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Synthetic strategies and biomedical applications of I-III-VI ternary quantum dots

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ABSTRACT

Surface modified and bioconjugated quantum dots (QDs) compromise interminable outlook to advance biomedical applications. In this regard, particularly I-III-VI QDs, are of a specific interest for biosensor, multimodal imaging, chemotherapy and for phototherapy as a whole theranostics application. Such surface modification used us to manage the physico-chemical properties, biocompatibility, and pharmacological properties. This review is anticipated to provide an introduction to novices about I-III-VI type QDs concerning to synthesis, optical properties, surface modification, bioconjugation, and accordingly formulate them for applications in biosensors, biological imaging, drug delivery, photothermal therapy and photodynamic therapy. We also highlight introducing magnetic metals and nanoparticles to these QDs for multimodal imaging applications and addressed to eliminate toxicity related issues. Finally, we summarize and give a short outlook on future directions of I-III-VI based QDs biomedical applications.

KEYWORDS I-III-VI QDs, Surface modification, optical property, multimodal imaging, photothermal therapy

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1. Introduction

Quantum dots (QDs) are semiconductor nanocrystals with size dependent optical and electronic properties and composed of inorganic core materials with organic outer layer of capping ligands. Colloidal QDs are characterised by their structures and band gap energies (less than 4 eV) between valance band (VB) and conduction band (CB). The electronic properties differ from the bulk crystals as the size decreases the band gap energy shifts to the higher energy (shorter wave length). The developments of different synthesis methods, size dependant optical properties in quantum confinement region have tremendous impacts on the advancements of wide range of applications including solar cell, photo catalysis, biosensing, drug delivery, detection and bioimaging.

To become biologically applicable, QDs should remain biocompatible and absorb in near infrared region (NIR). They are small fluorescent nanocrystals that have recently become a major issue in biological and medical sciences which enable high sensitivity imaging cells, tissues and biomolecules. These QDs, are of pronounced interest for ultimate studies and tremendous applications such as light emitting diodes,[1-5] light-harvesting systems,[6] lasers, and sensors,[7] biomedical labelling.[8-10] QDs usually refer to the II−VI, III−V, and IV−VI binary semiconductors such as CdS, CdSe, CdTe, PbS and PbSe and their alloys have been manly studied in the form of size- and shape-controlled NCs during the past decade.[11-13]

In comparison to the binary QDs, ternary I–III–VI (I=Cu, Ag; III=In, Sn, Ga, Al and VI=S, Se, Te etc.) chalcopyrite compounds, composed of less toxic elements (free from Cd, Hg etc.), considered as promising candidates on developing eco-friendly QDs.

Although, many reviews have been published, as the use of QDs in biology and biomedical fields, previously.[14-21] In this perspective, mainly we summarize the different kinds of I-III-VI QDs (such as $CuInS_2$ (CIS), $CuInSe_2$(CISe), $AgInS_2$ (AIS), $AgInSe_2$ (AISe)), which have been applied in biosensor, imaging, drug delivery, photothermal therapy (PTT) and photodynamic therapy (PDT). Most of the chosen reference papers in this review are related to ternary QD to biological applications. Moreover, a few representative papers not related to biological application is cited to show different synthesis approaches and optical properties of I-III-VI QDs. We hope to add some value to this review by revealing many practical aspects of synthesis approach, tuning optical properties, surface functionalization and use to biosensor, dual modal imaging, drug delivery and light-activated therapy, that are not clearly explained and discussed in the general literature. We begin at the beginning the quantum confinement effect, optical properties of ternary QDs and core/shell systems, doping heteroatom, different synthesis approaches, phase transfer strategies, and

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then functionalization and bioconjugation. Finally, the biological application of I-III-VI QDs specifically CIS, CISe, AIS and AISe QDs in biosensors, imaging, drug delivery, PTT and PDT with toxicity related issues are discussed. Every section provides with a brief historical outline, which is important to understand the follow up discussion in most recent progresses in the field. We will attempt to guide new researchers in terms of every methods advantages and disadvantages and what physical and chemical parameters the choice of synthetic roots and phase transfer strategies which leads to biocompatible QDs with high fluorescent intensity, are excellent candidates for a number of *in vivo* and *in vitro* studies.

