLS), laser exfoliation, etc. However, the works presented in this thesis are based on colloidal synthesis of II-VI semiconductor NCs and hence colloidal synthesis of such NCs will be discussed in this section.

Colloidal synthesis of NCs inevitably involves the process of precipitation of a solid phase from solution. Such an initiation of a phase change in a small region is known as
nucleation. A given solute has certain solubility for a particular solvent, thus for nucleation to occur, the solution must be supersaturated by adding the necessary amounts of required precursors during the reaction. Thus, the preparation of NCs usually comprises of two basic steps, namely, nucleation step followed by particle growth. Growth is nothing but the addition of solute to the already formed nuclei, resulting in an increase in particle size.

**Nucleation and growth**

There are two kinds of primary nucleation processes: homogeneous nucleation and heterogeneous nucleation; then there is also secondary nucleation. Homogenous nucleation takes place without the influence of any solid substance, for example, formation of CdSe nuclei in a solution containing Cd and Se precursors; whereas, heterogeneous nucleation is caused by foreign substances, which make the nucleation possible by increasing the rate of nucleation, for example, nucleation of shell material in the presence of already formed core NCs in a synthesis of core/shell NCs.

![Figure 1.8 Schematic diagram illustrating LaMer’s condition for nucleation. \(C_s\): solubility; \(C_{\text{min}}\): minimum concentration for nucleation; \(C_{\text{max}}\): maximum concentration for nucleation; I: prenucleation period; II: nucleation period; III: growth period. Adapted from reference 41.](image-url)
Figure 1.8 represents the famous LaMer diagram, which tells the nucleation and growth of colloids or NCs from a homogeneous, super-saturated medium. The concentration of solute (monomers) is built up in Stage-I, for example by decomposition of precursors generating the monomers. Nucleation does not take place during this step. When the monomer concentration C reaches $C_{\text{min}}$ the nucleation starts, which is specified as Stage-II. C still increases for a while and then decreases because of consumption of monomers by the pronounced nucleation. The nucleation then stops when C becomes less than $C_{\text{min}}$. Thus, $C_{\text{min}}$ is the critical concentration required for nucleation to start, below which, there is no nucleation. Remaining monomers then add on to the existing particles, leading the growth process, as represented by stage-III. Growth continues until the concentration of monomer is lowered close to the solubility level $C_s$. If the nucleation is very small, monomer concentration C lingers in between $C_{\text{min}}$ and $C_{\text{max}}$ for a longer time, which will lead to the coexistence nucleation and growth at the same time. In such a condition, a broad size distribution will be obtained. Thus the essential requirement to synthesis NCs with narrow size distribution is to separate the nucleation and growth processes. Injection of room temperature precursor solution to the hot reaction mixture results in thermal decomposition of the precursor reagents and sudden burst of nucleation take place. When the formed monomer concentration drops below a critical threshold, nucleation stops and remaining monomers add on to the existing particles, leading the growth process. The sudden temperature drop associated with injection of room temperature reagents also prevents further nucleation.

Growth processes mainly governed by two factors: diffusion of monomer toward the surface and the reaction of monomers on the surface. If the diffusion process is the rate determining step, then the growth is called diffusion-controlled growth, on the other hand if the growth rate is limited by the surface reaction of monomers, it is termed as reaction controlled growth. However, there also exists an intermediate regime, where growth process does not obey any one of the above mentioned two limits, instead has significant contributions from diffusion and surface reaction. But it has been shown that diffusion-controlled growth process is predominantly observed in the synthesis of mono-dispersed semiconductor NCs. The growth rate strongly depends upon size of the NC and for any given monomer concentration, there exists a critical size, which is at equilibrium. NCs
with size smaller than the critical size dissolve (negative growth rate), while larger ones grow at different rates depending on their size. When the size of NCs is slightly larger than the critical size, smaller particles in the distribution grow faster than the larger particles, this leads to the focusing of size distribution. After a certain time, the monomer concentration get depleted because of growth process and the critical radius becomes larger than the average size of present NCs; thus, distribution broadens since some of smaller NCs begin to shrink and eventually dissolve in favor of growth of larger particles. This is known as Ostwald ripening, which lead defocusing of particle size distribution. Injection of additional monomer at the growth temperature shifts the critical size back to a smaller value leading to a refocusing of size distribution. One can get rid off Ostwald ripening by adding additional monomer after nucleation is over but before the Ostwald growth begins. The concentration of the additional monomer has to be lower than the critical concentration of nucleation, such that additional monomers do not initiate any nucleation, instead, add to the existing particle and promote relatively faster particle growth.

