International Journal on Emerging Technologies **10**(1): 16-34(2019)

ISSN No. (Print) : 0975-8364
ISSN No. (Online) : 2249-3255

Development of Colloidal Semiconductor Nanocrystals: Synthesis, Properties and their Outlook for Light Emitting Diodes (LEDs)

Manpreet Kaur*[1]*, Paviter Singh*[1]*, Gurpreet Kaur*[1]*, Manjot Kaur*[1]*, Jeewan Sharma*[1]*, Manjeet Kumar*[2]*,
***Manoj Sharma*[3] *and Akshay Kumar*[1]**

[1]*Advanced Functional Materials Laboratory, Department of Nanotechnology, Sri Guru Granth Sahib World University,*
Fatehgarh Sahib-140406, India
[2]*Department of Electrical Engineering, Incheon National University, South Korea*
[3]*LUMINOUS! Center of Excellence for Semiconductor Lighting and Displays, School of Electrical and Electronics Engineering, School of Physical and Mathematical Sciences, School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue 639798, Singapore.*

(Corresponding author: Akshay Kumar, akshaykumar.tiet@gmail.com*)*

(Received 16 November 2018, Revised 02 February 2019 Accepted 08 February 2019)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: In recent years, the optimum properties of colloidal nanocrystals have widespread its usage in electronics and optoelectronics applications. The advancement in synthesis enables control over the size, shape, crystal structure and composition of nanocrystals. It facilitates control over optical and physical properties of colloidal nanocrystals. They have tremendous potential to be used in different applications. This review focuses on recent progress in the study of colloidal semiconductor nanocrystals. Here, we review the advances in the synthesis techniques, optical properties, surface modification with ligand treatment and doping in colloidal semiconductor nanocrystals. This enables their use in various applications such as light emitting diodes, lasers, solar cells, biomedical labelling and gas sensors. Literature studies reveal that the incorporation of any impurity element or defect into semiconductor affects its optical properties as well other physical properties. Binary semiconductor nanocrystals from different groups have high degree of ionicity making them suitable for various applications. With the advancement in technology, ternary semiconductor nanocrystals have replaced the binary nanocrystals as they possess tunable emission in the visible region of spectrum. In this review, we have summarized different ternary semiconductor nanocrystals which have been applied in light emitting diodes, biosensor, imaging, solar cell and drug delivery.

Keywords: Semiconductor nanocrystals, optical properties, binary nanocrystals, ternary nanocrystals, tunable emission

I. INTRODUCTION

Light emitting diodes (LEDs) have drawninordinateconsideration in research field as well in industries due to its energy saving potential. Their remarkable characteristics make them efficient for use in artificial lighting and displays. Now a days, white light emitting diodes (WLEDs) have been attained by integrating color converting material with commercial available blue LEDs. Previously, phosphor doped rare earth elements have been used along with blue LEDs to generate WLEDs which were inefficient. Semiconductor nanocrystal quantum dots exhibit the potential to replace therare earth phosphors as they possess high color rendering index (CRI), high luminous efficacy (LE), solution processibility, tunablecolor and their raw material is abundant in nature. WLEDs have replaced traditional light emitting systems (incandescent bulbs and CFLs) as they possess long lifetime and great economic significance. In order to achieve the full potential of WLEDs, advanced technologies must be developed to produce a high quality white light that is highly efficient, has a long lifetime, and is cost competitive. So the ideal WLEDs should emit a broad spectrum of white light that is similar to natural sunlight and most appealing to the human eyes. Based on the recent developments in semiconductor nanocrystals-based solid-state lighting (WLEDs), three different approaches are used to generate white light i.e. discrete color mixing, color conversion, and direct white light generation. The WLEDs first generated in 1996 were phosphor based. Semiconductor nanocrystal quantum dots exhibit the potential to replace therare earth phosphors as they possess high CRI, high LE, solution processibility, tunable color and their raw material is abundant in nature. As ideal white LEDs (WLEDs) should be highly efficient, cost competitive, having a long lifetime, hence high-efficiency light conversion materials are intensively required. The quality of white light generated from WLEDs can be evaluated by using several parameters, such as Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, color rendering index (CRI), correlated color temperature (CCT), and luminous efficacy (LE). The color rendering index mainly tests the color rendering ability of any test light source with respect to a reference light source. The reference source in such cases is assumed to possess perfect color rendition. The best CRI is considered as 100 whereas -100 is the representation of the worst color rendition. The CQS is the improved parameter as compare to CRI which is used to calculate the performance of the final color rendering of any light source with the scale lies between 0 to 100. Another parameter is correlated color temperature which defines the temperature of light source being tested. The warmer white light possess CCT value between 3000 and 4500 K is mostly desirable for use indoor lighting applications. This review will focus on the development of the semiconductor nanomaterials and their use in Semiconductor nanocrystals (NCs) exhibiting size dependent optical and electronic properties have been intensely investigated and developed for use in diverse applications i.e. optoelectronic devices, solar energy conversion, bioimaging and targeted drug delivery [1,2]. Quantum dots (QDs) are those three-dimensionally confined nano-crystalline semiconductor materials whose radius is equal to or less than the exciton bohr radius. Thus, quantum dots exhibit distinctive properties as a function of its size. The confined exciton in semiconductor precisely tune the band gap energy which depends upon the dimensionality and degree of confinement [3]. As emiconductor QD comprises atoms of group II–VI elements (e.g., CdTe, CdSe, CdS, ZnS, ZnSe, or ZnTe), group III–V elements (e.g., InP or InAs), group IV–VI elements (e.g., PbSe, PbS, or PbTe), or group IV elements (e.g., Si, C, or Ge).

Doping of transition elements is an important aspect to tune the properties of colloidal nanocrystals. The major problem in undoped semiconductor nanocrystals is the self-absorption. Therefore, transition metal ions-doped semiconductor NCs are increasingly being investigated. Doping of an impurity atom to the host matrix perturb the crystal structure by creating local quantum states light emitting diodes.

within the band gap of the material. Various transition atoms have been doped into the host matrix including Mn, Cu, Ag, Fe, Co etc. It is the amount of impurity element and its position in the structure that effects the properties of the nanocrystals. Along with maintaining the intrinsic advantages of QDs, the doped nanocrystals exhibit additional merits such as, large stokes shift, enhanced chemical and thermal stability, minimizes the issue of self-absorbance and longer state lifetime [4-5]. The main feature of dopant emission is that the energy is red shifted with respect to band gap energy of the host material which leads to overcome the problem of self-absorbance of dopant emission by host. The dopant or transition metal ions introduce discrete energy states or deep trap levels within the band gap of host semiconductor, which act as luminescent centers. As a result, they show different emission mechanisms as depicted in Fig. 1. For example, Mn^{2+} doped nanocrystals show emission in yellow-orange spectral window (580-600 nm) due to $^4T_1$–$^6A_1$ transition [6-7] and Cu doped nanocrystals shows tunable emission over the visible region that depends on the nature, composition and size of host nanocrystals [8].

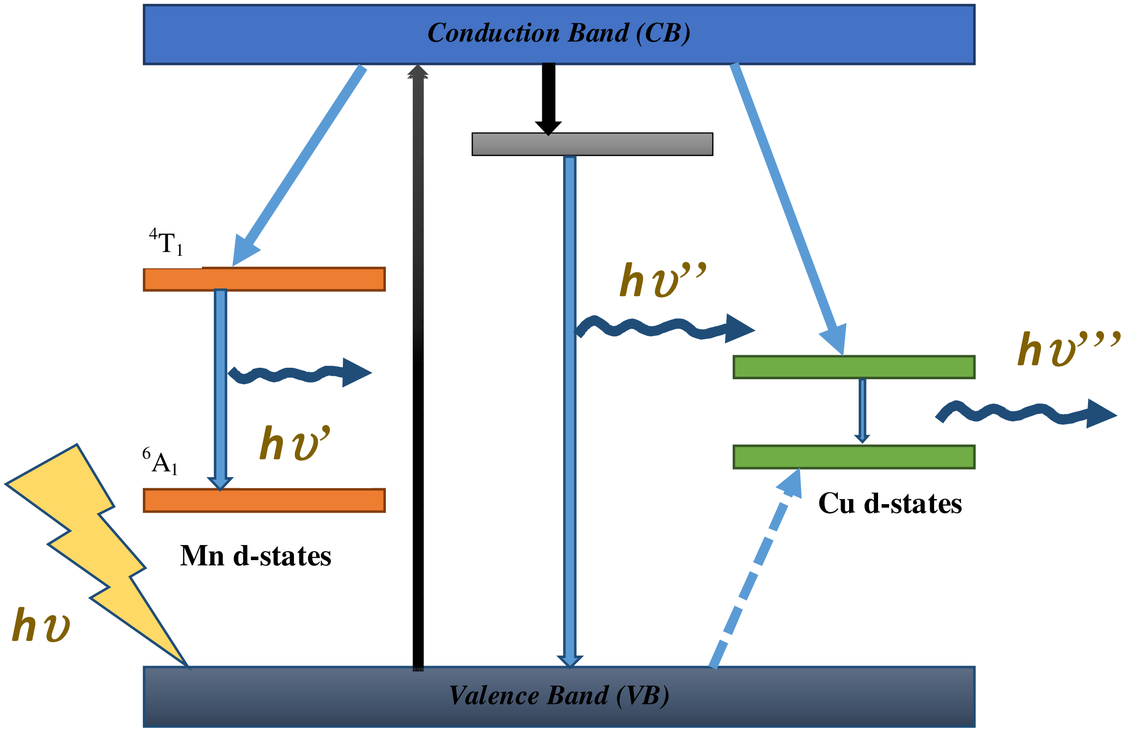

Fig. 1. Mechanism of emission in Cu- and Mn-doped colloidal nanocrystals.

In comparison to the binary nanocrystals, the ternary nanocrystals including I–III–VI (I = Cu, Ag; III = In, Sn, Ga, Al; VI = S, Se, Te etc.) or II-III-VI (II= Zn; III= Al, Ga or In; VI= S, Se or Te) chalcopyrite compounds have been considered as promising candidates to develop tunable emission by varying their composition. As the energy band gap of the alloyed nanocrystals can be engineered by varying the composition of the material [9], they show mixed or intermediate optoelectronic properties. For example, the band gap energy of ZnCdS semiconductor nanocrystals lies between the band gap of ZnS and CdS nanocrystals [10]. Generally, there are some unsatisfied or dangling bonds present at the surfacewhich may be due to non-stoichiometry or voids present in the structure that leads to the trap or surface state defects. These trap states quenches the radiative recombination and decreases the quantum yield (QY). Therefore, it is required to passivate or capped these trap states for the stability of nanocrystals. In order to passivate the surface, inorganic [11] as well as organic [12]. capping agents have been used. In case of inorganic agents, a material having higher energy band gap is chosen as a shell to passivate the core material.

The tunable emission covering the whole visible region (UV-vis-NIR), direct band gap, large stokes shift and longer fluorescence decay lifetime are the main features that enables the use of colloidal nanocrystals in energy efficient applications.

It is also notable that various methods had been reported for synthesizing the monodispersed and size controlled nanocrystals with the variation in reaction parameters. The temperature, reaction time and precursor ratio are the main parameters, which have been considered during synthesis of nanocrystals. The main approaches used to synthesize nanocrystals include hot injection method, solvo/hydro thermal method, non-injection method, refluxing, wet chemical synthesis, sol-gel process, micro-emulsion, molecular beam epitaxy (MBE) and physical vapor deposition (PVD) etc. Fig. 2 represents the methods used to synthesize colloidal nanomaterials of different structures.

In hot injection method (Fig. 3), a cool solvent is added into the hot solution of cationic precursors at appropriate high temperature, which is then followed by fast nucleation [13]. This is the most suitable method that allows the synthesis of controlled size nanocrystals. The injection temperature of precursor is the most important parameter as the size and morphology of the resultant nanocrystals depends on it [14]. Another synthesis method is wet chemical technique or aqueous synthesis approach that mainly follows the conventional precipitation process. This is the simplest method used to synthesize nanocrystals [15].

In sol-gel method, a sol of metal precursor is prepared followed by the polymerization to form gel. This method is cost effective, simple and can be used for large scale synthesis [16]. However, the rate of defects present in it is more. Many researchers have reported microemulsion method (reverse micelle) to synthesize nanocrystals [17]. Microreactor synthesis have also been proposed in which a metal precursor is passed to micromixer through microchannels that further passed to number of zones having specific temperature gradient. This method require small amount of precursor and short reaction time [18].

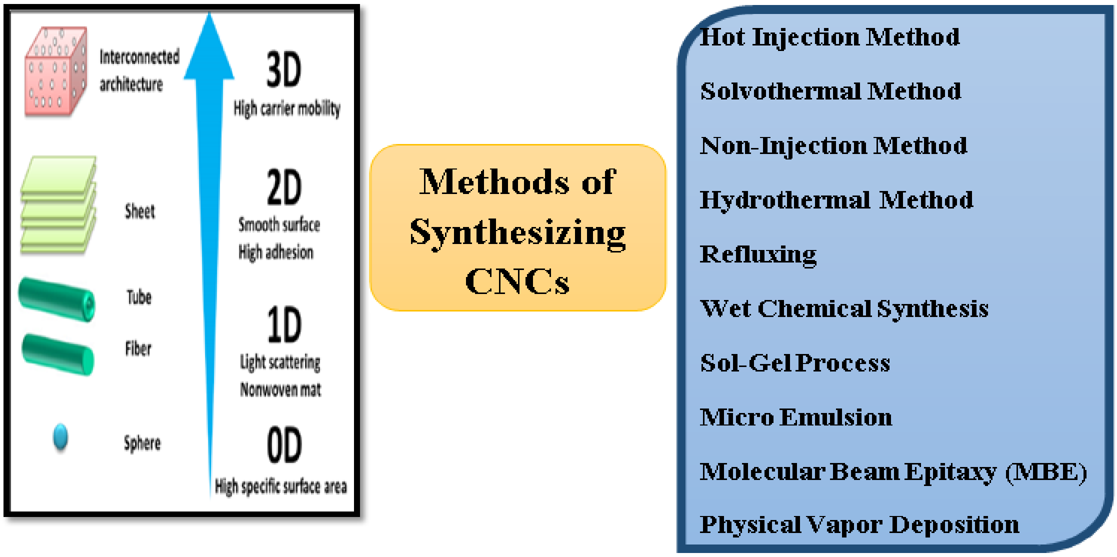

Fig. 2. Generic synthesis methods used to synthesize colloidal nanocrystals (CNCs).

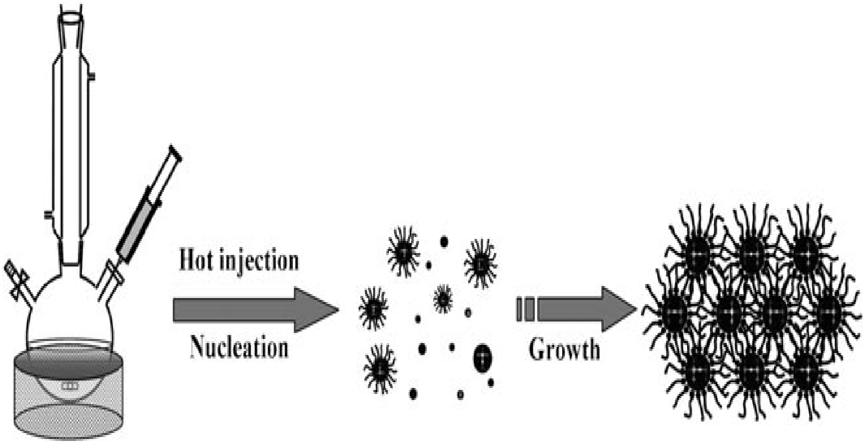

Fig. 3. Hot-injection method for the synthesis of monodisperse nanoparticles. (Adapted from ref 13. Copyright2007 Wiley-VCH Verlag GmbH).