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2. Over-view of I-III-VI QDs

2.1 The Need for I-III-VI QDs

Studies focusing on I-III-VI QDs are growing in number and attracting researchers from different areas:(i) the diode lasers are a subject to a wide spectrum of vagarious studies in that range from their physics of operation, to device engineering. (ii) The synthesis with different chemical composition and spectroscopic aspects from chemistry. (iii) Developing novel device designing for the conversion of solar to electrical energy from engineering. (iv) Their applications in biosensing, imaging phototherapy and chemotherapy attracts biologists and medical sciences. The interplay among these subjects could lead to a great contribution towards potential improvements of semiconductor materials in the future.

Biological applications with highly fluorescent and photostable QDs requires, QDs with NIR emission, small size, aqueous solution soluble and nontoxic. Ternary chalcopyrite QDs can achieve these desires; hence they are good candidates for this application. Particle size and stoichiometric compositions variations allow to tune the emission wave length in the windows for biological applications from 600-900 nm.

2.2 The quantum confinement, optical properties, and core/shell structure of I-III-VI QDs

QDs are constructed from semiconductor materials, their optical properties are greatly affected by the interactions among electrons, holes and surroundings. Absorption of photons in QDs is observed when the energy difference of CB and VB is lower than the energy of absorbance. At this time, VB electrons are excited to the CB leaving a 'hole'. The average physical distance between conduction electrons and valence holes is stated as the exciton Bohr radius (α_B). Once the electron excited to CB, it falls back down across the band gap towards the VB. At this time electromagnetic radiation energy is loses and its corresponding wavelength in the transition is emitted. Increase in band gap energy is related to size, composition and shape of quantum confinement. This is due to quantum confinement and it will happen when the QDs is in size of exciton Bohr radius.[22, 23] Quantum confinement in QDs is defined as decreasing QDs size and widening the band gaps. In the case of QDs the energy between VB and CB is discrete due to quantum effect and the energy band gap increases as the QDs size decreases which affects the properties. There are two major effects which varies the QDs size. Frist, the surface atom ratio in the QDs which contribute to the free energy and accountable for changes in thermodynamic properties. Second, intrinsic properties of QDs which are transformed by quantum size effects. Since, QDs optical and

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electrical properties have strong variations with size effects. The most interesting properties of QDs is tunable optical and electrical properties as a function of particle size (Figure 1).[24] The intrinsic electron and hole carriers leads to increased band gap energy and to the splitting of continuous energy bands in the discrete energy levels in spatial confinement. This absorption and emission property of QDs is particularly valued property for biological imaging and therapy.[25]

Unlike binary copper chalcogenides, ternary I–III–VI materials display a chance of a direct band gap in the visible region with band gaps of 1.05 eV (CISe) and 1.5 eV (CIS),[5, 26, 27] 1.87eV(AIS) and 1.2 eV(AISe).[28, 29] Ternary I-III-VI QDs also have a large optical absorption coefficient for CIS ($\alpha > 10^5$ cm^{-1}),[30] and high photostability (excited state life time).[8] In addition to this, these QDs have been reported with high quantum yield (QY),[31-34] long luminescence decay time and a large Stokes shift (wide energy separation between absorption and emission maxima).[8, 35, 36]

Moreover, composition variation consequences on the defects of I-III-VI QDs can directly tune the optical properties. The presence of different atoms in their composition challenges tuning of the absorption spectra. Several works show that the non-stoichiometry of ternary I-III-VI QDs could be controlled by the molar ratios of precursors.[8, 37, 38] The tunable emission is a pronounced properties of I-III-VI QDs which attracts various researchers to biomedical application since the fluorescence is normally used in cell, tissue and animal experiments.

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 bonds on 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 of semiconductor QDs. Deng *et al.*[39] proven that increasing Zn on AISe system also effecting on blue shift on PL emission, which improve QY up to 50%. Separately, Deng also investigate optical properties of AISe after hot injected with ZnS.[40] On the results, QY of AISe QDs can reach to 40% with emission tunable from 700 to 820 nm. The emission range makes these QDs suitable to be applied on biological application.