1.6 Transition metal doped semiconductor nanocrystal (d-dot)

Different types of nanocrystals with different photo-physical properties are described above. Apart from this, these nanocrystals show less thermal stability, self-absorption and also photo-bleaching which makes them less reliable for wide spread applications. Therefore, the extreme search for alternate and environment kind system has been focused to develop new materials which can provide similar intense and tunable emission with or without having Cd like heavy metals, and also possibly be associated with some additional new properties. One such possibility is deliberate introduction of very small amount of optically active different transition metal ion impurities in semiconductor nanocrystal hosts. These newly developed doped materials (d-dots) show their potentials as an alternative of highly emitting Cd–based nanocrystals and they can be used for various applications like LED and display devices, spintronics and biomedical imaging. Doped semiconductor nanocrystals show several advantages over the normal quantum dot which suffers from several disadvantages such as thermal instability, self-absorption and toxicity. Thus d-dots are promising new materials for several applications. The emission results
from q-dots is band edge emission (Figure 1.9a) where stokes shift is very less. Hence some part of the emission energy is absorbed by the other molecules which are in the ground state and thus reducing the quantum efficiency. But doped semiconductor are devoid of this emission quenching problem due to large stokes shift as shown in Figure 1.9b as the exciton recombination process in doping dots is different from the traditional quantum dots.\textsuperscript{51-54}

![Figure 1.9 Typical absorption and emission spectra of CdSe (a) and Mn doped ZnS nanocrystal (b). The CdSe QDs show very small stokes shift whereas the Mn:ZnS nanocrystals show large stokes shift.](image)

To get different interesting properties related with the d-dots, it is obvious to introduce dopant ions inside the hosts as the optical properties of the d-dots highly dependent on the environment of the dopant ions. However, it is very difficult to get homogeneously doped nanocrystals as there is always a possibility to get undoped host nanocrystals. In addition, when the size of the crystal reduces to the nanometer regime, it is relatively more difficult to dope the dopant ions compared to the bulk counterpart. For example, some compound which could be easily doped in bulk form is rather un-dopable in quantum confined size regime. However, for all practical applications uniformly doped nanocrystals are required. In order to get homogenously doped nanocrystals in solution it is important to decouple the doping process from the host nucleation and/or growth process and for this different synthetic strategies are developed: nucleation doping and growth doping.
1.6.1 Nucleation doping

In this technique, dopant nanoclusters are synthesized first which are then overcoated with the host precursors (Figure 1.10a). This procedure ensures uniform doping as the host nanocrystals are grown on the dopant core. For example, high quality Mn doped ZnSe nanocrystals are synthesized following nucleation doping strategy. First, MnSe nanoclusters are synthesized and then zinc precursor is injected to overcoat the dopant core to get high quality doped nanocrystals which emit orange yellow emission upon UV-radiation. However, there is always a chance for separate nucleation of the host nanocrystals. Therefore it is extremely important to optimize the reaction condition to avoid separate nucleation of the host nanocrystals. For Mn doped ZnSe nanocrystals, during the overcoating of ZnSe using Zn-carboxylate salt, always calculated amount of corresponding carboxylic acid is injected to reduce the reaction rate of Zn-carboxylate to avoid separate nucleation of ZnSe nanoparticles.$^{55,56}$

![Figure 1.10](image-url) Schematic representation of two different doping strategies; (a) Nucleation and (b) growth doping.
1.6.2 Growth Doping