The non-injection method also called heating up method includes the addition of precursors in one pot followed by rapid heating to specific temperature at which nucleation occurs (Fig. 4) [16]. This is also a best method for large scale synthesis [17]. Solvothermal method is used to synthesize nanocrystals by using autoclave. The anionic and cationic precursors are added at low temperature and the sealed autoclave is heated to desired temperature [18]. Thermolysis is a fast synthetic process where metal precursors are heated at high temperature. During the synthesis of nanocrystals, the reaction parameters play a significant role for getting nanocrystals of desired shape and size. The change in precursor ratio has a significant effect on the optical properties. The reaction time and temperature are crutial parameters as the prolonged reaction time leads to aggregation and effect the stability of nanocrystals. The high temperature and more reaction time results precipitation of the nanocrystals. The capping ligand used and the pH of the reaction also effects the optical properties. Afterwards, these high quality nanocrystals can be used in various applications. Sometimes, their hydrophobic nature makes them unsuitable for use in some applications. So, surface modification is required to change their medium from oil based to water soluble. Ligand exchange and encapsulation of the nanocrystals are the main approaches used by researchers for the surface modification of nanocrystals. They improve their water solubility and make them efficient for use in biological applications. Unique properties of nanocrystals makes them effective for use in various applications like optoelectronics, photonics and biomedicine. Some of them are represented in Fig. 5.

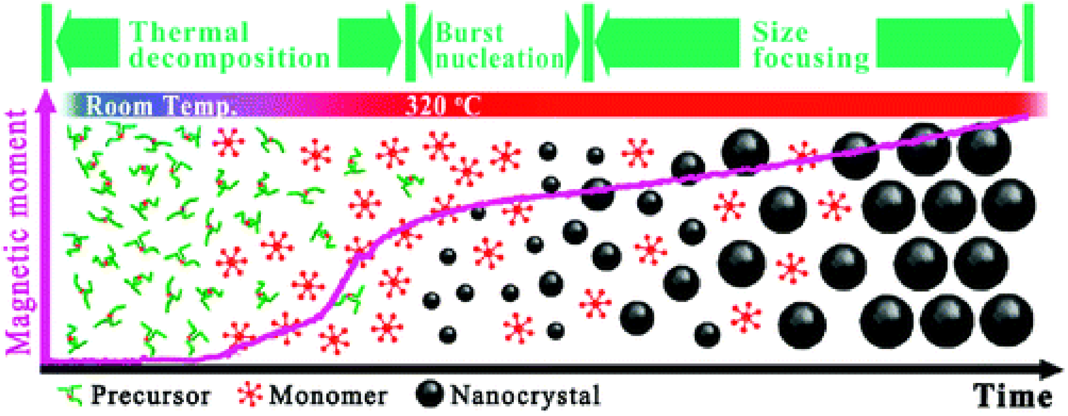

Fig. 4. Noninjection heat-up method. All precursors are present from thebeginning of the reaction, and are steadily heated to initiate nucleationand growth stages. (Adapted from ref 16. Copyright 2007 American Chemical Society).

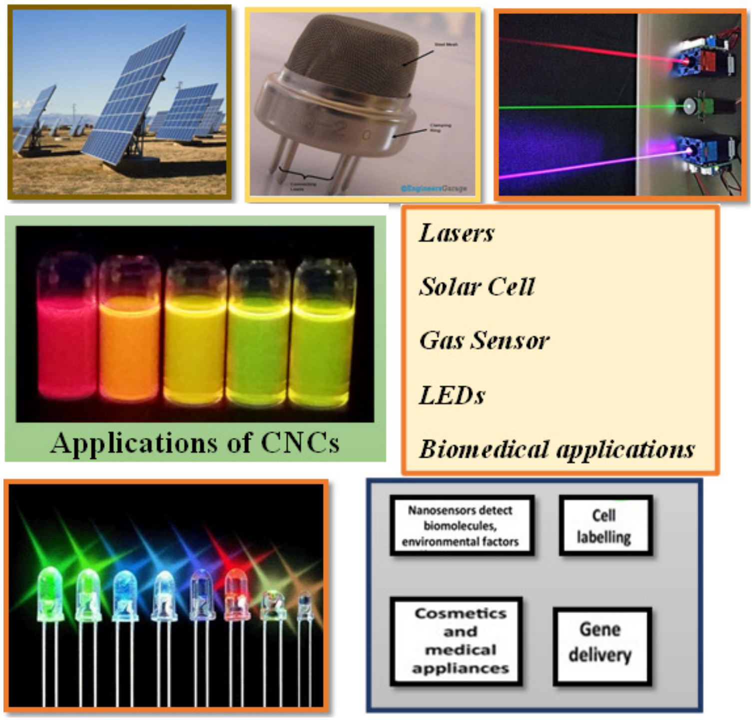

Fig. 5. Illustrates various applications of colloidal nanocrystals.

II. DEVELOPMENT OF SEMICONDUCTOR NANOCRYSTALS (NCs)

A. Binary semiconductor nanocrystals

The unique optical properties of the colloidal nanocrystals makes them proficient as they exhibit bandgap tunability, wide absorption range, high luminescence, spectral purity and photo-/chemical stability [19]. Their novel applications in various fields such as light emitting diodes (LEDs), laser diodes, integrated circuits, photodetectors have generated their technological interest. The most common binary semiconductor compounds consisting of II-VI elements, include cadmium sulfide (CdS), cadmium selenide (CdSe), cadmium telluride (CdTe), zinc selenide (ZnSe) and mercury sulfide (HgS), etc. These materials mostly reveal wurzite and zinc blende tetrahedral crystal structures. II-VI semiconductors nanocrystals show emission in blue-green spectral region and has been used as blue lasing material in optical wave guide [20]. The oxides from II-VI group like ZnO has been used in biological [21]. There are some QDs comprising III-V elements, i.e., indium phosphide (InP), gallium nitride (GaN), indium arsenide (InAs), etc. These materials have direct band gap, high refractive index and possess tetrahedral crystal structure. Therefore, they have been considered as proficient materials for optoelectronics and photovoltaic applications. These materials have been used in fabrication of high efficiency solar cells [22]. Various nitrides from III-V group such as GaN, InN and AlN possess high thermal conductivities and electron transport properties, which make them efficient for use in optoelectronic properties.

(a) Binary Undoped semiconductor nanocrystals

Among II–VI semiconductors, ZnS, CdS, ZnO, CdTe, etc. are the main candidates as they exhibit favorable electronic and optical properties for optoelectronic applications. Among them, ZnS is a commercially important semiconductor having a wide optical band gap, which makes it very attractive material for optical application especially in nanocrystalline form. The luminescent material ZnS was developed by Theodor Sidot in 1866 [23]. Murray, Norris and Bawendi [24]. were the first who reported high-temperature colloidal synthesis of monodispersed CdSe, CdS and CdTe colloidal NCs of uniform size via the hot-injection technique in 1993. Cho *et al.* [25]. synthesized PbSe nanowires and nanorings by adjusting the reaction conditions (i.e. temperatures of 190-250°C and mixture of surfactants). They have successfully synthesized straight, zigzag, helical, branched, and tapered nanowires as well as single-crystal nanorings by using one-pot reactions in a controlled way by careful adjusting the reaction conditions (Fig. 6).

The II–VI binary systems including CdSe, CdS, and PbS magic-sized or regular sized quantum dots (MSQDs) have gained more interest in recent years. The solvothermal synthesis of CdS, CdSe and CdSe/CdS core/shell, PbSe and InP quantum dotsin organic solvents had been reported [15, 26-31].

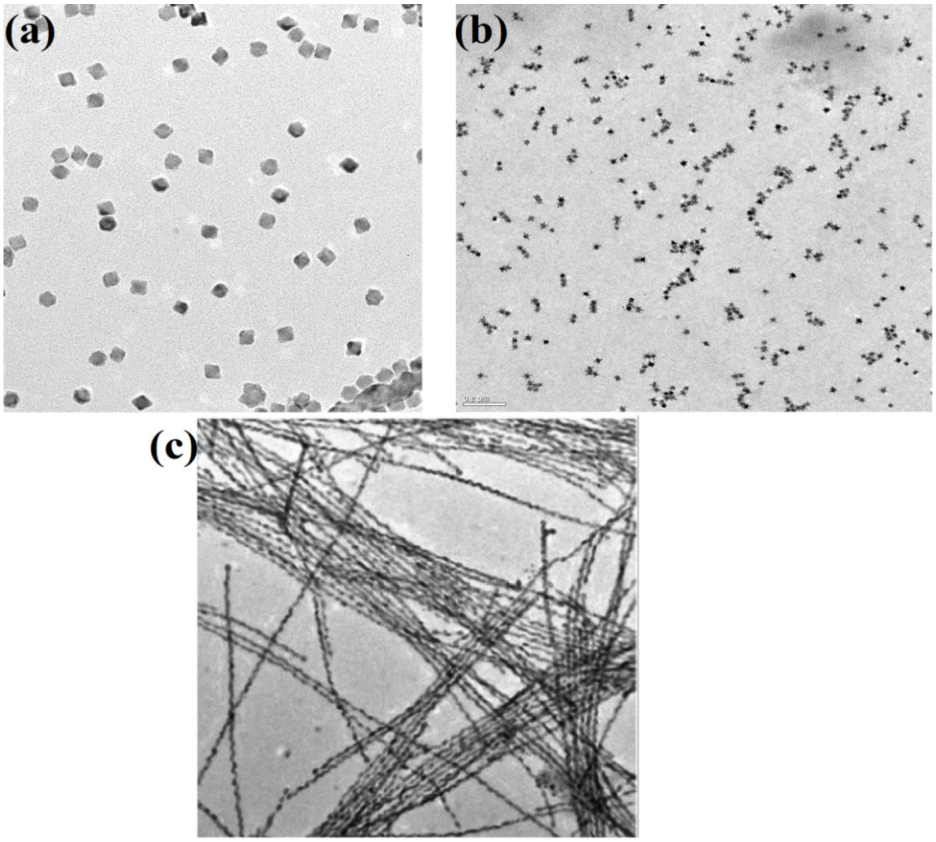

Fig. 6. (a) Octahedral shape PbSe nanocrystals, (b) Star-shape PbSe nanocrystals and(c) Helical nanowires formed upon annealing of straight PbSe nanowires.Reprinted with permission from ref 25. Copyright 2005 American Chemical Society.

It required adequate temperature and pressure which provide the suitable condition for the reaction to takes place for the growth of nanocrystals. The nanocrystals of different sizes have been synthesized by changing the concentration of ligands in noncoordinating solvents. Another approach used for the synthesis of quantum dots is aqueous route that is simple and cost effective. The quantum dots synthesized by this method are attractive for biological applications due to their water dispersibility property. Various materials including CdSe, CdTe, CdTe/ZnTe, CdTe/CdS, CdTe/CdSe, ZnS and ZnSe had been synthesized by this method [32]. Moreover, the most popular stabilizers used for aqueous synthesis of quantum dots are thiols and thioalkyl acids which includes thioglycolic acid (TGA) and 3-mercaptopropionic acid (MPA). It has been found that the synthesized QDs are homogeneous, spherical, and small but their quantum yield is low.

The high-quality quantum dots had been synthesized by hydrothermal method including CdTe, CdTe/CdS core/shell, CdTe/CdSe core/shell, and CdTeS alloyed [33-36]. In this, the precursors containing anions and cations react at high temperature followed the nucleation and growth stages. An another approach that had also been used to produce high-quality colloidal semiconductor nanocrystals both in organic as well in aqueous media is microwave-assisted method. The materials synthesized by this method include CdTe, CdTe/CdS/ZnS, CdSe, ZnSe(S) alloyed, and CdSe(S) alloyed [37-41].

Peng *et al.* used Cd-phosphonate or Cdcarboxylate complexes in place of dimethyl cadmium which were previously used by Murray *et al.* to obtain tunable emission ranging between blue to the near UV region [42]. The same group then replaced the coordinating solvent TOPO by the non-coordinating 1-octadecene (ODE) and obtain monodispersed CdS NCs [28]. Henglein *et al.* coated CdS particles with $Cd(OH)_2$ and increased the quantum yield to 50% by eliminating the trap state emission which was due to high surface to volume ratio [43]. Hines and Guyot-Sionnest [44]. synthesized CdSe/ZnS nanoparticles with quantum yield of 50%. ZnS shell growth had been achieved by the injection of a mixture of the organometallic precursors diethylzinc and hexamethyl disilathianeat high temperature (300˚C). After that Bawendi *et al.* synthesized size series of CdSe/ZnS NCs by growing shell at different temperatures of 140–220˚C (depending on the core size), and reported their in-depth characterization [45]. A similar approach had been applied for depositing ZnS shell on Cd Senano rods with lengths up to 30 nm [46]. The addition of hexadecylamine (HDA) to the traditionally used solvent system i.e. trioctylphosphine oxide /trioctylphosphine(TOPO/TOP) led to abetter control of the growth kinetics during CdSe core and ZnS shell synthesis, results a lower size distribution and increased quantum yields (QYs) of theorder of 60% [21]. An extremelysmall CdSe/ZnS core shell (CS) NCs had been synthesized by Kudera *et al.*, making blue spectral region accessiblewith this system [47]. The synthetic approach was based on the sequentialgrowth of Cd Semagic-sized clusters in a mixture of trioctylphosphine, dodecylamine, and nonanoic acid ata temperatures of 80˚C and their subsequent coating with ZnS. Jun and Jang suggested an anothermethod to access this spectral region [48]. The precursors such as zinc acetate and octanethiol having relatively low reactivity were used to grow ZnS shell at 300℃. The shell material was diffused into the core, resulting in a significant hypsochromic shift of the emission wavelength. The obtained NC gives emission at 470nm with a QY of 60%. Generally, shell growth on wurtzite CdSe core NCs obtained with hot-injection method, is kinetically driven along the c-axis. Therefore, to enhance the growth and uniformity of shell, Lim *et al.* had used zinc blende CdSe NCs forovergrowth with ZnS and achieved 50% PL efficiency in water [49].

With the advancement in synthesis techniques of colloidal nanostructures, the self assembly of colloidal components had also been extended from micrometer size to nanometer with distinctive intrinsic properties. Chen *et al*. [50] obtained a superlattice by self-assembly of CdTe and CdSe and estimated the pair interaction energies due to core-core and ligand-ligand vander Waals (VDW) forces. Bang *et al*. [51] synthesized ZnTe/ZnSe (core/shell) quantum dots (QDs) with PL emission extended from blue to amber (Fig. 7). They have passivated QDs by ZnS layers that maintained their optical and chemical stabilities and demonstrated their potentials of heavy-metal leakage free QDs toward nontoxic biological or medical applications. They have also explored their use in photovoltaic applications. Talapin *et al*. [52] synthesized CdSe NCs with low size distribution by using Hexadecylamine (HDA) in the TOPO/trioctylphosphine(TOP) mixed solvent. Ding *et al*. synthesized water soluble and highly luminescent ZnSe/ZnS core/shell nanocrystals using aqueous method. The tunable emission had been achieved with quantum yield in range of 23% to 62.8% [53]. Fu *et al*. synthesized CdSe/ZnS/ZnS core/shell nanocrystals [54]. Hu *et al*. used an effective approach for better quality and stability by using an outer shell that coated the inner core/shell QDs. They had utilized a double outer shell for inner CdSe/CdS core/shell QDs and with an optimal outer shell thickness, the QY was increased to 72% and the QDs show stability even after purification and exposure to UV [55].