For example, we have shown the PL QY of AIS is dependent on the ratio of the cations ([Ag]:[In]). The fluorescent emission was strongly dependent on QDs size as the ratio of [Ag]:[In] increases the crystal growth is faster. Whereas the concentration of indium increase

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it reduces nonradiative recombination.[41] Furthermore, recently Jara *et al.*[42] investigates the copper deficient CIS QDs shows two independent optical transition absorptions, which is related to exctonic and Cu-related sub band gap state respectively (Figure 2). Hence depth knowledge of photo-physical mechanisms will support to control properties of I-III-VI QDs and helps to improve the photovoltaic, light emitting devices and biological performances. Hence, the band gap of QDs can be altered by lattice stress created from the lattice mismatch between the core and shell systems.[43] The shelling material should possess; larger band gap than core to deliver effective charge carrier, the crystal structure and the lattice parameters should be closer to the core to facilitate the epitaxial-like growth on the shell. The band gaps and lattice parameters of various Semiconductors usually used in shelling the core are listed in Ref.11.[11] As illustrated in Figure 3, Core/shell systems can be Type-I, Type-II and quasi-type-II in reference to their band alignments valance and conduction bands of their constituent materials. In Type-I (e.g. CdSe/ZnS, InP/ZnS, CIS/ZnS, AIS/ZnS) core/shell systems the CB of the core is lower in energy than the shell whereas the VB of the core is higher in energy than the shell. Consequently, both holes and electrons confined within the core. Coating of core materials with wide band gap materials usually employed to deduct nonradiative recombination which enhances PL QY and the chemical stability. For example, Li *et al.* improved the QY of CIS materials from 5-10% to 86% by adding CdS shell [31]. In the case of Type-II QDs (Figure 3C) one of the material have both VB and CB higher in energy than the other material. Unlike Type-I QDs one of either the electron holes mainly confined to the core and while the other is confined to the shell. In Type I/II core/shell structures CdS,[44] CdSe,[45] ZnTe[46] and ZnS [47,48] used as shell materials.

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. Frist, it has wide band gap (3.7eV) [49] and smaller ionic radii which forms good band alignment with I-III-VI QDs. Second, its Zinc blende structure allows to eliminate the surface trap states and avoid leakage created charge carriers in ternary core QDs. Xie *et al.*[50] demonstrated one layer of ZnS over the CIS core improved the PL QY to 30%. Jang *et al.*[51] Synthesized CIS core and passivated with two layers of ZnS shell, the fluorescence QY is upgraded to 92%. These double Layer shelling of ZnS shows a remarkable blue shift from 660 to 559 nm. Speranskaya *et al.*[52] recently synthesize core CIS core with a PL QY 28% and after shelling with ZnS the PL QY value reaches to 80% with the stoichiometric ratios of Cu:In showed high photostability under UV illumination both in toluene and aqueous solutions. In addition to this surface reconstruction with ZnS provides good stability by decreasing the size of core

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and shows a shift in the absorption and emission spectra (Figure 4).[53]

2.3 Doping heteroatoms to I-III-VI QDs

Precise and purposeful insertion of atoms in to QDs in the bulk form is known as doping. Doped QDs can introduce multichannel imaging application by introducing multiple emission peaks. For instance, Zinc (Zn) doped CIS/ZnS QDs which shows a blue shift and applied for tumour targeted bioimaging.[54] Tang *et al*. [55]synthesized Zn doped AIS and compared with a pure AIS QDs which indicated the incorporation of Zn dopant shows higher structure stability and crystallinity. Doping also performed to introduce magnetic functionality to the QDs to afford contrast agent in MRI and multimodal imaging. Typically for these purpose paramagnetic metal ions can be doped to get spin-lattice relaxation and spin-spin relaxation dynamics of protons in nearby water molecule which extends the array of physical properties of the host QDs. For example Yang *et al*.[56] used Gd^{3+} to CIS/ZnS QDs for fluorescent MR/*in vivo* imaging.

More fundamentally doping can control the electronic, optical, magnetic, to produce n-type and p-type QDs which could be applied for solar cell devices to fabricate highly conductive NCs and other physical properties of the QDs. Most of the focus has been on transition metal dopants such as Cu, Mn, and Zn which can serve as a center to tune the properties of the host QDs. In this respect, when paramagnetic dopants are introduced into the lattices of ternary QDs, escape of ions into the surrounding medium is suppressed. One should consider that several synthetic methods critically influence the doping efficiency as well as the optical properties of the host QDs. Moreover, doping to core QDs requires to consider "had and soft acids and bases" (HSAB) for example, Mn^{2+} and Zn^{2+}, Mn^{2+} has harder nature than Zn^{2+} hence there is a difference in solubility products which reduces their corresponding metal sulfide co-precipitation during synthesis of ternary QDs. In this regard, doping of soft acids to the ternary system may facilitate the incorporation into the lattice crystal and reaction with the anion precursor rather than hard base solvents present in the reaction media. So as having the platforms of HSAB, during synthesis of doped ternary QDs it is necessary to target the acid strength of the dopant and choosing appropriate ligands most specifically in aqueous phase synthesis approaches.