In growth doping technique, dopant ions are chemically embedded on the growing host nanocrystals as shown in Figure 1.10b. At first, a small size host nanocrystal is synthesized and then dopant ions are introduced which are adsorbed on the surface of the host. These surface doped nanocrystals are then further over-coated with the host precursors to get uniform doped nanocrystals. From the past literature it has been observed that the dopant ion adsorption occurs on the particular facet of the host nanocrystals which depends on the binding energy of the dopant ions with that particular surface. For example, in Mn doped ZnSe nanocrystals, the Mn$^{2+}$ dopant ions bind on (001) facets of zincblende (ZB) structure and then further growth of the ZnSe buried them inside the nanocrystals.$^{35}$

1.6.3 Electronic structure of Mn$^{2+}$ ions in II-VI semiconductor lattices

A major motivation for investigation of transition metal doped semiconductors has been the use of luminescence activators such as Mn$^{2+}$ or Cu$^{2+}$ for sensitized photoluminescence and electroluminescence applications last two decade. Mn$^{2+}$ is among the most common dopants for luminescence applications, and Mn$^{2+}$ doped ZnS for example is a widely used commercial phosphor. In most cases, like Mn$^{2+}$:ZnS, the large absorption cross sections of the semiconductor host lattices combine with rapid energy transfer to the dopants to yield efficient sensitized Mn$^{2+}$ emission.$^{57}$ Bulk semiconductors are doped at very high temperatures (> 1100 °C), whereas, synthesis temperature of colloidal NCs are restricted to a higher limit of ~320 °C because of the boiling points of the organic chemicals used and the size of the NCs becomes larger than quantum confinement regime at higher temperature. Doping Mn$^{2+}$ in semiconductor NCs was first achieved by low temperature synthetic methods, such as room-temperature condensation of organometallic precursor in presence of coordinating surfactant or room-temperature inverse-micelle methods.$^{52,58}$ But NCs prepared at low temperature exhibit poor crystallinity and hence poor physical properties, for example, low PL efficiency. When the reaction temperature was increased, the products became more crystalline but at the same time the dopant impurities were excluded from the NC core towards the surface, a phenomenon, known as self-purification. These synthetic challenges to dope a
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semiconductor NC provided fertile grounds to chemists for investigating the homogeneous nucleation and crystal growth in the presence of impurity.

The local electronic structures of Mn$^{2+}$ ions in such II-VI semiconductor crystals are generally described well by ligand field theory. The most stable free-ion electronic configuration of Mn$^{2+}$ corresponds to the five 3d orbitals being uniformly filled with one electron each, which leads to an orbitally non-degenerate spin sextet ground state ($6S$, $S = 5/2$, $L = 0$). Because the 3d orbitals are half filled, all excitations within the 3d manifold must be associated with spin-flip transitions at energies approximately 3 eV above the ground state, with the major consequence that there are no spin-conserving transitions from the 6S ground state. This situation remains true in tetrahedral (or pseudo-tetrahedral) ligand fields, which are encountered in the cationic sites of every II-VI semiconductor lattice.$^{59}$

![Figure 1.11](image)