Different materials had been used for double outer shells which improved the luminescence efficiency [56]. The device performance of the alloyed core [57] and alloyed intermediate shell [58] had been significantly improved by coating the inner core/shell QD with single outer shell. With optimally graded alloyed intermediate shell, anexternal quantum efficiency (EQE) exceeding 20% and a current efficiency higher than 80 cdA^{-1} had been achieved [59]. Boonsin *et al*. investigated the optical properties ofgradient alloyed $(CdSe)_x(ZnS)_{1-x}$ and $(CuInS_2)_x(ZnS)_{1-x}$QDs. The optical properties of composite films based on these QDs were also studied. The combination of both QDs revealed that it is possible to produce a warm white light by combining with UV commercial LED [60]. Wang *et al*. synthesized highly luminescent silica coated CdS/CdSe/CdS nanoparticles having quantum yield of 72%. The synthesized nanoparticles having spherical quantum well type structure show excellent stability of silica suggesting their use in real-life applications such as bio-imaging and light emitting devices [61].

(b) Binary Doped semiconductor nanocrystals

The metal ions such as Mn, Cu, Co, Ni and Fe doped nanocrystals had gained significant interest and used for many applications including light emitting diodes and solar cells [62-63].

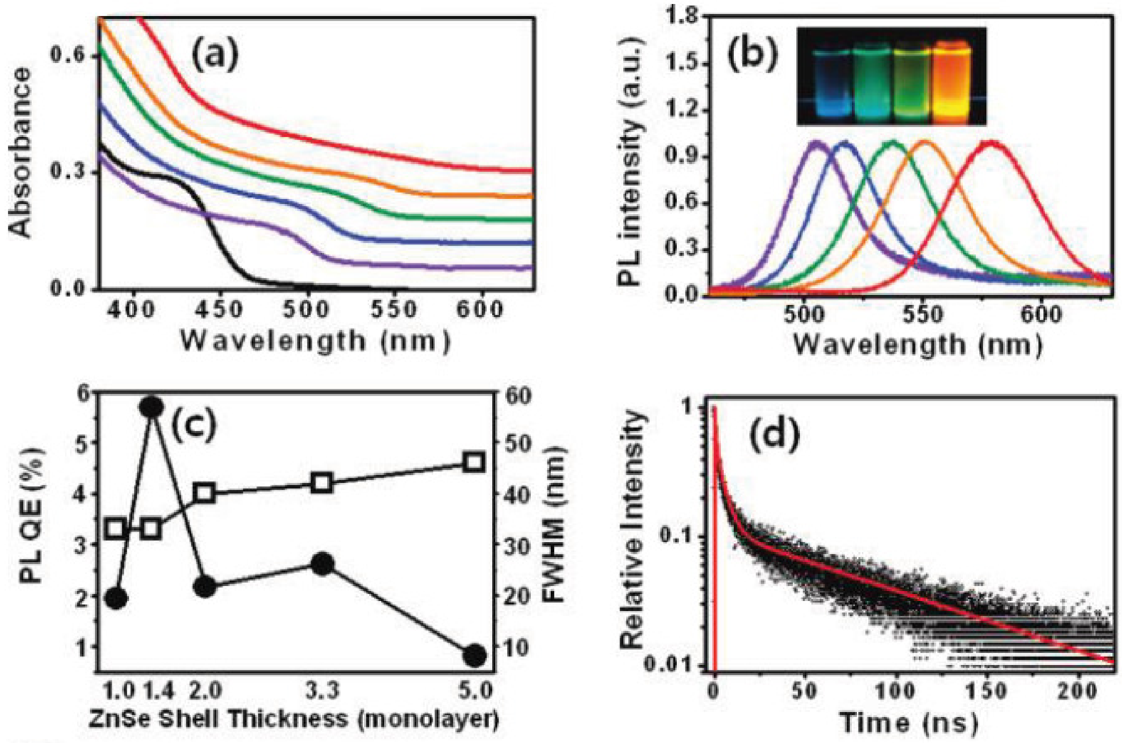

Fig. 7. Absorption and (b) emission spectra of ZnTe/ZnSe (core/shell) QDs. The inset in panel (b) shows various ZnTe/ZnSe (core/shell) QD samples under UV illumination. (c) Photoluminescence (PL) quantum efficiencies (closed circle, b) and full widths at half-maximum (open squares, 0) for ZnTe/ZnSe (core/shell) QDs with 2.2-nm-radius cores and different thicknesses of ZnSe shells. (d) Room-temperature normalized photoluminescence decay of ZnTe/ZnSe QD. (Reprinted with permission from ref 51. Copyright 2010 American Chemical Society).

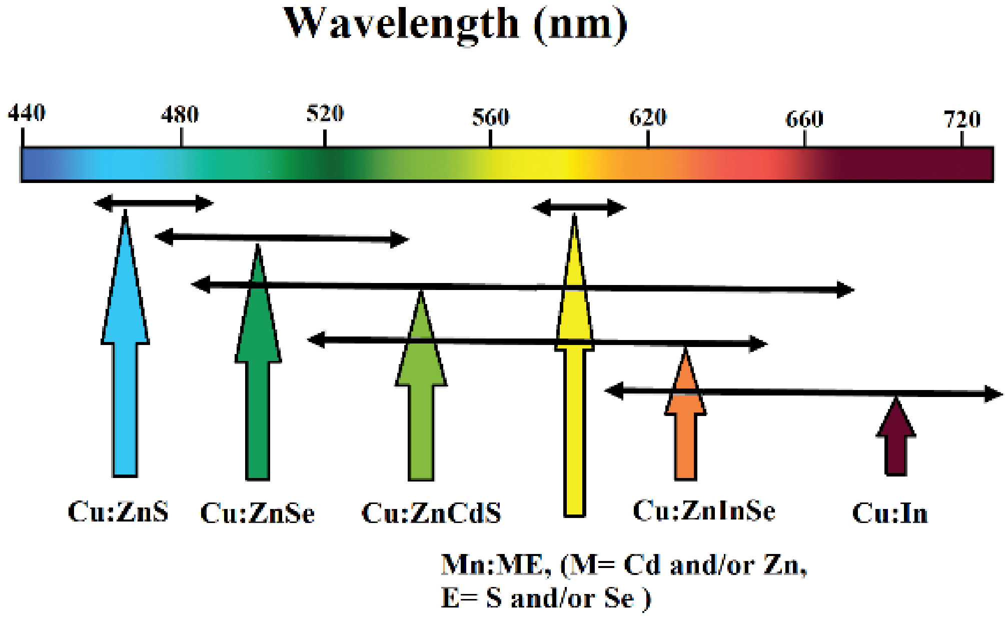

Fig. 8. “Demonstrate the colloidal nanocrystals covering the whole visible spectrum”.

They covered the whole visible spectrum as demonstrated in Fig. 8. Other materials like ZnS:Tb (efficient green emission) [64], ZnS:Sm (weak red emission) [65] and ZnS:Ho (white) [66] had received some interest in later years. Mn-doped ZnS was probably the most studied doped sulfide in nano-sized form. The chemical similarity between Zn^{2+} and Mn^{2+} facilitates the incorporation of the dopant ions into the host crystal. Nevertheless, the incorporated concentration was consistently lower than the intended dopant concentration [67] and part of the Mn^{2+} ions reside near the surface of the nanoparticle. The work by Bol *et al.* showed that the lifetime of Mn^{2+} in $ZnS:Mn^{2+}$ quantum dots is very similar to the bulk lifetime, in spite of earlier work stating a considerable shortening of the lifetime [68-69]. Also the emission spectrum itself was almost size-independent [67]. Hence, growing an inorganic (ZnS) shell around ZnS:Mn effectively reduces non-radiative decay paths and enhances the luminescence [70], more efficiently than organic passivation of the surface [67]. Synthesis techniques, luminescence properties and possible applications of Mn-doped ZnS nanoparticles had been explained in detail in the reviews by Chen *et al*. [71, 67]. The luminescence properties of nano-sized ZnS:Eu had been studied and the results show deviation with the presence of both Eu^{3+} and (assumed) Eu^{2+} emission [72]. Bulk ZnS:Eu was not luminescent and it was proposed that increasing the band gap of the host would allow the 5d-4f transition in Eu^{2+}. Incorporation of Eu in ZnS appears difficult as the Zn^{2+} and Eu^{2+} ions possess different ionic radius [73]. Xie *et al.* [74]. In 2005 synthesized high qualtiy Cu:InP and Cu:InP/ZnSe core/shell quantum dotsby varying the size of the InP host nanocrystals for biomedical applications that covered the red and near-infrared (NIR) window (i.e. from 630 to 1100 nm) (Fig. 9). The PL QY ofthe resulting efficient pure dopant emissioni.e. Cu:InP/ZnSe core/shell quantum dotsreached close to 40% by the complete elimination of InPb and gap emission.

AC electroluminescence (EL) was reported by using ZnSe/ZnS:Mn/ZnS core/shell nanoparticles having high photoluminescence quantum efficiency of 65% [75]. The semiconductor part of the ACTFEL devices consisted of a multi-layer of spin-casted nanoparticles layers (thickness of 30 nm) and sputtered (undoped) ZnS layers (12 nm). The typical orange emission (ZnS:Mn) was obtained for these structures having of 2 cd/m² at 30 kHz. The devices without the sputtered ZnS layers did not show EL emission. Toyama *et al.* [76] also obtained electroluminescence of ZnS: Mn nanoparticles with a 150 nm thick printed layer and suggested that5 kHz, and 45 V above threshold were sufficient to obtain a luminance of 1cd/m^2 for the smallest particles having size 3 nm.Corrado *et al.* [77]. synthesized Cu-doped ZnS nanocrystals by using mercaptopropionic acid (MPA) as a capping agent. The incorporation of Cu ions into the crystal structure red shifted the emission band in PL spectra. They had suggested that the optical and structural properties make this material as potential candidate for use insolid state lighting, imaging, and other photonic devices. Xin *et al.* [77] synthesized Cu, Tm-doped ZnS nanocrystals at 200℃ by using hydrothermal method. They have found that for long time treatment, it showed low luminous intensity. They have obtained a broad emission band with blue and green emission. Hazarika *et al.* [79] synthesized Mn doped ZnS-CdS alloys with narrow energy window ≤150meV in the orange-red emission region. They carried the single crystal PL emission and found that it vary over wide range (~370 meV) which covers the deep green to deep red region of spectrum.

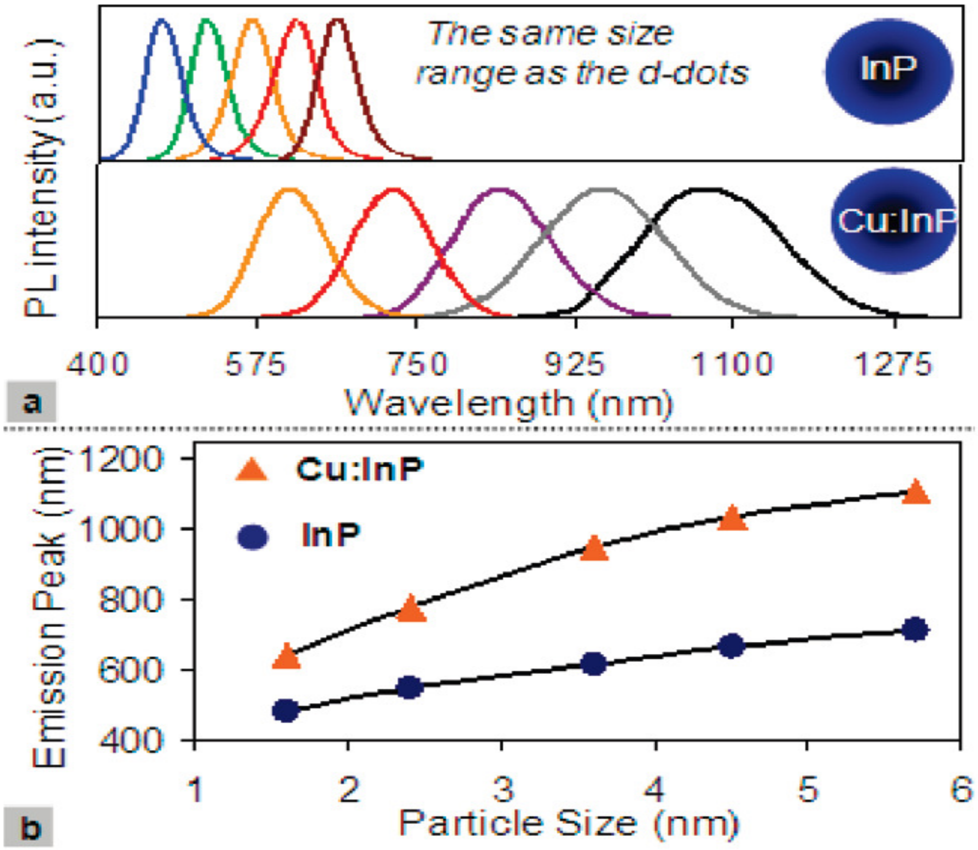

Fig. 9. PL spectra (a) and PL peak positions (b) of differently sized InP q-dots and Cu: InP d-dots. (Reprinted with permission from ref 74. Copyright 2009 American Chemical Society).