3. Synthesis of I-III-VI QDs

Now a days, several researches on the synthesis of I-III-VI QDs and an effective way to highly luminescent core/shell ternary QDs were reported.[31, 57-60] Fabrication of I-III-VI QDs are adapted from the methods used in II−VI binary QDs understanding from the literatures.[61-63] During synthesis of QDs, the reaction temperature and time,[8, 64] injection temperature in

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hot-injection methods,[65] the reactivity and the stoichiometric ratios of precursors, the solvent type used, surfactant, and pH,[66] etc. are important parameters to adjust the size. A number of metal salts and sulphur precursors used for the preparation of luminescent I-III-VI QDs by thermolysis in hot organic solvents.[35, 64, 67-69]

Difficulties faced in the synthesis of ternary QDs arises from the chemistry of I–III–VI QDs can be particularly complex chemical properties of the two cations. Cu^{+} and Ag^{+} is a soft Lewis acid, whereas In^{3+} is a hard one; consequently, there is a difference in their reactivity towards sulphur compounds (a soft Lewis bases). Unbalanced cationic precursors will lead to the formation of copper sulphides or silver sulphides and Indium sulphides, rather than growth of ternary QDs. Regulating the reactivity of Cu and In precursors at the same time can be achieved by having more than one kind of capping ligands, e.g., a thiol and a carboxylic acid, for controlling the reactivity of Cu^{+} and In^{3+} cations, respectively.[50, 70] Also using one excess stabilizer as a solvent and ligand, e.g., thiol,[31, 35, 71] is another alternative to reduce the cations in forming side reaction products. Another strategy to avoid the problem of different reactivities is the use of single precursors having both precursor cations, which provides the same amount of Cu and In at once, which maintain the formation of CIS or CISe instead of metal sulphides.[67, 72] In 2003 Castro *et al.*[67] synthesized CIS and CISe QDs through single precursors using $PPh_3)_2CuIn(SEt)_4$ And $PPh_3)_2CuIn(SePh)_4$ respectively. Although the particle size of CIS they synthesized is not small enough (larger than 8 nm) to exhibit quantization effects, these precursors provides a root to colloidal chalcopyrite QDs. In 2004 they modify the experimental conditions and successfully synthesized CIS QDs smaller than 4 nm size by increasing the reaction temperature.[68] Ternary QDs have enhanced significance as compared to binary QDs. Since they have large stokes shifts, enhanced PL lifetime and size tunable emissions and low toxicity. However, the PL QY is mostly less than 10%, which is not sufficient for further investigation.[31, 50, 73] Based on those studies numerous efforts has been done for finding solution, for example, Uehara *et al.*[37] enhanced the fluorescence of CIS QDs by introducing crystal defects through a highly Cu defect composition from CIS. This enhanced fluorescence was due to large number of donor or acceptor defects required for ''donor–acceptor pair recombination (DAP)'' of excited charge carriers.[35, 74] Hamanaka *et al.*[75] report shows the decrease in PL QY in CIS QDs is associated with deep surface trap rather than DAP. These opens a way for researchers to construct efficient approach for modifying the surface of ternary core QDs.

Table 1. Overview experimental synthesis procedures for CIS and CISe QDs.