**Figure 1.11** (a) Approximate evaluation between band gap energies of common II-VI semiconductor and the energy of the Mn$^{2+}$ $^4T_1$ ligand-field excited state (~2.1–2.2 eV, dotted line) in these lattices (Mn$^{2+}$ has an anomalously high $E(4T_1) \sim 3$ eV in ZnO). The principal electronic configurations relevant to the ligand field luminescence transition of Mn$^{2+}$ are shown at the bottom. Adapted from reference 59 (b) Tanabe-Sugano ligand field energy level diagram for Mn$^{2+}$ (d5) in a cubic ligand field, showing several of the lowest ligand-field excited states, and indicating the emissive $^4T_1 \rightarrow ^6A_1$ transition observed in many Mn$^{2+}$ doped II-VI semiconductor nanocrystals. Adapted from reference 60.
The tetrahedral ligand field provided by the four anions around the cation in II-VI semiconductors removes the fivefold degeneracy of the 3d orbitals, splitting them into a twofold degenerate \( e \) set (\( d_{xy} \) and \( d_{yz} \)) and a threefold degenerate \( t_2 \) set (\( d_{zx}, d_{yz}, \) and \( d_{zx} \)). The energy difference between the more stable \( e \) and the less stable \( t_2 \) sets is defined as \( \Delta \) (\( \Delta \propto D_q \)), which, for a given cation, depends on the ligands surrounding it. Because of the high energy associated with spin pairing, the lowest energy \( \text{Mn}^{2+} \) configuration in every II-VI lattice corresponds to a uniform filling of the five 3d orbitals, as illustrated at the bottom of Figure 1.11a. The lowest energy \( \text{Mn}^{2+} \) excited-state configuration corresponds to the promotion of one \( t_2 \) electron down into the \( e \) set, where it must be paired with another electron. The first configuration gives rise to the ground state \( ^6A_1 \), whereas the lowest-energy excited state (the splitting of the 5-fold degenerate 3d orbitals into \( t_2 \) and \( e \) sets splits the orbital degeneracy of the \( 4G \) and higher-energy free-ion terms) derived from the second configuration is a \( ^4T_1 \) state. These two states are responsible for the characteristic PL of \( \text{Mn}^{2+} \) ions in doped crystals, namely, the \( ^4T_1 \rightarrow ^6A_1 \) ligand field transition. The lowest-energy ligand field excited state in weak cubic fields is the \( ^4T_1 \) state, which is further split by axial low symmetry, spin-orbit, and Jahn-Teller interactions. The \( ^4T_1 \rightarrow ^6A_1 \) ligand field transition, marked with an arrow in the cubic energy-level diagram of Figure 1.11b, is responsible for the characteristic luminescence of \( \text{Mn}^{2+} \) ions in doped II-VI. Increasing \( \Delta \) has the effect of destabilizing the ground state configuration while stabilizing the excited state configuration, leading to the negative slope of the \( ^4T_1 \) excited state energy relative to the \( ^6A_1 \) ground state as illustrated in the ligand-field energy level diagram of Figure 1.11b. The negative dependence on \( \Delta \) is responsible for the shift of the \( ^4T_1 \rightarrow ^6A_1 \) transition to lower energies with decreasing lattice parameter across each II-VI series sharing a common anion (e.g., \( \text{ZnS} \rightarrow \text{CdS} \), crystals. Although formally forbidden by spin selection rules, the \( ^4T_1 \rightarrow ^6A_1 \) transition can gain some intensity by spin-orbit coupling at the \( \text{Mn}^{2+} \) (\( \zeta = 300 \text{ cm}^{-1} \) for the free \( \text{Mn}^{2+} \) ion), and to a lesser extent also at the coordinated anion (e.g., \( \zeta(S^{2-}) = 300 \text{ cm}^{-1}, \zeta(Se^{2-}) = 1400 \text{ cm}^{-1}, \zeta(Te^{2-}) = 3600 \text{ cm}^{-1} \)). Spin-orbit coupling for \( \text{Mn}^{2+} \) is too weak to mix strongly the spin states, and transitions between the \( ^6A_1 \) ground state and all ligand-field excited states remain only weakly allowed. As a result, the oscillator strength of the \( ^6A_1 \rightarrow ^4T_1 \) transition is on the order of \( 10^{-6} \rightarrow 10^{-5} \), corresponding to a \( ^4T_1 \rightarrow ^6A_1 \) radiative transition rate constant of \( \sim 10^{-2} \rightarrow 10^{-3} \text{ s}^{-1} \).
or a radiative lifetime of $\tau = 0.1-1.0$ ms. Anion spin-orbit contributions decrease this radiative lifetime e.g. for Mn$^{2+}$ dope ZnS the radiative lifetime is $\sim 1.8$ ms while for Mn$^{2+}$ doped ZnSe this is 8 time less $\sim 0.2$ ms. With such low oscillator strengths, Mn$^{2+}$ ligand-field transitions are typically not observed in electronic absorption spectra of dilute doped crystals unless long optical path lengths are used.$^{60-64}$

1.6.4 Electronic transition of Mn$^{2+}$ ions in II-VI semiconductor host

Mn$^{2+}$ doped II-VI semiconductor nanocrystals are systematized into three distinct categories according to the nature of their lowest energy excited state, which determines their resulting photo-physical properties. These three situation termed as Situation-I, Situation-II and Situation-III.