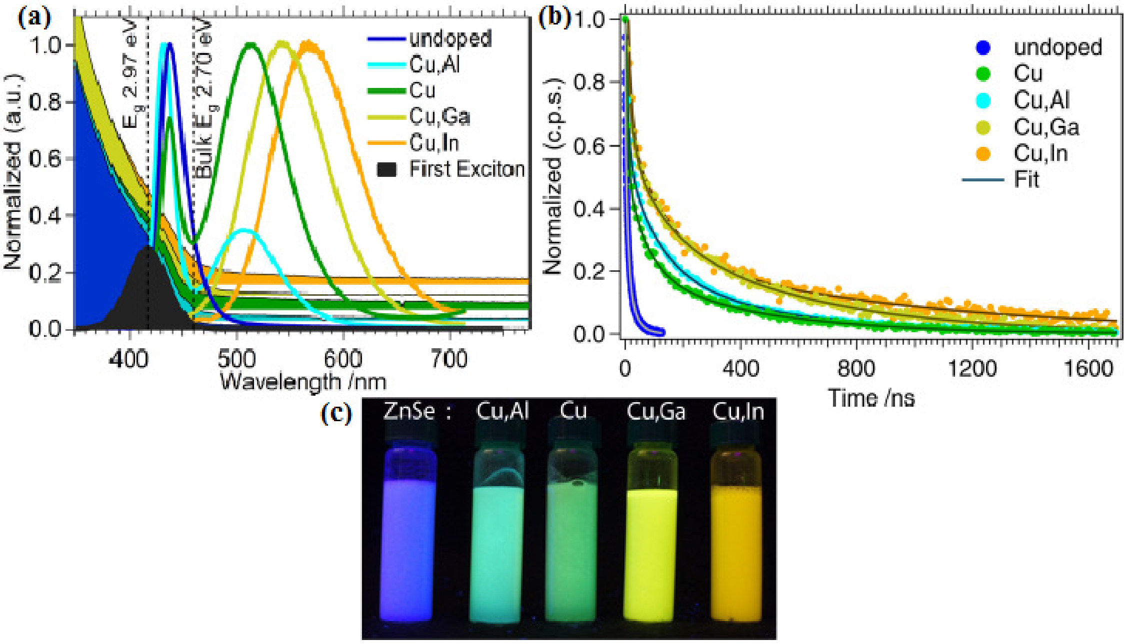

Fig. 10. (a) Normalized absorption and PL spectra (λex = 380 nm) of undoped ZnSe/ZnS, ZnSe:Cu,Al/ZnS (Cu,Al), ZnSe:Cu/ZnS (Cu), ZnSe:Cu,Ga/ZnS (Cu,Ga), and ZnSe:Cu,In/ZnS (Cu,In). Excitation wavelength for photoluminescence is 380 nm.(b) Photograph of the codoped ZnSe/ZnS QD system as excited by UV light. (c) Time-resolved photoluminescence of undoped ZnSe/ZnS(undoped), ZnSe:Cu,Al/ZnS (Cu,Al), ZnSe:Cu/ZnS (Cu), ZnSe:Cu,Ga/ZnS (Cu,Ga), and ZnSe:Cu,In/ZnS (Cu,In). (Reprinted with permission from ref 82. Copyright 2015 American Chemical Society).

Mei *et al*. [80] synthesized highly luminescent ZnS:Cu, Eu semiconductor nanocrystals by using hydrothermal method and their results demonstrate that this material can be effectively used for optoelectronic applications. Gao *et al.* [81] fabricated white light emitting diodes by using Mn-doped CdS/ZnS core/shell nanocrystals. They had reported an improvement in the intensity, stability, and achieved color rendering index of 88 and luminous efficiency of 108lm/W. Cooper *et al.* [82]. in 2015 synthesized a series of ZnSe/ZnS QDs by using Cu^+ as theprimary dopant and trivalent cations (Al^{3+}, Ga^{3+}, and In^{3+}) as codopants with tunable PL emission covering 430–570 nm with average full width at half maximum of 80 nm (Fig. 10).

B. Ternary semiconductor nanocrystals

The ternary semiconductor compounds have been widely investigated. The ternary NCs provide tunable emission fromNIR region through visible and covers the ultraviolet (UV) region.

(a) I-III-VI CNCs

Recently, ternary I-III-VI (I=Cu, Ag; III=In, Sn, Ga, Al; VI=S, Se, Te etc.) semiconductor NCs came into view due to their innovative properties. They are less toxic as compared to other Cd based materials. Along with large stokes shift, high photo stability, high quantum yield and longer photoluminescence lifetime, they also exhibit wide range of optical and electronic properties which can be achieved by varying their composition and altering structure [83]. As compared to binary CNCs, the ternary I–III–VI compounds have been considered as promising candidates for light emitting and biological applications as they composed of less toxic elements. They have direct band gap in the visible region as $CuInSe_2$ (CISe), CuInS (CIS), $AgInS_2$ (AIS) and $AgInSe_2$ (AISe) have band gap of 1.05 eV, 1.5 eV, 1.87eV and 1.2 eV, respectively [84]. Various metal salts and sulfur sources had been used to synthesize I-III-VI type CNCs (CIS, AIS, CISe and AISe etc.). Various methods such as electrode position, spray pyrolysis, sputtering, ionized cluster beam technique and chemical vapour deposition had been used to synthesize colloidal CuInS CNCs[2].

Moreover, composition variation consequences on the defects of I-III-VI QDs can directlytune the optical properties. The presence of different atoms in their composition challenges tuning of the absorption spectra. Several works showed that the non-stoichiometry of ternary QDs could be controlled by the molar ratios of precursors [85]. The tunable emissionis a pronounced properties of I-III-VI QDs which attracts various researchers to make their use in light emitting applications. Fabrication of I-III-VI QDs were adapted from the methods used in II–VI binary QDs [13,20]. During synthesis of QDs, the reaction temperature and time [86], injection temperature in hot-injection methods [87], the reactivity and the stoichiometric ratios of precursors, the solventtype used, surfactant, and pH [88] etc. are important parameters to adjust the size. A number of metal salts and sulphur precursors were used for the preparation of luminescent I-III-VI QDs by thermolysis in hot organic solvents [86,89]. Ternary I-III-VI QDs prepared as core QDs exhibit poor PL QYs of less than 20% and are not stable to photon-irradiation. Surface coating of the QDs with a materials having large band gap is a suitable way to enhance the PL QY as well as the stability. The surface-to-volume ratio is higher due to their small size, as a result surface defects on unsaturated bondson the surface provide non radiative decay for the photo created charge carriers.

Efficient surface passivation is required to eliminate surface defects, improve the fluorescence QY and stability. Introducing Zn or ZnS also was adjusted on optimizing optical properties ofsemiconductor QDs. The growth of ZnS shell layer around the surface of core enhances the PL QY of the QDs. Most researchers choose ZnS as a shelling material due to its chemical properties. First, ithas wide band gap (3.7eV) [90] and smaller ionic radii which forms good band alignment withI-III-VI QDs. Second, its Zinc blende structure allows to eliminate the surface trap states andavoid leakage created charge carriers in ternary core QDs.

Jaffe *et al*. [91] studied the electronic structure of Cu based ternary semiconductors i.e. $CuAlS_2$, $CuGaS_2$, $CuInS_2$, $CuAlSe_2$, $CuGaSe_2$, and $CuInSe_2$. They had studied their band structure, density of states, electronic charge densities. Gurin [92] prepared ternary I-III-VI compounds having chalcopyrite structure. He had synthesized $CuInS_2$,$CuInSe_2$, $CuGaS_2$, $CuFeS_2$, and $AgInS_2$ in aqueous or acetonitrile medium and studied their quantum size effect. Parkin *et al*. [93] synthesized CIS nanocrystals by reflux method. Lu *et al*. [94] synthesized CIS by using solvothermal method. They had used CuCl, In and S as reagents and synthesized at 200˚C. Malik *et al*. [95] synthesized tri-n-octylphosphine oxide(TOPO)-capped $CuInSe_2$ nanoparticles. They had carried out the reaction in two steps. In first step, $InCl_3$ and CuCl were reacted in tri-n-octylphosphine (TOP) and injected into TOPO at 100 ℃. In second step, at an elevated temperature of 250 ℃, tri-n-octylphosphineselenide (TOPSe) was added to the reaction mixture.Li *et al*. [96] prepared $CuInSe_2$ nanowhiskers and nanoparticles at 180℃. Jiang *et al*. [97] synthesized CIS nanorods by solvothermal route by setting the reaction temperature at 280˚C for 48 hrs. In 2001, Xiao *et al*. [98] prepared CIS nanorods with length 400 to 450 nm and diameter 20 to 25 nm by using hydrothermal technique at 180˚C for 15 hrs. Castro *et al*. [99] synthesized CIS and CISe chalcopyrite compounds by thermal decomposition of single source precursors but the resultant nanocrystals were not small enough to exhibit quantization effect. Therefore, in 2004 they had slightly modified their method and successfully synthesized CIS nanoparticles of size 2-4 nm at 200˚C [100]. Grisaru *et al*. [101] prepared $CuInTe_2$ (CIT) and $CuInSe_2$ (CISe) nanoparticles of tetragonal structure by microwave assisted method. Wei *et al*. [102] synthesized cube shaped CIS nanoparticles by using a simple wet chemical process. Vittalet *et al*. [103] produced wurtzite or sphalerite CIS nanocrystals by the thermal decomposition of single source precursors. Dutta and Sharma [104] synthesized CIS nanoparticles by thermolysis of precursors at 196˚C. Gardner *et al*. synthesized 3-5 nm CIS nanoparticles using microwave irradiation of single source precursors. The other material or compounds which comes in I-III-VI group are $CuGaS_2$(CGS), $AgInS_2$ (AIS), $AgInSe_2$ (AISe) and $AgGaS_2$ (AGS) [105].

Tang *et al*. [106] synthesized Zn doped AIS QDs and studied that the incorporation of Zn dopant leads to increased structure stability and crystallinity. Shapiro *et al*. [107] synthesize dultrafine $CuInS_2$ nanoparticles from the photolytic decomposition of a molecular single source precursor. Vittal *et al*.[108] synthesized orthorhombic $AgInSe_2$ nanorods at 185˚C. Monodispersed $AgInS_2$ nanoparticles were successfully synthesized by Tian and co-workers using direct thermal decomposition of the single-source precursor in a bisurfactant system [109]. Later on, the same group synthesized polyhedral shaped $AgInS_2$ nanocrystals from dual-source precursors [110]. Wang *et al*. [111] demonstrated one-pot synthesis strategy for the preparation of ternary nanocrystals. They had synthesized $AgInS_2$ nanocrystals having different morphologies by controlling the reaction conditions. They had also synthesized $CuInS_2$ and $AgInSe_2$ nanocrystals by replacing the precursors and provided a controlled way for the synthesis of ternary nanocrystals.

Xie *et al*. [112] synthesized CIS and AIS nanocrystals of size range from 2 to 20 nm at 180˚C by using hot injection method. Norako *et al*. [113] had prepared CIS nanoparticles of size 6.9 nm by hot injection method at 180˚C. Park and Kim [114] synthesized CIS/ZnS core/shell QDs by cation exchange reaction with quantum yield of 65% and studied their blue shifted photoluminescence. Mao *et al*. [115] synthesized highly luminescent AIS nanocrystals by one pot reaction and study their photocatalytic and photovoltaic applications.Li *et al*. [116] synthesized CIS nanocrystals and deposited CdS or ZnS layers over the nanocrystals to improve their quantum efficiency. They demonstrated that the method used by them produced nanocrystals with high yield and revealed the time resolved spectroscopic studies of core and core/shell nanoparticles. They had found that the core-only particles were promising candidates for PV applications, while core/shell particles could be used in displays, solidstatelighting, and bioimaging.

Allen *et al*. [117] achieved tunable emission from red to near-infrared region by varying the stoichiometric ratio of CISe QDs via hot injection method. They had demonstrated that the synthetic method can be used for the synthesis of ternary I-III-VI nanomaterials. They had also synthesized AISe QDs with emission in orange to red region of spectrum by following same synthesis method and replacing the precursors with AgI and InI_3. Pan *et al*. [86] synthesized monodispersed CIS ternary nanocrystals by using mixed precursors via a hot injection method. They had synthesized NCs having zincblende to wurtzite structure by varying the precursor composition and concentration of capping agent. Later, [118] the same group synthesized (CIS)(ZnS) alloyed nanocrystals by using wet chemical method. They have achieved tunable band gap by varying the composition of the precursors. Zhong *et al*. [119] synthesized CISe nanocrystals with controlled stoichiometric composition and size. The synthesized CISe/ZnS core/shell QDs exhibited 26% quantum yield with excellent PL properties. Thus, they had used this material as light emitter for the fabrication of electroluminescent devices. Omata *et al*. [120] synthesized CISe/ZnSe core/shell QDs with PL quantum yield of 16%. They have demonstrated that there is blue shift in the emission after the deposition of ZnSe that can be attributed due to the partial alloying of CISe core with the ZnSe shell around their interfaces. They also synthesized ZnSe/CISe inverted core/shell QDs and studied their optical properties. Yarema *et al*. [121] synthesized high yield CISe QDs with precisely controlling the shape and size. These QDs exhibited bright luminescence and quantum yield of 50%-60%

after coating ZnS and ZnSe shell suggesting their use in bioimaging, biolabeling and lighting applications.

Deng *et al*. [122] had proven that increasing Zn on AISe system also effect theblue shift on PL emission, which improve QY up to 50%. Separately, Deng [123] also investigated optical properties of AISe deposited with ZnS shell. As a result, QY of AISe QDs canreach to 40% with emission tunable from 700 to 820 nm. Xie *et al*. [112] demonstrated that one layer of ZnS over the CIS core improved the PL QY to 30%. Jang *et al*. [124] synthesized CIS coreand passivated with two layers of ZnS shell and fluorescence QY was upgraded to 92%. These double Layer shelling of ZnS shows a remarkable blue shift from 660 to 559 nm. The stoichiometric ratios of Cu:In showed high photostability under UV illumination both in toluene and aqueous solutions. Tang *et al*. [106] compared Zn doped AIS with pure AIS QDs and indicated that the incorporation of Zn dopant shows higher structure stability and crystallinity. Uehara *et al*. [125] enhanced the fluorescence of CIS QDs by introducing crystal defects through a highly Cu defect composition of CIS. This enhanced fluorescence was due to large number of donor or acceptor defects requiredfor donor-acceptor pair recombination (DAP) of excited charge carriers. Hamanaka *et al*. [126] reported the decrease in PL QY in CIS QDs and associated it with deep surface traprather than DAP. These reports open a way for researchers to construct efficient approach for modifying the surface of ternary core QDs.

Dai *et al*. [85] and Kameyama *et al*. [127] reported utilization of non-injection or pyrolysis method on synthesis of AIS and AISe QDs. However, even prepared with precisely stoichiometric composition, difficulty to get QDs with single crystal structure commonly occured on this type. For instance, in synthesis of AIS proposed by Dai *et al*. [85], they obtained the AIS QDs with tetragonal and orthorhombic crystal along with cubic $AgIn_5S_8$ (Fig. 11). Torimoto *et al*. [128] synthesized ZnS-AIS nanoparticles with broad and tunable emission spectrum which makes them competent for use in solar cells and photocatalysis.

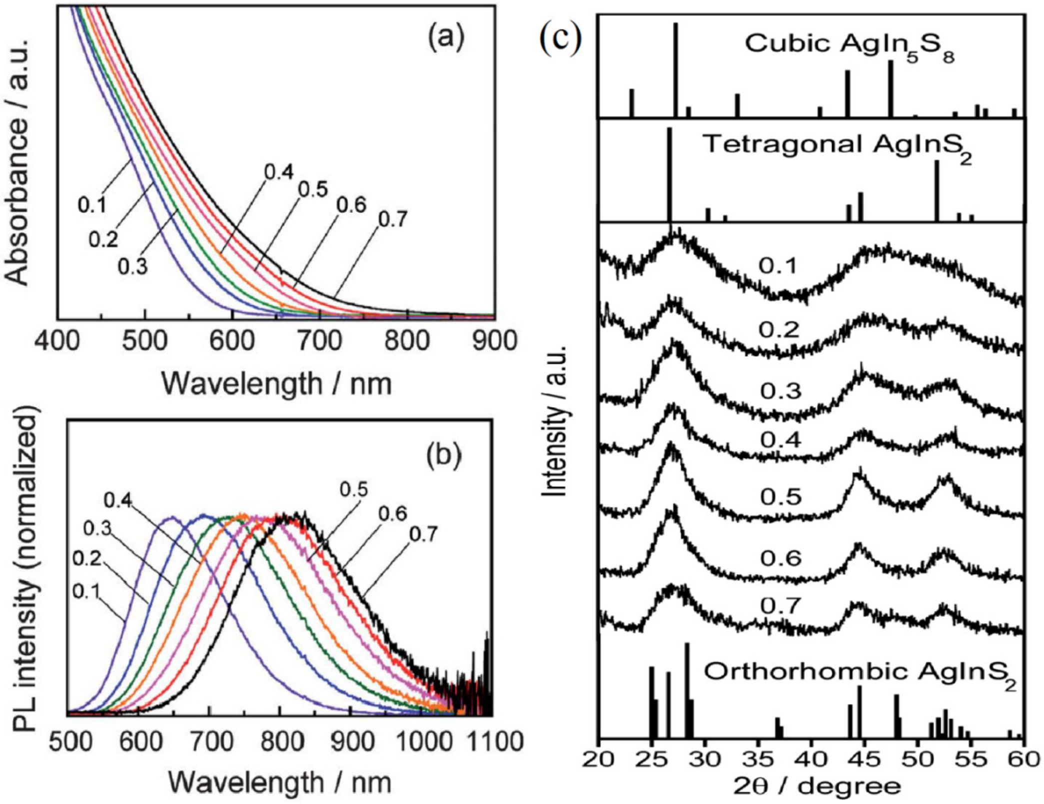

Fig. 11. Absorption spectra (a) and PL emission spectra (b) of AIS nanoparticles. The excitation wavelength in PL spectra was 430 nm. (c) XRD patterns of AIS nanoparticles. (Reprinted with permission from ref 85. Copyright 2012 The Royal Society of Chemistry).

Later on, in 2010 the same group synthesized ZnS-AIS nanoparticles with photoluminescence intensity of 80% using thermal decomposition of precursor at 180˚C [129]. Ogawa *et al*. synthesized orthorhombic AIS by thermolysis and studied their photoluminescence properties [130]. Tang *et al*. [131] synthesized AIS–ZnS heterodimers by using hot injection method that showed tunable emission from green to red and also showed two photonfluorescence (TPF) properties. Hamanaka *et al*. [132] studied the photoluminescent properties of AIS QDs. They had investigated that the PL emission is attributed due to the donor-acceptor (DA) pair recombination. They suggested thatthe large Stokes shift observed in PL band was due to the strong interactions between the carriers which were trapped at the donor or acceptor levels. Dai *et al*. [85] synthesized $AgInS_2$ (AIS) semiconductor nanoparticles by the thermalde composition of single-source precursors. They had varied the ratio of Ag content and achieved maximum quantum yield of 70% with tunable emission from visible to near infrared region.

Chung *et al*. used carbon dots and Zn-doped $AgInS_2$ nanocrystals for the fabrication of white LED. Carbon dots were prepared by thermal carbonization of citric acid whereas $AgInS_2$ nanocrystals were prepared by thermal decomposition at a low temperature. Then, they fabricate a white LED by combining a UV LED with thecarbon dots and Zn-doped $AgInS_2$ NCs which exhibit warm color temperature with an excellent color rendering index 95, and verify its potential for use in solid state lighting [133]. Wang *et al*. prepared Ag doped ZnInSe ternary quantum dots by following aqueous route and refluxed at 100˚C. They exhibited high stability, good biocompatibility, low cytotoxicity, and broad tunable emission scope suggesting their use in optical coding, white LED, and bio-imaging [134].

Kameyama *et al*. [127] synthesized nanocrystals of ZnSe-AlSe and used them for the fabrication of quantum-dot-sensitized solar cells (QDSSC) with maximum energy conversion efficiency of 1.9%. Langevin *et al*. [135] synthesized air stable AlSe NCs through thermolysis followed by anion exchange reaction. These pyramid shaped NCs with quantum yield of 21% showed emission in range of 800 to 1300 nm. Lu *et al*. [136] fabricated white LED by using AIS/ZnS quantum dots. They had deposited the red emitting QDs over the yellow emitting phosphor layer and achieved white light having color temperature of 3500 K, luminous efficiency of 72.1 lm/W and color rendering index of 85.

(b) Other Ternary CNCs

There are other ternary nanocrystals that include II-III-VI semiconductor compounds (II:Zn, Cd or Hg; III: Al, Ga or In; VI:S, Se or Te). These compounds have gained much interest in few decades due to their tunable emission, large full width half maxima (FWHM), long decay lifetime and large stokes shift. These properties make these compounds suitable for various applications.

Chen *et. al* successfully synthesized porous ZnInS microspheres by thermal solution method at low temperature. The resultant product showed enhanced visible light photocatalytic activity. This low cost method was highly suitable for large scale industrial production [137]. Kim *et al*. [138]. fabricated white light emitting diode (WLED) by using different composition of Mn-doped $Zn_{1-x}Cd_xS$ quantum dots (QDs). They obtained the color rendering index (CRI) of 62 and CIE chromaticity coordinates of (0.529, 0.459) and (0.316, 0.264) for QD-based orange and white LEDs respectively. Gou *et. al* synthesized ZnInS, CuInS, and CuInSe nano- and microstructures vis a facile solution-based route.They synthesized ZnInS nanotubes and nanoribbons by solvothermal method and ZnInS hollow microspheres by hydrothermal method in the presence of cetyltrimethylammoniumbromide (CTAB) or poly(ethylene glycol) (PEG) surfactant [139].

Shen *et. al* synthesized ZnInS nanocrystals by hydrothermal method and studied their photocatalytic activity for hydrogen evaluation [140]. Cao *et al*. [141] synthesized high-qualified Cu-doped Zn–In–Se nanocrystals by using hot injection method. They have achieved composition dependent tunable emission by varying Zn to In ratio with PL quantum yield of 38%. They fabricate LED by using these QDs with maximum luminance of 320 cd m^{-2} and a luminous efficiency (LE) of0.97 cd A^{-1}. Peng *et al*. in 2013 synthesized ternary hexagonal ZnInS with controlled size and shape. Nanocrystals of different sizes i.e. 2.1 nm to 9.2 nm had been obtained at different reaction temperature. They demonstrated the photocatalytic activity of the ZnInS nanocrystals for degradation of methyl orange in visible region [142].

Xu *et al*. [143] synthesized Mn-doped $Zn_xCd_{1-x}S$ QDs using nucleation-doping approach and studied their optical properties. They have found that the emission arises from Mn-ion states and defect states. The achieved quantum yield is 29% that can be improved by decreasing non-radiative centers through growing ZnS shell. Goutam De *et al*. [144] fabricated films of Cu-doped $Cd_{0.5}Zn_{0.5}S$ alloyed QDs incorporated with organically modified SiO_2 and capped with P123. The concentration of QDs was 40 mol% higher than equivalent SiO_2. The fabricated films show high luminescence and covers the entire visible region.

Zeng *et al*. [145] synthesized Ag-doped ZnCdS/ZnS core/shell nanocrystals at 250˚C. Then, they treated the synthesized NCs with Se to prepare Ag doped ZnCdSSe nanocrystals. The size, shape, crystallity and optical properties were unchanged. Ouyang *et al*. [146] synthesized CdS and CdZnS quantum dots by hot injection method and observed upconversion luminescence. In 2008, they synthesized alloyed ZnCdS quantum dots by non-injection method [147]. The cubic shaped ZnCdS nanoparticles with intense luminescence and narrow full width at half maxima can be considered as blue emitting material for various applications. Shen *et al*. [148] fabricated quantum dots based LED by using ZnCdS/ZnS core/shell quantum dots. They had attained maximum external quantum efficiency >10% with low turn on voltage of ~2.6V. They had suggested that further optimizing the capping ligands and the electron and hole transport layers help in improving the quantum efficiencies.

Chen *et al*. [149] synthesized water soluble Mn-doped ZnCdS/ZnS core/shell quantum dots. They have synthesized these QDs by using an aqueous route and achieved quantum yield of 20% after coating with ZnS shell. These quantum dots having tunable emission could be used for preparing QD-based LEDs. Wang *et al*. [150] synthesized monodisperse zinc indium sulfide (ZIS) alloy and tuned the optical properties by varying the indium content in the nanocrystals. Li *et al*. [151] in 2016 synthesized transition metal ion (Mn^{2+} or Cu^{+}) doped ZnInS/ZnS core/shell quantum dots (QDs) and studied their photoluminescence properties in solution as well as in films forms. Their results showed them efficient for photoelectronic devices.Shen *et al*. [152] in 2011 synthesized transition metals (Cr, Mn, Fe, Co) doped ZnInS and studied their photocatalytic activity. Sarkar *et al*. [153] in 2011 synthesized Cu-doped ZnInSe ternary alloy nanocrystals by precipitation and surface cation-exchange method and achieved emission over visible region. The synthesized ultrasmall nanocrystals had versatile characteristics which makes it useful in biomedical, solar cell, and LED applications.

Yuan *et al*. [154] fabricated white light emitting diodes by using Cu-doped ZnInS/ZnS core/shell nanocrystals. The QDs synthesized by hot injection method showed emission in deep red to green region. The QDs based LEDs showed high photoluminescence quantum yields

(PL QYs), low scattering and good colour saturation as compared to traditional phosphors based LEDs. They obtained device parameters as high CRI up to 96, luminous efficacy of 70–78 lmW^{-1}, CCTof 3800–5760 K, and CIE colour coordinates (0.3388, 0.3337). Zhang *et al*. [155] synthesized Cadmium-Free Cu-Doped ZnInS/ZnS Nanocrystals by non-injection method and achieved quantum yield of 85%. They studied the electroluminescent devices performance of the fabricated QD-based light-emitting diodes with a maximum luminance of 220 cdm^{-2}, low turn-on voltages of 3.6 V.

Yuan *et al*. [156] synthesized manganese and copper co-doped Zn–In–S Quantum Dots and used them for the fabrication of white LED. The fabricated device showed color rendering index of 95, luminous efficacy of 73.2 lm/W, and color temperature of 5092 K. Huang *et al*. [157] in 2016 synthesized dual emissive Ag,Mn:ZnInS Quantum dots and used to fabricate temperature sensor device. The emission achieved at 485 nm was attributed to Ag-related anion vacancies while emission at 585 nm was attributed to the Mn^{2+} transition from $^4T_1$ to $^6A_1$.

Jiang *et al*. [158] synthesized Cu doped ZnInS/ZnS nanoparticles with tunable emission in the whole visible region by aqueous method. They had found them biocompatible to use in biomedical applications. Xuan *et al*. [159] synthesized Ag-doped ZnInS/ZnS nanocrystals and achieved quantum yield of 43.5%. They used the synthesized nanocrystals for bioimaging by changing their media to aqueous via ligand exchange. Yuan *et al*. [160] studied the luminescence properties of Cu-doped ZnInS/ZnS core/shell nanocrystals. They discussed the thermal quenching mechanism and used the synthesized quantum dots for fabrication of white LEDs.

Yakoubi *et al*. [161] synthesized high quality Cu:CdZnS/ZnS core/shell QDs with a PL quantum yield (PLQY) of 42% and studied their optical and structural properties. These stable and water dispersible QDs could be potential candidate for biolabelling applications. Yadav *et al*. [162] synthesized Cu-doped $Cd_{1-x}Zn_xS$ quantum dots by using chemical co-precipitation method and studied their structural properties. These QDs exhibit hexagonal crystal structure with size in the range of 2-12 nm. Levchuk *et al.* [163] synthesized highly efficient Mn-doped ZnCdS/ZnS core/shell QDs with high reproducibility in large quantities by using a non-injection method. They have deposited these QDs on top of a commercial monocrystalline silicon (mono-Si) solar cell and significantly enhanced its external quantum efficiency (EQE) to 12% and thus power conversion efficiency (PCE) also increases by nearly 0.5 percentage points. Thus, the production costs of mono-Si solar cell modules reduced by around 3.33%.

C. Quaternary semiconductor nanocrystals

Quaternary QDs have also been exploited to fabricate white LEDs. Zhang *et al*. successfully developed quaternary Cu–Zn–In–S (CZIS) QDs, and studied the optical performance of quantum dots. A new synthetic approach was exploited to fabricate various homogeneous CZIS QDs by varying reaction temperature and the ratios of the precursors, respectively. These as-prepared QDs exhibited not only broad PL spectra with emission color tuned from the visible to the NIR region but also high QY (over 70%) without coating the wide band gap shell materials. Further studies revealed good thermal stability, where the CZIS QDs did not show any obvious variation in emission intensity upon heating to 150˚C [164].

Song *et al*. [165] recently developed color-tunable Cu-In-Ga-S (CIGS) QDs and CIGS–ZnS core–shell QDs by adjusting the ratios of In:Ga to apply in white LEDs. The EL spectra of CIGS–ZnS QD based LEDs with different In:Ga ratios had been collected at 20 mA input current. With increasing In content in the CIGS–ZnS QDs, the conversion efficiency of the LED increased from 74 to 96%. Lately, Liu *et al*. [166] in 2015 synthesized quaternary $ZnCuInS_2$/ZnSe/ZnS QDs (ZCIS/ZnSe/ZnS) to exploit themfor fabricating white LEDs.Despite this recent progress, there are still remaining challenges: compared to the binary QDs, the ability to control the size, size distribution, and optical properties of quaternary QDs is still poor.

McDaniel *et al.* [167] synthesized CISeS QDs and used them as a sensitizer to enhance the photovoltaic performance of solar cell. The cation exchanged QDs increased the photovoltage and photocurrent in QDs based solar cell. They had achieved 3.45% of photovoltaic efficiency without optimizing the absorption in the film by refining QDs loading. Panthani *et al*. [168] synthesized CISeS/ZnS core/shell QDs with bright photoluminescence and quantum yield of 40%. These QDs did not contain toxic heavy metal and showed emission in red to near infrared region. Thus, they can be considered as promising candidates for biocompatible medical imaging.

Jie Wang *et al.* [169] synthesized ZAISe QDs with tunable emission and QY 30%. Xiang *et al*. [170] in 2014 synthesized AIS and AZIS QDs using hot injection method. The AIS QDs showed tunable emission with PL QY of 62% with Ag/Zn ratio of 1/4. They had blue shifted emission spectra by introducing Zn ions i.e. AZIS. They fabricated QD based LEDs and studied their electroluminescence properties.Yoon *et al*. [83] in 2015 synthesized eco-friendly Zn–Ag–In–S (ZAIS) and Zn–Cu–In–S (ZCIS) QDs by hot injection methodwith qunaum yield of 61% and 53%, respectively. These QDs were used to fabricate white down-converted light-emitting diodes (DC-LEDs). The various parameters were calculated with luminous efficacy (LE) of 31.2 lm/W, color rendering index (CRI) of 97, color quality scale (CQS) of 94 with warm white at a correlated color temperature (CCT) of 3500 K. Chung *et al*. [171] in 2011 fabricated white LED by using highly luminescent deep red emitting CuInS-ZnS (ZCIS) alloy nanocrystals. They had tuned the emission wavelengths by varying the Zn concentration in alloyed nanocrystals and studied their optical properties. They had calculated the device parameters of the fabricated white LED with luminous efficacy of 4.15 lm/W and CIE chromaticity coordinates of (0.3891, 0.3357) at 20 mA.