**Situation-I: Mn$^{2+}$ photoionization excited states are lowest in energy and within the gap**

This situation occurs in wide-gap semiconductors, where the existence of donor or acceptor type photoionization states within the gap can introduce nonradiative relaxation pathways that entirely quench the nanocrystal emission. Among Mn$^{2+}$-doped II-VI semiconductors, the presence of such levels within the gap appears to occur only for Mn$^{2+}$-doped ZnO. Still now Mn$^{2+}$ 4$^2$T$_1$-$^6$A$_1$ emission has not been observed in Mn$^{2+}$:ZnO QDs. The PL attributed to the Mn$^{2+}$ 4$^2$T$_1$-$^6$A$_1$ ligand field transition in nanocrystalline Mn$^{2+}$:ZnO powders is indistinguishable from the visible surface trap emission, and it is likely that this is not Mn$^{2+}$ ligand-field emission. This transition has instead been assigned as a donor-type photoionization transition (Mn$^{2+}$ $\rightarrow$ Mn$^{3+}$ + e$_{CB}$, or ML$_{CB}$CT) of Mn$^{2+}$:ZnO on the basis of optical electronegativity considerations, and the ligand-field transitions are likely obscured by this band because of the $10^2$–$10^3$ difference in extinction coefficients. This charge-transfer excited state configuration is formally equivalent to a hole-trapped exciton and is related to proposed Zhang–Rice-like states in p-type Mn$^{2+}$:ZnO. Because this photoionization state is the lowest energy excited state, it largely defines the photophysical properties of Mn$^{2+}$:ZnO nanocrystals. Specifically, it provides an efficient pathway for nonradiative relaxation back to the ground state, as in Figure 1.12 (left panel). The details
of this nonradiative relaxation are not yet understood, but multi-phonon relaxation often makes the greatest contribution to the overall nonradiative relaxation rate constant.\textsuperscript{65,66}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1_12.png}
\caption{Schematic presentation of different electronic transition related of Mn\textsuperscript{2+} doped semiconductor nanocrystals. In the first situation (I), excitons are quenched by Mn\textsuperscript{2+} photoionization states which relax nonradiatively to the ground state. In the second situation (II), efficient energy transfer to the Mn\textsuperscript{2+} and quenches excitonic emission and sensitizes Mn\textsuperscript{2+} \textsuperscript{6}A\textsubscript{1}, \textsuperscript{4}T\textsubscript{1} emission. In the third situation (III), all Mn\textsuperscript{2+} excited states are situated outside of the bandgap, and the nanocrystals show excitonic emission. Adopted from reference 60.}
\end{figure}

\textbf{Situation-II: Mn\textsuperscript{2+} ligand-field excited states are lowest in energy and within the gap}

The most commonly studied of Mn\textsuperscript{2+}-doped semiconductor nanocrystals are those where the Mn\textsuperscript{2+} ligand-field excited states reside within the band gap of the host semiconductor. The ground state of Mn\textsuperscript{2+} is \textsuperscript{6}A\textsubscript{1} and first ligand-field excited state is \textsuperscript{4}T\textsubscript{1} derived from the 4G free ion term. Transitions from the \textsuperscript{6}A\textsubscript{1} ground state to this ligand-field excited state are spin forbidden and gain only slight allowedness through spin–orbit coupling. This is the transition most commonly described in PL studies of Mn\textsuperscript{2+} doped semiconductor
nanocrystals (Figure 1.12 middle panel). The large energy gap between the \(^4T_1\) excited state and the ground state contributes to the high PL quantum yields and nearly radiative excited state lifetimes that can be achieved in Mn\(^{2+}\) doped nanocrystals of this type. \(^4T_1\) to \(^6A_1\) energy gap is very large compared to the low phonon energies provided by most II–VI semiconductor lattices restricting the nonradiative recombination of the electron-hole pair involving these Mn\(^{2+}\) states resulting in strong PL efficiency of this \(^4T_1 \rightarrow ^6A_1\) transition.  