Peng *et al.* [172] synthesized Mn-doped ZnCuInS/ZnS core/shell nanocrystals that showed band edge emission along with dopant emission. Mn-doped ZnCuInS/ZnS nanocrystals with various band gaps had been prepared with controlled experiment conditions. Zhang *et al*. [164] synthesized quartenary CuZnInS nanocrystals of various sizes and composition by simply changing reaction temperature and the ratio of the precursors. The results demonstrate its efficient use in fabrication of quantum dots based LEDs. Kim *et al.* [173] produced quaternary Zn-Cu-Ga-S (ZCGS) QDs by alloying Zn into Cu-Ga-S (CGS) host QDs. The variation in composition gives tunable emissions in the azure-to-bluerange with quantum yields in the range of 78–83%. Their efficient properties makes them practically applicable for the fabrication of optoelectronic devices .

Therefore, the basic understanding of the photophysical process that takes place in colloidal nanocrystals is important. The emission mechanism for ternary and quatnary nanocrystals is different from binary nanocrystals. The composition variation in ternary nanocrystals enables stokes shifted tunabe emission spectra. Moreover, deposition of shell of higher band gap material enhances the intensity and stability of nanocrystals. Thus, alloying, doping and functionalization of nanocrystals makes them efficient for use in different applications.

III. CONCLUSION

In this review, the binary, ternary and quaternary semiconductor nanocrystals have been investigated in detail and their role for the development of light emitting diodes have been discussed. This review focuses on the development of nanocrystals. The various synthesis methods to synthesize nanocrystals and their optical properties have been explored. The inclusion of dopant element into the crystal structure induces new energy states in the band gap of nanocrystals, thus changes the emission pathway. Ternary nanocrystals have been used in wide range of applications as compared to binary nanocrystals. They show tunability in their photoluminescence behaviour, broad absorbance band, large stoke-shift. These crucial optical properties facilitates their use in light emitting diodes, solar cells, bioimaging etc. The significant work has been done to improve the quantum yield of nanocrystals to make their efficient use in various applications. The white light emitting diodes have been successfully fabricated by using these nanocrystals. Although, researchers have got success in obtaining good device parameters. However, the research is going on to obtain even better external quantum efficiency of fabricated LEDs along with other device parameters.

ACKNOWLEDGEMENTS

This study was funded by the SERB, Department of Science and Technology India, Project No. EMR/2016/002815.

REFERENCES

[1]. Aboulaich A., Michalska M., Schneider R., *et al.*, (2014). "Ce-Doped YAG Nanophosphor and Red Emitting $CuInS_2$/ZnS Core/Shell Quantum Dots for Warm White Light-Emitting Diode with High Color Rendering Index", *ACS Appl Mater Interfaces*, **6**(1): 252-258.

[2]. Bai Z., Ji W., Han D., et al., (2016). "Hydroxyl-Terminated $CuInS_2$ Based Quantum Dots: Toward Efficient and Bright Light Emitting Diodes", *Chem Mater*, **28**(4): 1085-1091.

[3]. Brus L., (1986). "Electronic wave functions in semiconductor clusters: experiment and theory", *J Phys Chem.*, **90**(12): 2555-2560.

[4]. Norris D.J., Efros A.L., Erwin S.C., (2008). "Doped Nanocrystals", *Science,* **319**(5871): 1776-1779.

[5]. Cao S., Li C., Wang L., et al., (2014). "Long-lived and Well-resolved Mn($^{2+}$) Ion Emissions in CuInS-ZnS Quantum Dots", *Sci Rep.*, **4**: 7510.

[6]. Wang C., Gao X., Ma Q., Su X., (2009). "Aqueous synthesis of mercaptopropionic acid capped Mn^{2+}-doped ZnSe quantum dots", *J. Mater Chem.*, **19**(38): 7016-7022.

[7]. Zheng J., Ji W., Wang X., et al., (2010). "Improved Photoluminescence of MnS/ZnS Core/Shell Nanocrystals by Controlling Diffusion of Mn Ions into the ZnS Shell", *J Phys Chem C*, **114**(36): 15331-15336.

[8]. Chen Y., Huang L., Li S., Pan D., (2013). "Aqueous synthesis of glutathione-capped Cu+ and Ag+-doped ZnxCd1-xS quantum dots with full color emission", *J Mater Chem C.*,**1**(4), 751-756.

[9]. Gurusinghe N.P., Hewa-Kasakarage N.N., Zamkov M., (2008). "Composition-Tunable Properties of CdSxTe1−x Alloy Nanocrystals", *J Phys Chem C*, **112**(33): 2795-12800.

[10]. Korgel B.A., Monbouquette H.G., (2000). "Controlled Synthesis of Mixed Core and Layered (Zn,Cd)S and (Hg,Cd)S Nanocrystals within Phosphatidylcholine Vesicles", *Langmuir*, **16**(8): 3588-3594.

[11]. Reiss P.B., Pron J. A., (2002). "Highly luminescent {CdSe}/ZnSe core/shell nanocrystals of low size dispersion", *Nano Lett.*, 2002, **2**.

[12]. Colvin V.L., Goldstein A.N., Alivisatos A.P., (1992). "Semiconductor nanocrystals covalently bound to metal surfaces with self-assembled monolayers", *J Am Chem Soc.*,**114**(13): 5221-5230.

[13]. Park J., Joo J., Kwon S.G., Jang Y., Hyeon T., (2007). "Synthesis of Monodisperse Spherical Nanocrystals", *Angew Chemie Int Ed.*, **46**(25): 4630-4660.

[14]. Peng X., Manna L., Yang W., et al., (2000). "Shape control of CdSe nanocrystals", *Nature*. **404**: 59.

[15]. Burda C., Chen X., Narayanan R., El-Sayed M.A., (2005). "Chemistry and Properties of Nanocrystals of Different Shapes", *Chem Rev.*, **105**(4), 1025-1102.

[16]. Kwon S.G., Piao Y., Park J., et al., (2007). "Kinetics of Monodisperse Iron Oxide Nanocrystal Formation by “Heating-Up” Process", *J Am Chem Soc.*, **129**: 12571-12584.

[17]. Yu K., Ouyang J., Zaman M.B., et al., (2009). "Single-Sized CdSe Nanocrystals with Band gap Photoemission via a Noninjection One-Pot Approach", *J Phys Chem C.*, **113**(9): 3390-3401.

[18]. Arellano I.H.J., Mangadlao J., Ramiro I.B., Suazo K.F., (2007). "3-component low temperature solvothermal synthesis of colloidal cadmium sulfide quantum dots", *Mater Lett.*, **64**(6), 785-788.

[19]. Paskov P.P. (1997). "Refractive indices of InSb, InAs, GaSb, InAs x Sb1-x, and In1- xGaxSb: Effects of free carriers", *J Appl Phys*, **81**(4): 1890-1898.

[20]. Haase M.A., Qiu J., DePuydt J.M., Cheng H., (1991). "Blue-green laser diodes", *Appl Phys Lett.*, **59**(11): 1272-1274.

[21]. Groneberg D.A., Giersig M., Welte T., Pison U., (2006)."Nanoparticle-based diagnosis and therapy", *Curr Drug Targets*, **7**(6): 643-648.

[22]. Afzaal M., O’Brien P., (2006). "Recent developments in II--VI and III--VI semiconductors and their applications in solar cells", *J Mater Chem.*, **16**(17): 1597-1602.

[23]. Sidot T., (1866). "Recherches sur la crystallisation de quelque sulphures m{é}talliques et sur les propri{é}t{é}s de la blende hexagonale", *Comptes Rend Ac Sci*., **62**: 999-1001.

[24]. Murray C.B., Norris D.J., Bawendi M.G., (1993). "Synthesis and characterization of nearly monodisperse CdE (E= sulfur, selenium, tellurium) semiconductor nanocrystallites", *J Am Chem Soc*., **115**(19): 8706-8715.

[25]. Cho K., Talapin D.V., Gaschler W., Murray C.B., (2005). "Designing PbSe Nanowires and Nanorings through Oriented Attachment of Nanoparticles", *J AM CHEM SOC*., **127**: 7140-7147.

[26]. Ouyang J., Kuijper J., Brot S., et al., (2009). "Photoluminescent colloidal CdS nanocrystals with high quality via noninjection one-pot synthesis in 1-octadecene", *J Phys Chem C*.,**113**(18): 7579-7593.

[27]. Liu T.Y., Li M., Ouyang J., et al., (2009). "Non-injection and low-temperature approach to colloidal photoluminescent PbS nanocrystals with narrow bandwidth", *J Phys Chem C*., **113**(6): 2301-2308.

[28]. Yu W.W., Peng X., (2002). "Formation of high-quality CdS and other II--VI semiconductor nanocrystals in noncoordinating solvents: tunable reactivity of monomers", *Angew Chemie Int Ed*., **41**(13): 2368-2371.

[29]. Wang Q., Pan D., Jiang S., Ji X., An L., Jiang B., (2006). "Luminescent CdSe and CdSe/CdS core-shell nanocrystals synthesized via a combination of solvothermal and two-phase thermal routes", *J Lumin*., **118**(1), 91-98.

[30]. Xu J., Ge J.P., Li Y.D., (2006). "Solvothermal synthesis of monodisperse PbSe nanocrystals", *J Phys Chem B*., **110**(6): 2497-2501.

[31]. Nag A., Sarma D.D., (2009). "Solvothermal synthesis of InP quantum dots". *J Nanosci Nanotechnol*., **9**(9): 5633-5636.

[32]. Talapin D.V., Lee J.S., Kovalenko M.V., Shevchenko E.V., (2010). "Prospects of Colloidal Nanocsrystals for Electronic and Optoelectronic Applications", *Chem Rev*., **110**: 389-458.

[33]. Yang W., Li W., Dou H., Sun K., (2008). "Hydrothermal synthesis for high-quality CdTe quantum dots capped by cysteamine", *Mater Lett*., **62**(17-18), 2564-2566.

[34]. Zhao D., He Z., Chan W.H., Choi M.M.F, (2008). "Synthesis and characterization of high-quality water-soluble near-infrared-emitting CdTe/CdS quantum dots capped by N-acetyl-L-cysteine via hydrothermal method", *J Phys Chem C*., **113**(4): 1293-1300.

[35]. Wang J., Han H., (2010). "Hydrothermal synthesis of high-quality type-II CdTe/CdSe quantum dots with near-infrared fluorescence", *J Colloid Interface Sci*., **351**(1): 83-87.

[36]. Mao W., Guo J., Yang W., Wang C., He J., Chen J., (2007). "Synthesis of high-quality near-infrared-emitting CdTeS alloyed quantum dots via the hydrothermal method", *Nanotechnology*, **18**(48): 485611.

[37]. Li L., Qian H., Ren J., (2005). "Rapid synthesis of highly luminescent CdTe nanocrystals in the aqueous phase by microwave irradiation with controllable temperature", *Chem Commun*., (**4**), 528-530.

[38]. He Y., Lu H.T., Sai L.M., et al., (2008). "Microwave Synthesis of Water-Dispersed CdTe/CdS/ZnS Core-Shell-Shell Quantum Dots with Excellent Photostability and Biocompatibility", *Adv Mater*., **20**(18): 3416-3421.

[39]. Chu M., Shen X., Liu G., (2005). "Microwave irradiation method for the synthesis of water-soluble CdSe nanoparticles with narrow photoluminescent emission in aqueous solution", *Nanotechnology*, **17**(2): 444.

[40]. Qian H., Qiu X., Li L., Ren J., (2006). "Microwave-assisted aqueous synthesis: a rapid approach to prepare highly luminescent ZnSe (S) alloyed quantum dots", *J Phys Chem B*., **110**(18): 9034-9040.

[41]. Qian H., Li L., Ren J., (2005). "One-step and rapid synthesis of high quality alloyed quantum dots (CdSe--CdS) in aqueous phase by microwave irradiation with controllable temperature", *Mater Res Bull*., **40**(10): 1726-1736.

[42]. Peng Z.A., Peng X., (2001). "Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor", *J Am Chem Soc*.,**123**(1): 183-184.

[43]. Spanhel L., Haase M., Weller H., Henglein A., (1987). "Photochemistry of colloidal semiconductors. 20. Surface modification and stability of strong luminescing CdS particles", *J Am Chem Soc*., **109**(19): 5649-5655.

[44]. Hines M.A., Guyot-Sionnest P., (1996). "Synthesis and characterization of strongly luminescing ZnS-capped CdSe nanocrystals", *J Phys Chem*., **100**(2): 468-471.

[45]. Dabbousi B.O., Rodriguez-Viejo J., Mikulec F.V., et al., (1997). "(CdSe) ZnS core- shell quantum dots: synthesis and characterization of a size series of highly luminescent nanocrystallites", *J Phys Chem B*., **101**(46): 9463-9475.

[46]. Mokari T., Banin U., (2003). "Synthesis and properties of CdSe/ZnS core/shell nanorods",*Chem Mater*., **15**(20): 3955-3960.

[47]. Kudera S., Zanella M., Giannini C., et al., (2007). "Sequential Growth of Magic-Size CdSe Nanocrystals", *Adv Mater*., **19**(4): 548-552.

[48]. Jun S., Jang E., (2005). "Interfused semiconductor nanocrystals: brilliant blue photoluminescence and electroluminescence", *Chem Commun*., (**36**): 4616-4618.

[49]. Lim S.J., Chon B., Joo T., Shin S.K., (2008). "Synthesis and characterization of zinc-blende CdSe-based core/shell nanocrystals and their luminescence in water", *J Phys Chem C*., **112**(6): 1744-1747.

[50]. Chen Z., Moore J., Radtke G., et al., (2007). "Binary Nanoparticle Superlattices in the Semiconductor - Semiconductor System : CdTe and CdSe", *J AM CHEM SOC*., **129**: 15702-15709.

[51]. Bang J., Park J., Lee J.H., et al., (2010). "ZnTe/ZnSe (Core/Shell) Type-II Quantum Dots : Their Optical and Photovoltaic Properties", *Chem Mater*., **22**(13), 233-240.

[52]. Talapin D.V., Rogach AL., Kornowski A., Haase M., Weller H., (2001). "Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine- trioctylphosphine oxide- trioctylphospine mixture", *Nano Lett*., **1**(4): 207-211.

[53]. Ding Y., Sun H., Liu D., Liu F., Wang D., Jiang Q., (2013). "Water-soluble, high-quality ZnSe@ ZnS core/shell structure nanocrystals", *J Chinese Adv Mater Soc*., **1**(1): 56-64.

[54]. Fu Y., Kim D., Jiang W., Yin W., Ahn T.K., Chae H., (2017). "Excellent stability of thicker shell CdSe@ ZnS/ZnS quantum dots", *RSC Adv*., **7**(65): 40866-40872.

[55]. Xu S., Shen H., Zhou C., et al., (2011). "Effect of Shell Thickness on the Optical Properties in CdSe/CdS/Zn0.5Cd0.5S/ZnS and CdSe/CdS/ZnxCd1-

xS/ZnS Core/Multishell Nanocrystals", *J Phys Chem C*., **115**(43): 20876-20881.

[56]. Jun S., Jang E., (2013). "Bright and stable alloy core/multishell quantum dots", *Angew Chemie Int Ed*., **52**(2): 679-682.

[57]. Fitzmorris B.C., Pu Y.C., Cooper J.K., et al., (2013). "Optical Properties and Exciton Dynamics of Alloyed Core/Shell/Shell Cd1--x Zn x Se/ZnSe/ZnS Quantum Dots", *ACS Appl Mater Interfaces,* **5**(8): 2893-2900.