Figure 1.13 Low-temperature (5 K) photoluminescence spectra of colloidal \(d = 2.5\)nm(top) and \(d = 4.2\) nm (bottom) Mn\(^{2+}\):CdSe quantum dots. The dotted line marks the energy of the Mn\(^{2+}\) emission maximum (2.11 eV), which is observed only in small Mn\(^{2+}\):CdSe QDs. Adopted from reference 60.

**Situation-III: Semiconductor conduction band is lowest in energy (Mn\(^{2+}\) ligand-field excited states are outside the gap)**

This third situation can be identified when no impurity states exist within the gap of the host semiconductor and the conduction band is lower than Mn\(^{2+}\) excited state (Figure 1.12 right panel). These observation was made for colloidal Mn\(^{2+}\):CdSe QDs. The colloidal Mn\(^{2+}\):CdSe QDs differ from all other colloidal doped semiconductor nanocrystals reported to date in that are the first that have allowed tuning of the semiconductor band gap energy across the dopant excited state levels. Fig. 1.13 presents PL spectra of small (d=2.5 nm) and large (d=4.2 nm) Mn\(^{2+}\):CdSe QDs. The characteristic Mn\(^{2+}\) emission is observed when
the bandgap energy (conduction band) is greater than the Mn$^{2+}$ $^4T_1$ excited state energy, but only excitonic emission is observed when the conduction is reduced to below the $^4T_1$ energy in larger Mn$^{2+}$:CdSe QDs. The excitonic emission observed in the small Mn$^{2+}$:CdSe nanocrystal sample arises predominantly from undoped nanocrystals, which occur with greater probability as the nanocrystal diameter is reduced.$^{60,63}$

1.6.5 Other transition metal ion doped semiconductor nanocrystals

Insertion of transition metal dopants (e.g., Mn, Cu ions, etc.) creates intermediate energy state/s between the valence and conduction band of host semiconductor nanocrystal and changes its photophysical relaxation process. As a result, the dopant emission evolves with new optical properties whose nature and position vary with that of chosen hosts and dopants. For Mn-doped nanocrystals, the dopant emission has been restricted within the yellow-orange spectral window, but in case of Cu doping, a wide range of tunable emission has been observed due to the tunability of the size of the hosts.$^{55,70-74}$ As compared to the Mn-doped system, the study of Cu doping is still in a very nascent stage, even though it was reported decades before. The insensitivity of the dopant emission energy to the particle size is due to the fact that these electronic transitions involve wave functions localized on the dopant cation and the neighboring ligand anions. The localized wave functions are not influenced by quantum size effects. For other dopant ions emission of light may involve recombination of a delocalized charge carrier and the dopant. The emission from Cu$^{2+}$ centers in ZnS and ZnSe is assigned to recombination of a delocalized electron (in the conduction band or a shallow trap) with Cu$^{2+}$ (Figure 1.14).$^{55,75}$ These dopants form deep trap levels and act as luminescence centers. Literature reports on Cu-doped nanocrystal hosts show, for example, ZnS results in blue-green emission, in ZnSe it is a little more extended to greenish yellow spectral window, in CdS it is orange-red, and in InP, it has been extended to near IR.$^{76,77}$