[58]. Lee K.H., Lee J.H., Kang H.D., et al., (2014). "efficient green quantum dot electroluminescent device comprising uniquely large-sized quantum dots", *ACS Nano*. **8**(5): 4893-4901.

[59]. Yang Y., Zheng Y., Cao W., et al., (2015). "High-efficiency light-emitting devices based on quantum dots with tailored nanostructures", *Nat Photonics*., **9**(4): 2015.

[60]. Boonsin R., Barros A., Donat F., et al., (2017). "Optical Properties and Reliability Studies of Gradient Alloyed Green Emitting (CdSe)x(ZnS)1-x and Red Emitting (CuInS$_2$)x (ZnS)1-x Quantum Dots for White Light-Emitting Diodes". *ACS photonics*, 2017.

[61]. Wang N., Koh S., Jeong B.G., et al., (2017). "Highly luminescent silica-coated CdS/CdSe/CdS nanoparticles with strong chemical robustness and excellent thermal stability", *Nanotechnology,* **28**(18): 185603.

[62]. Yang Y., Chen O., Angerhofer A., Cao Y.C., (2006). "Radial-position-controlled doping in CdS/ZnS core/shell nanocrystals", *J Am Chem Soc,* **128**(38): 12428-12429.

[63]. Schwartz D.A., Norberg N.S., Nguyen Q.P., Parker J.M., Gamelin D.R., (2003). "Magnetic quantum dots: synthesis, spectroscopy, and magnetism of Co^{2+}-and Ni^{2+}-doped ZnO nanocrystals", *J Am Chem Soc*., **125**(43): 13205-13218.

[64]. den Bossche J., Neyts KA., De Visschere P., et al., (1994). "XPS study of TbF3 and TbOF centres in ZnS", *Phys status solidi*., **146**, (2).

[65]. Tohda T., Fujita Y., Matsuoka T., Abe A., (1986). "New efficient phosphor material ZnS: Sm, P for red electroluminescent devices", *Appl Phys Lett*., **48**(2): 95-96.

[66]. Kuk V.K., Kynev K.D., (1989). "Luminescence of ZnS: Dy, Cu, ZnS: Pr, Cu and ZnS: Ho, Cu phosphors depending on the activator and coactivator concentration",*J Mater Sci Lett*., **8**(6): 711-715.

[67]. Yang H., Santra S., Holloway P.H., (2005). "Syntheses and applications of Mn-doped II-VI semiconductor nanocrystals",*J Nanosci Nanotechnol*., **5**(9): 1364-1375.

[68]. Bol A.A., Meijerink A., (2001). "Luminescence quantum efficiency of nanocrystalline ZnS: Mn^{2+}1 Surface passivation and Mn^{2+} concentration", *J Phys Chem B*., **105**(42): 10197-10202.

[69]. Bhargava R.N., Gallagher D., Hong X., Nurmikko A., (1994). "Optical properties of manganese-doped nanocrystals of ZnS", *Phys Rev Lett*., **72**(3): 416-419.

[70]. Quan Z., Wang Z., Yang P., Lin J., Fang J., (2007). "Synthesis and Characterization of High-Quality ZnS, ZnS:Mn^{2+}, and ZnS:Mn^{2+}/ZnS (Core/Shell) Luminescent Nanocrystals", *Inorg Chem*., **46**(4): 1354-1360.

[71]. Chen, W., Zhang, Jin Z., Joly A.G., (2004). "Optical properties and potential applications of doped semiconductor nanoparticles", *J Nanosci Nanotechnol*., **4**: 919-947.

[72]. Cheng B.C., Wang Z.G., (2005). "Synthesis and Optical Properties of Europium-Doped ZnS: Long-Lasting Phosphorescence from Aligned Nanowires", *Adv Funct Mater*., **15**(11): 1883-1890.

[73]. Bol A.A., van Beek R., Meijerink A., (2002). "On the Incorporation of Trivalent Rare Earth Ions in II–VI Semiconductor Nanocrystals", *Chem Mater*., **14**(3): 1121-1126.

[74]. Xie R., Peng X., (2009). "Synthesis of Cu-doped InP nanocrystals (d-dots) with ZnSe diffusion barrier as efficient and color-tunable NIR emitters". *J Am Chem Soc*., **131**(30): 10645-10651.

[75]. Wood V., Halpert J.E., Panzer M.J., Bawendi M.G., Bulović V., (2009). "Alternating Current Driven Electroluminescence from ZnSe/ZnS:Mn/ZnS Nanocrystals", *Nano Lett*., **9**(6): 2367-2371.

[76]. Toyama T., Hama T., Adachi D., Nakashizu Y., Okamoto H., (2009). "An electroluminescence device for printable electronics using coprecipitated ZnS:Mn nanocrystal ink", *Nanotechnology*, **20**(5): 55203.

[77]. Corrado C., Jiang Y., Oba F., Kozina M., Bridges F., Zhang J.Z., (2009). "Synthesis, Structural, and Optical Properties of Stable ZnS:Cu,Cl Nanocrystals", *J Phys Chem A*., **113**(16): 3830-3839.

[78]. Xin M., Liu D.P., Yu N. Sen, Qi X.H., Li H., (2012). "Luminescence Properties of ZnS:Cu,Tm Semiconductor Nanocrystals Synthesize by a Hydrothermal Process", In: *Advanced Materials, ICAMMP 2011*. Vol **415.** Trans Tech Publications, 499-503.

[79]. Hazarika A., Layek A., De S., et al., (2013). "Ultranarrow and Widely Tunable Mn+-Induced Photoluminescence from Single Mn-Doped Nanocrystals of ZnS-CdS Alloys", *Phys Rev Lett*., **110**(26): 267401.

[80]. Mei X., Li-Zhong H., (2013). "Luminescence properties of ZnS:Cu, Eu semiconductor nanocrystals synthesized by a hydrothermal process",*Chinese Phys B*., **22**(8): 87804.

[81]. Gao X., Zhuo N., Liao C., et al., (2015)."Industrial fabrication of Mn-doped CdS/ZnS core/shell nanocrystals for white-light-emitting diodes",*Opt Mater Express*, **5**(10): 2164-2173.

[82]. Cooper J.K., Gul S., Lindley S.A., Yano J., Zhang J.Z., (2015). "Tunable Photoluminescent Core/Shell Cu+ Doped ZnSe/ZnS Quantum Dots Codoped with Al^{3+} , Ga^{3+}, or In^{3+}", *ACS Appl Mater Interfaces*, **7**: 10055–10066.

[83]. Yoon H.C., Oh J.H., Ko M., Yoo H., Do Y.R., (2015). "Synthesis and Characterization of Green Zn–Ag–In–S and Red Zn–Cu–In–S Quantum Dots for Ultrahigh Color Quality of Down-Converted White LEDs",*ACS Appl Mater Interfaces*, **7**(13): 7342-7350.

[84]. Koitabashi K., Ozaki S., Adachi S., (2010). "Optical properties of single-crystalline chalcopyrite semiconductor AgInSe$_2$",*J Appl Phys*., **107**(5): 53516.

[85]. Dai M., Ogawa S., Kameyama T., et al., (2012). "Tunable photoluminescence from the visible to near-infrared wavelength region of non-stoichiometric AgInS$_2$ nanoparticles", *J Mater Chem*, **22**(25): 12851-12858.

[86]. Pan D., An L., Sun Z., et al., (2008). "Synthesis of Cu–In–S Ternary Nanocrystals with Tunable Structure and Composition", *J Am Chem Soc*., **130**(17): 5620-5621.

[87]. Raffaelle R.P., Castro S.L., Hepp A.F., Bailey S.G., (2002). "Quantum dot solar cells", *Prog Photovoltaics Res Appl*., **10**(6): 433-439.

[88]. Liu S., Zhang H., Qiao Y., Su X., (2012). "One-pot synthesis of ternary $CuInS_2$ quantum dots with near-infrared fluorescence in aqueous solution", *RSC Adv.*, **2**(3): 819-825.

[89]. Panthani M.G., Akhavan V., Goodfellow B., et al.,(2008). "Synthesis of $CuInS_2$, $CuInSe_2$, and $Cu(In_xGa_{1-x})Se_2$ (CIGS) Nanocrystal “Inks” for Printable Photovoltaics", *J Am Chem Soc.*, **130**(49): 16770-16777.

[90]. Fang X.S., Bando Y., Shen G.Z., et al., (2007). "Ultrafine ZnS Nanobelts as Field Emitters", *Adv Mater.*, **19**(18): 2593-2596.

[91]. Jaffe J.E., Zunger A., (1983). "Electronic structure of the ternary chalcopyrite semiconductors $CuAlS_2$, $CuGaS_2$, $CuInS_2$, $CuAlSe_2$, $CuGaSe_2$, and $CuInSe_2$", *Phys Rev B*, **28**(10): 5822-5847.

[92]. Gurin V.S., (1998). "Nanoparticles of ternary semiconductors in colloids: Low-temperature formation and quantum size effects", *Colloids Surfaces A Physicochem Eng Asp*, **142**(1): 35-40.

[93]. J. Carmalt C., E. Morrison D., P. Parkin I., (1998). "Solid-state and solution phase metathetical synthesis of copper indium chalcogenides", *J Mater Chem.*, **8**(10): 2209-2211.

[94]. Lu Q., Hu J., Tang K., Qian Y., Zhou G., Liu X., (2000). "Synthesis of Nanocrystalline $CuMS_2$ (M= In or Ga) through a Solvothermal Process", *Inorg Chem.*, **39**(7): 1606-1607.

[95]. Malik M.A., O’Brien P., Revaprasadu N., (1999). "A Novel Route for the Preparation of CuSe and $CuInSe_2$ Nanoparticles", *Adv Mater.*, **11**(17): 1441-1444.

[96]. Li B., Xie Y., Huang J., Qian Y., (1999). "Synthesis by a Solvothermal Route and Characterization of $CuInSe_2$ Nanowhiskers and Nanoparticles", *Adv Mater.*, **11**(17): 1456-1459.

[97]. Jiang Y., Wu Y., Mo X., Yu W., Xie Y., Qian Y., (2000). "Elemental Solvothermal Reaction To Produce Ternary Semiconductor $CuInE_2$ (E=S, Se) Nanorods", *Inorg Chem.*, **39**(14): 2964-2965.

[98]. Xiao J., Xie Y., Tang R., Qian Y., (2001). "Synthesis and Characterization of Ternary CuInS2 Nanorods via a Hydrothermal Route", *J Solid State Chem.*, **161**(2): 179-183.

[99]. Castro S.L., Bailey S.G., Raffaelle R.P., Banger K.K., Hepp A.F., (2003). "Nanocrystalline Chalcopyrite Materials ($CuInS_2$ and $CuInSe_2$) via Low-Temperature Pyrolysis of Molecular Single-Source Precursors", *Chem Mater.*, **15**(16): 3142-3147.

[100]. Castro S.L., Bailey S.G., Raffaelle R.P., Banger K.K., Hepp A.F., (2004). "Synthesis and Characterization of Colloidal $CuInS_2$ Nanoparticles from a Molecular Single-Source Precursor", *J Phys Chem B.*, **108**(33): 12429-12435.

[101]. Grisaru H., Palchik O., Gedanken A., Palchik V., Slifkin M.A., Weiss A.M. (2003). "Microwave-Assisted Polyol Synthesis of $CuInTe_2$ and $CuInSe_2$ Nanoparticles. *Inorg Chem.*, **42**(22): 7148-7155.

[102]. Wei Q., Mu J. (2005). "Synthesis of $CuInS_2$ Nanocubes by a Wet Chemical Process",*J Dispers Sci Technol.*, **26**(5): 555-558.

[103]. Batabyal S.K, Tian L., Venkatram N., Ji W., Vittal J.J. (2009). "Phase-Selective Synthesis of $CuInS_2$ Nanocrystals", *J Phys Chem C.*, **113**(33): 15037-15042.

[104]. Dutta D.P., Sharma G. (2006). "A facile route to the synthesis of $CuInS_2$ nanoparticles",*Mater Lett.*, **60**(19): 2395-2398.

[105]. Gardner J.S, Shurdha E., Wang C., Lau L.D, Rodriguez R.G, Pak J.J. (2008). "Rapid synthesis and size control of $CuInS_2$ semi-conductor nanoparticles using microwave irradiatio", *J Nanoparticle Res.*, **10**(4): 633-641.

[106]. Tang X., Ho W.B.A., Xue J.M. (2012). "Synthesis of Zn-Doped $AgInS_2$ Nanocrystals and Their Fluorescence Properties", *J Phys Chem C.*, **116**(17): 9769-9773.

[107]. Nairn J.J, Shapiro P.J, Twamley B., et al. (2006). "Preparation of Ultrafine Chalcopyrite Nanoparticles via the Photochemical Decomposition of Molecular Single-Source Precursors", *Nano Lett.*, **6**(6): 1218-1223.

[108]. Tian L, Elim H.I., Ji W., Vittal J.J. (2006). "One-pot synthesis and third-order nonlinear optical properties of $AgInS_2$ nanocrystals",*Chem Commun.*, (**41**): 4276-4278.

[109]. Ng M.T, Boothroyd C.B, Vittal J.J. (2006). "One-Pot Synthesis of New-Phase $AgInSe_2$ Nanorods", *J Am Chem Soc.*, **128**(22): 7118-7119.

[110]. Tian L., Vittal J.J. (2007). "Synthesis and characterization of ternary $AgInS_2$ nanocrystals by dual- and multiple-source methods",*New J Chem.*, **31**(12): 2083-2087.

[111]. Wang D., Zheng W., Hao C., Peng Q., Li Y. (2008). "General synthesis of I-III-VI_2 ternary semiconductor nanocrystals", *Chem Commun.*, **0**(22): 2556-2558.

[112]. Xie R., Rutherford M., Peng X. (2009). "Formation of High-Quality I–III–VI Semiconductor Nanocrystals by Tuning Relative Reactivity of Cationic Precursors". *J Am Chem Soc.*, **131**(15): 5691-5697.

[113]. Norako M.E, Franzman M.A, Brutchey R.L. (2009). "Growth Kinetics of Monodisperse Cu–In–S Nanocrystals Using a Dialkyl Disulfide Sulfur Source", *Chem Mater.*, **21**(18): 4299-4304.

[114]. Park J., Kim S.W. (2011). "$CuInS_2$/ZnS core/shell quantum dots by cation exchange and their blue-shifted photoluminescence", *J Mater Chem.*, **21**(11), 3745-3750.

[115]. Mao B., Chuang C.H., Wang J., Burda C. (2011). "Synthesis and Photophysical Properties of Ternary I–III–VI $AgInS_2$ Nanocrystals: Intrinsic versus Surface States", *J Phys Chem C.*, **115**(18): 8945-8954.

[116]. Li T.L., Lee Y.L, Teng H. (2012). "High-performance quantum dot-sensitized solar cells based on sensitization with $CuInS_2$ quantum dots/CdS heterostructure", *Energy Environ Sci.*, **5**(1): 5315-5324.

[117]. Allen P.M, Bawendi M.G. (2008). "Ternary I–III–VI Quantum Dots Luminescent in the Red to Near-Infrared",*J Am Chem Soc.*, **130**(29): 9240-9241.

[118]. Pan D., Weng D., Wang X., et al. (2009). "Alloyed semiconductor nanocrystals with broad tunable band gaps", *Chem Commun.*, **0**(0): 4221-4223.