Except Cu there is other dopant ion which is used for electronic dopant ion. Electronic impurity doping is the process in which impurity atoms are intentionally added to bulk semiconductors to provide either extra electrons (n-type doping) or extra holes (p-type doping). The carriers’ then enable electrical transport through an otherwise poorly
conducting material. However, studies of electronic impurity doping in colloidal nanocrystals have been fairly limited. Development has been impeded by the broader synthetic challenge of incorporating an impurity into a nanoscale particle. While progress has been made with magnetic substitutional impurities in II–VI semiconductor nanocrystals, these dopants (e.g., Mn and Co) are isovalent with the cations that they replace, and no additional carriers are introduced.\(^78,79\) Recently, efforts have attempted to incorporate heterovalent impurities that can provide these carriers, most notably in InAs.\(^80\) In Cu-, Ag-, and Au-doped samples, shifts in the valence and conduction bands were observed through scanning tunneling microscopy on individual nanocrystals, and a simple model assuming interstitial Cu and substitutional Ag and Au was proposed. These electronic doping not only changes the optical properties of the host also changes the other properties like magnetic, electronic etc.\(^81\)

1.7 Scope of the present work

Doped semiconductor nanocrystals are the potential alternative nanocrystal emitters which are substantially different from QDs. Even though there are several successful reports on Mn and Cu doped nanocrystals in various group II–VI and III–V semiconductor
hosts, but the origin of doping, mechanism of dopant insertion and stability of impurity in host lattice, crystal phase dependent dopant adsorption, the allowed photo-physical recombination process, different properties of dopant emission, tuning the dopant energy state, and study of the allowed transition processes etc. are not yet clear. **Chapter 2** is divided in two parts where in the first part the synthesis methods of different types of high quality colloidal nanocrystals are described. In the second part different types of experimental techniques used for the characterization of the nanocrystals are described.

In **Chapter 3** of this thesis, doping of Cu$^{2+}$ in a ZnSe host nanocrystal and stabilization of their emission are discussed. It has been observed, unfortunately the Cu dopant emission suffers from a serious photostability problem because of photooxidation in the presence of air and light. Hence the emission resulting from Cu doped ZnSe degrades nearly to a non-emissive state on exposure of a few seconds in air, making even the usual spectroscopic measurements difficult. In order to address such issues while simultaneously achieving a technologically important milestone of obtaining stable photoluminescence from Cu doped samples, we analyzed the Cu doping in ZnSe nanocrystals thoroughly. We found here that the photo-oxidation facilitated by surface selenium atoms is the root cause of quenching of the Cu dopant emission and this is successfully protected against by introducing a calculated amount of S anions towards the end of the growth of doped nanocrystals.

Although doped semiconductor are strong candidate to replace the Cd-based nanocrystal emitter and in between different transition metal dopant ion Mn$^{2+}$ is the well-studied. But for Mn$^{2+}$ doped non-cadmium and selenium based material is only ZnS which is well studied. But the size of the particle is very small ~4.5 nm. Growing of the larger size nanocrystal is difficult to synthesis in colloidal method. In **Chapter 4** we report the synthesis of large size ZnS nanocrystal by colloidal method and also doping with Mn$^{2+}$ ion. We use here the different sulfur precursor e.g. thiourea, thioacetamide etc. These precursors are formed a different complex in presence of amine and release the sulfide ion to grow the nanocrystals larger.

After having the high quality Mn and Cu doped semiconductor nanocrystals, we move to the other transition metal which can also doped in the different semiconductor nanocrystals. In **Chapter 5** we discussed about synthesis and characterization Ni$^{2+}$, Cr$^{3+}$,
Ag$^{+1}$ doped different semiconductor host nanocrystals (ZnSe, CdZnS, CuInS$_2$ etc.). These dopant ions create their own state near the valence band of the host nanocrystals. Depending of the dopant state the emission is tuned from their own visible window.

These transition metal dopant emission is tunable depending of the host, except Mn$^{2+}$ which is non-tunable. To study the photo-physical recombination process we put two dopant ions in one semiconductor nanocrystals where one is Mn$^{2+}$ and another is Cu$^{2+}$. As two dopant ions are there we expect two emission but we got only one emission. We studied this single emission in Chapter 6. Not only Mn and Cu also we put two same kind of dopant ion like Ag-Cu, Ag-Ni there also we got single emission. From their emission properties we studied how the exciton recombines in dual doped semiconductor nanocrystals. The summary of all the results are described in Chapter 7.
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Bibliography

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