[119]. Zhong H., Wang Z., Bovero E., L.Z, Van Veggel F.C.J.M., Scholes G.D. (2011). "Colloidal $CuInSe_2$ Nanocrystals in the Quantum Confinement Regime: Synthesis, Optical Properties, and Electroluminescence", *J Phys Chem C.*, **115**(25): 12396-12402.

[120]. Omata T, Nosel K O-Y-MS. (2011). "Fabrication of CoreShell-Type Copper Indium Selenide and Zinc Selenide Composite Quantum Dots and Their Optical Properties",. *J Nanosci Nanotechnol.*, **11**(6): 4815-4823.

[121]. Yarema O, Bozyigit D, Rousseau I, et al. (2013). "Highly Luminescent, Size- and Shape-Tunable Copper Indium Selenide Based Colloidal Nanocrystals", *Chem Mater.*, **25**(18): 3753-3757.

[122]. Deng D., Qu L., Zhang J., Ma Y., Gu Y. (2013). "Quaternary Zn–Ag–In–Se Quantum Dots for Biomedical Optical Imaging of RGD-Modified Micelles", *ACS Appl Mater Interfaces*., **5**(21): 10858-10865.

[123]. Deng D., Qu L., Gu Y. (2014). "Near-infrared broadly emissive $AgInSe_2$/ZnS quantum dots for biomedical optical imaging", *J Mater Chem C*., **2**(34): 7077-7085.

[124]. Bachmann V., Ronda C., Meijerink A. (2009). "Temperature Quenching of Yellow Ce^{3+} Luminescence in YAG:Ce", *Chem Mater*., **21**(10): 2077-2084.

[125]. Nakamura H., Kato W., Uehara M., et al. (2006). "Tunable Photoluminescence Wavelength of Chalcopyrite $CuInS_2$-Based Semiconductor Nanocrystals Synthesized in a Colloidal System", *Chem Mater*., **18**(14): 3330-3335.

[126]. Hamanaka Y., Kuzuya T., Sofue T., Kino T., Ito K., Sumiyama K. (2008). "Defect-induced photoluminescence and third-order nonlinear optical response of chemically synthesized chalcopyrite $CuInS_2$ nanoparticles",*Chem Phys Lett*., **466**(4): 176-180.

[127]. Kameyama T., Douke Y., Shibakawa H., et al. (2014). "Widely Controllable Electronic Energy Structure of ZnSe–$AgInSe_2$ Solid Solution Nanocrystals for Quantum-Dot-Sensitized Solar Cells", *J Phys Chem C*., **118**(51): 29517-29524.

[128]. Torimoto T., Adachi T., Okazaki K., et al. (2007). "Facile Synthesis of ZnS–$AgInS_2$ Solid Solution Nanoparticles for a Color-Adjustable Luminophore", *J Am Chem Soc*., **129**(41): 12388-12389.

[129]. Torimoto T., Ogawa S., Adachi T., et al. (2010). "Remarkable photoluminescence enhancement of ZnS-$AgInS_2$ solid solution nanoparticles by post-synthesis treatment", *Chem Commun*., **46**(12): 2082-2084.

[130]. Ogawa T., Kuzuya T., Hamanaka Y., Sumiyama K. (2010). "Synthesis of Ag-In binary sulfide nanoparticles-structural tuning and their photoluminescence properties", *J Mater Chem*., **20**(11), 2226-2231.

[131]. Chang J.Y., Wang G.Q., Cheng C.Y., Lin W.X., Hsu J.C. (2012). "Strategies for photoluminescence enhancement of $AgInS_2$ quantum dots and their application as bioimaging probes", *J Mater Chem*., **22**(21): 10609-10618.

[132]. Hamanaka Y., Ogawa T., Tsuzuki M., Kuzuya T. (2011). "Photoluminescence Properties and Its Origin of $AgInS_2$ Quantum Dots with Chalcopyrite Structure", *J Phys Chem C*., **115**(5): 1786-1792.

[133]. Chung W., Jung H., Lee C.H., Kim S.H. (2014). "Extremely high color rendering white light from surface passivated carbon dots and Zn-doped $AgInS_2$ nanocrystals", *J Mater Chem C*., **2**(21): 4227-4232.

[134]. Wang C., Xu S., Shao Y., Wang Z., Xu Q., Cui Y. (2014). "Synthesis of Ag doped ZnInSe ternary quantum dots with tunable emission", *J Mater Chem C*., **2**(26): 5111-5115.

[135]. Langevin M-A, Ritcey AM, Allen CN. (2014). "Air-Stable Near-Infrared $AgInSe_2$ Nanocrystals", *ACS Nano*., **8**(4): 3476-3482.

[136]. Lu M., Bai X., Lin Y., et al. (2016). "Liquid-type $AgInS_2$/ZnS quantum dot-based warm white light-emitting diodes",*Chem Phys Lett*., **661**: 228-233.

[137]. Chen Z., Li D., Zhang W., et al. (2008). "Low-Temperature and Template-Free Synthesis of ZnIn2S4 Microspheres", *Inorg Chem*., **47**(21): 9766-9772.

[138]. Kim J., Lee M., Yang H. (2008). "Synthesis of $Zn_{1-x}Cd_xS$:Mn/ZnS quantum dots and their application to light-emitting diodes", *Nanotechnology*., **19**, 465605.

[139]. Gou X., Cheng F., Shi Y., Zhang L., Peng S., Chen J. (2006). "Shape-Controlled Synthesis of Ternary Chalcogenide $ZnIn_2S_4$ and $CuIn(S,Se)_2$ Nano-/Microstructures via Facile Solution Route", *J Am Chem Soc*., **128**(12): 7222-7229.

[140]. Shen S., Zhao L., Guo L. (2010). "$ZnmIn_2S^{3+}m$ (m=1- 5, integer): A new series of visible-light-driven photocatalysts for splitting water to hydrogen", *Int J Hydrogen Energy*., **35**(19): 10148-10154.

[141]. Cao S., Zhao J., Yang W., Li C., Zheng J. (2015). "Mn^{2+}-doped Zn--In--S quantum dots with tunable bandgaps and high photoluminescence properties", *J Mater Chem C*., **3**(34): 8844-8851.

[142]. Peng S., Li L.., Wu Y., et al. (2013). "Size- and shape-controlled synthesis of $ZnIn_2S_4$ nanocrystals with high photocatalytic performance",*Cryst Eng Comm*., **15**(10): 1922-1930.

[143]. Wei Xu, Xiangdong Meng, Wenyu Ji, Pengtao Jing, Jinju Zheng, Xueyan Liu, Jialong Zhao HL. (2012). "Photoluminescence properties of Mn-doped $ZnxCd_{1-x}S$ nanocrystals synthesized via nucleation-doping strategy",*Chem Phys Lett*., **532**: 72–76.

[144]. De M.K.M. and G. (2013). "Fabrication of $Cd_{0.5}Zn_{0.5}S$:Cu QDs incorporated organically modified SiO_2 films showing entire visible colour emission with high quantum yield", *J Mater Chem C*., **1**: 4816-4820.

[145]. Zeng R., Sun Z., Cao S., et al. (2015). "Facile synthesis of Ag-doped ZnCdS nanocrystals and transformation into Ag-doped ZnCdSSe nanocrystals with Se treatment", *RSC Adv*., **5**(2): 1083-1090.

[146]. Ouyang J., Ripmeester J.A., Wu X., *et al.* (2007). "Upconversion Luminescence of Colloidal CdS and ZnCdS Semiconductor Quantum Dots", *J Phys Chem C*., **111**(44): 16261-16266.

[147]. Ouyang J., Ratcliffe C.I., Kingston D., et al. (2008). "Gradiently Alloyed ZnxCd1-xS Colloidal Photoluminescent Quantum Dots Synthesized via a Noninjection One-Pot Approach", *J Phys Chem C*., **112**(13): 4908-4919.

[148]. Shen H., Cao W., Shewmon N.T., Yang C., Li L.S., Xue J. (2015). "High-Efficiency, Low Turn-on Voltage Blue-Violet Quantum-Dot-Based Light-Emitting Diodes", *Nano Lett*., **15**(2): 1211-1216.

[149]. Chen Z., Lian C., Zhou D., et al. (2010). "Greatly enhanced and controlled manganese photoluminescence in water-soluble ZnCdS:Mn/ZnS core/shell quantum dots", *Chem Phys Lett*., **488**(1-3): 73-76.

[150]. Wang X., Damasco J., Shao W., Ke Y., Swihart M.T. (2016). "Synthesis of Zn–In–S Quantum Dots with Tunable Composition and Optical Properties",*Chem Phys Chem*., **17**(5): 687-691.

[151]. Li J., Liu Y., Hua J, Tian L, Zhao J. (2016). "Photoluminescence properties of transition metal-doped Zn-In-S/ZnS core/shell quantum dots in solid films", *RSC Adv*., **6**(50): 44859-44864.

[152]. Shen S., Chen J., Wang X., Zhao L., Guo L. (2011). "Microwave-assisted hydrothermal synthesis of transition-metal doped $ZnIn_2S_4$ and its photocatalytic activity for hydrogen evolution under visible light", *J Power Sources*., **196**(23): 10112-10119.

[153]. Sarkar S., Karan N.S., Pradhan N. (2011). "Ultrasmall Color-Tunable Copper-Doped Ternary Semiconductor Nanocrystal Emitters", *Angew Chemie Int Ed*., **50**(27): 6065-6069.

[154]. Yuan X., Hua J., Zeng R., et al. (2014). "Efficient

white light emitting diodes based on Cu-doped ZnInS/ZnS core/shell quantum dots", *Nanotechnology.*, **25**(43): 435202.

[155]. Zhang W., Lou Q., Ji W., Zhao J., Zhong X. (2014). "Color-Tunable Highly Bright Photoluminescence of Cadmium-Free Cu-Doped Zn–In–S Nanocrystals and Electroluminescence", *Chem Mater.*, **26**: 1204-1212.

[156]. Yuan X., Ma R., Zhang W., et al. (2015)."Dual Emissive Manganese and Copper Co-Doped Zn – In – S Quantum Dots as a Single Color-Converter for High Color Rendering White- Light-Emitting Diodes", *Appl Mater Interfaces.*, **7**: 8659–8666.

[157]. Huang G., Wang C., Xu X., Cui Y. (2016). "An optical ratiometric temperature sensor based on dopant-dependent thermal equilibrium in dual-emitting Ag&Mn: ZnInS quantum dots", *RSC Adv.*, **6**(63): 58113-58117.

[158]. Jiang T., Song J., Wang H., et al. (2015). "Aqueous synthesis of color tunable Cu doped Zn-In-S/ZnS nanoparticles in the whole visible region for cellular imaging", *J Mater Chem B.*, **3**(11): 2402-2410.

[159]. Xuan T.T., Liu J.Q., Yu C.Y., Xie R.J., Li H.L. (2016). "Facile Synthesis of Cadmium-Free Zn-In-S:Ag/ZnS Nanocrystals for Bio-Imaging", *Sci Rep.*, **6**: 24459.

[160]. Yuan X., Ma R., Hua J., et al. (2016). "Thermal stability of photoluminescence in Cu-doped Zn-In-S quantum dots for light-emitting diodes", *Phys Chem Chem Phys.*, **18**(16): 10976-10982.

[161]. Yakoubi A., Ben T., Aboulaich A., et al. (2016). "Aqueous synthesis of Cu-doped CdZnS quantum dots with controlled and efficient photoluminescence", *J Lumin.*, **175**: 193-202.

[162]. Yadav I., Singh D., Rachna A. (2016). "Cu-doped $Cd_{1-x}Zn_xS$ alloy: synthesis and structural investigations", *Appl Phys A.*, **122**(3): 1-6.

[163]. Levchuk I., Würth C., Krause F., *et al.* (2016). "Industrially scalable and cost-effective Mn^{2+} doped $ZnxCd_{1-x}S/ZnS$ nanocrystals with 70% photoluminescence quantum yield, as efficient down-shifting materials in photovoltaics", *Energy Environ Sci.*, **9**(3): 1083-1094.

[164]. Zhang J., Xie R., Yang W.A. (2011)."Simple Route for Highly Luminescent Quaternary Cu-Zn-In-S Nanocrystal Emitters", *Chem Mater.*, **23**: 3357-3361.

[165]. Song W.S, Kim J.H., Lee J.H, Lee H.S, Do Y.R, Yang H. (2012). "Synthesis of color-tunable Cu-In-Ga-S solid solution quantum dots with high quantum yields for application to white light-emitting diodes", *J Mater Chem.*, **22**(41): 21901-21908.

[166]. Wenyan L., Yu Z., Cheng R., Dan W., Tieqiang Z., Yi F, Wenzhu G., Jingzhi Y., Yiding W., Alexis P.R, Michael Z.H. (2015). "ZnCuInS/ZnSe/ZnS Quantum Dot-Based Downconversion Light-Emitting Diodes and Their Thermal Effect",*J Nanomater.*, 2015: 298614.

[167]. McDaniel H., Fuke N., Pietryga J.M., Klimov VI. (2013)."Engineered $CuInSe_xS_{2-x}$ Quantum Dots for Sensitized Solar Cells". *J Phys Chem Lett.*, **4**(3): 355-361.

[168]. Panthani M.G., Khan T.A., Reid D.K., et al. (2013). "In Vivo Whole Animal Fluorescence Imaging of a Microparticle-Based Oral Vaccine Containing $(CuInSexS_{2-x})/ZnS$ Core/Shell Quantum Dots", *Nano Lett.*, **13**(9): 4294-4298.

[169]. Wang J., Zhang R., Bao F., Han Z., Gu Y., Deng D. (2015). "Water-soluble Zn-Ag-In-Se quantum dots with bright and widely tunable emission for biomedical optical imaging", *RSC Adv.*, **5**(108): 88583-88589.

[170]. Xiang W., Xie C., Wang J., et al. (2014)."Studies on highly luminescent $AgInS_2$ and Ag–Zn–In–S quantum dots", *J Alloys Compd.*, **588**: 114-121.

[171]. Chung W., Jung H., Lee C.H., Park S.H., Kim J., Kim S.H. (2011). "Synthesis and Application of Non-Toxic $ZnCuInS_2/ZnS$ Nanocrystals for White LED by Hybridization with Conjugated Polymer", *J Electrochem Soc.*, **158**(12): H1218-H1220.

[172]. Peng L., Huang K., Zhang Z., et al. (2016). "Bandgap- and Radial-Position-Dependent Mn-Doped Zn–Cu–In–S/ZnS Core/Shell Nanocrystals", *Chem Phys Chem.*,**17**(5): 752-758.

[173]. Bu-Yong K., Jong-Hoon, Ki-Heon L., Eun-Pyo J., Chang-Yeol H., Jung-Ho J., Ho Yang S. and H.Y., (2017). "Synthesis of highly efficient azure-to-blue-emitting Zn–Cu–Ga–S quantum dots", *Chem Commun.*, **53**: 4088-4091.

How to cite this article: Kaur, Manpreet; Singh, Paviter; Kaur, Gurpreet; Kaur, Manjot; Sharma, Jeewan; Kumar, Manjeet; Sharma, Manoj and Kumar, Akshay (2019). Development of Colloidal Semiconductor Nanocrystals: Synthesis, Properties and their Outlook for Light Emitting Diodes (LEDs). *International Journal on Emerging Technologies,* **10**(1): 16-34.