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Precursors	Synthesis method	Reaction temperature (°C)	PL emission peak (nm)	QY (%)	Material	Application	Ref. No
$Cu(S_2COEt)$, $In(S_2COEt)_3$, EG	Heating up	196	642	-	CIS	-	76
$[P(i\text{-}But)_3]_2CuIn(SEt)_4$ or $(PPh_3)_2CuIn(SEt)_4$, DOP	Microwave	140−170	603.5-656.5	-	CIS	-	77
Cu(ac)*H_2O, $InCl_3$*$4H_2O$, CS_2	Solvothermal	200	835	-	CIS	-	78
CuAc, $In(OAc)_3$, DDT,ODE	Solvothermal	240	600-750	-	CIS	-	35
CuI, $InCl_3$, $(Me_3Si)_2Se$, OA, TOP	Hot injection	200-280	640-975	25	CIS	-	79
$Cu(S_2CNEt_2)_2$, $In(S_2CNEt_2)_3$, OA, ODE	Hot injection	200	-	-	CIS	Solar cell	64
CuI, InI_3, DDT,OA, ODE	Heating up	160−240	702	5	CIS	-	37
CuI, $In(OAc)_3$, $ZnSt_2$, DDT,ODE	Heating up	200-270	650-830	60	CIS/ZnS	In vivo imaging	8
$Cu(dedc)_2$, $In(dedc)_3$, $Zn(dedc)_2$, DDT	Hot injection	120-200	-	-	CIS/ZnS	Photovoltaic and photocatalytic	80
CuI, $In(OAc)_3$, DDT, ODE	Heating up	120-200	700-850		CIS	Light emitting and solar cell	70
CuCl, $InCl_3$, S,OA	Solvothermal	110−170	-	-	CIS	Solar cell	81
CuI, $In(OAc)_3$, Zn(OAC), DDT,ODE	Solvothermal	180	647-664	65	CIS/ZnS	-	82
CuI, $In(OAc)_3$, DDT, $ZnSt_2$, MA,ODE	Heating up	110-250	645	65	CIS/ZnS	-	83
CuI, $In(OAc)_3$, $ZnSt_2$, DDT	Heating up	100-230	630-780	86	CIS	-	84
CuI, $In(OAc)_3$, DDT, ODE	Heating up	120-230	683	-	CIS	-	85
$CuCl_2$*$2H_2O$, $InCl_3$*$4H_2O$, $CS(NH_2)_2$, MPA	Hydrothermal	150	660	3.3	CIS	Biomedical imaging	66
$Cu(NO_3)_2$,$In(OAc)_3$,S, $Zn(OAC)_2$OA	Hot injection	90-170	650-800	30	CIS/ZnS	In vivo imaging	86
CuI, $In(OAc)_3$, DDT	Solvothermal	180	654-659		CIS	White LED	5
$InCl_3$, $CuCl_2$, Na_2S, $Zn(OAc)_2$	Hydrothermal	100	532-655		CIS/ZnS		87
$CuCl_2$*$2H_2O$, $InCl_4$*$4H_2O$, $Zn(OAC)_2$, DDT, ODE	Heating up	100-250	450-559	80	CIS/ZnS/ZnS	White LED	88
$Cu(NO_3)_2$*$3H_2O$, $In(NO_3)_2$*$5H_2O$, Na_2S*$9H_2O$), GSH	Hydrothermal	100	654-800	-	CIS	In vivo imaging	89
CuCl, $InCl_3$, Se powder, DPP, OA	Hot injection	100-240	735-800		CISe	solar cells	90
CuI, $In(OAc)_3$, Se powder, DDT, ODE, TBP	Hot injection	200	600-850	26	CISe/ZnS	LEDs, Biolabeling	91
CuI, InI_3, $(TMS)_2Se$, TOPO, HDA, $(TMS)_2S$, diethyl zinc, DDT	Hot injection	270, 130	700-900	60	CISe/ZnS	Biomedical Imaging	92
CuI, $InCl_3$, Se powder, TOP, $(Zn(CH_3COO)_2$, HDA, OLA	Hot injection	200-280	619	16	CISe/ZnSe	solar cells and LEDs	93
CuCl, $InCl_3$, TOPSe, $(LiN(SiMe_3)_2$, $ZnEt_2$, TOPS	Hot injection	285, 320	700-1200	60	CISe/ZnSe	Bioimaging, biolabeling, and lighting applications	94
$Cu(acac)_2$, $In(acac)_3$, Se powder, TBP, DDT, S source, ODE, zinc (II) oleate	Hot injection	220	750	40	$CISe_xS_{2-x}$/ZnS	Bioimaging	95
CuCl, $InCl_3$, Seleneourea, ODE, TOP, DDT, $Zn(OA)_2$	Heating up	140-250	700-1040	50	CISe/ZnS	Biomedical imaging	96
CuI, $(In(OAc)_3$, Se powedr, DDT, ODE, OLA	Hot injection	130, 180, 200	709		CISe/ZnS	Bioimaging	97
CuI, InI_3, $(Me_3Si)_2Se$, TOP, OA	Hot injection	280, 210	650-975	25	CISe	Bioimaging	98
CuI, $InCl_3$, Se powder, TOP, ODE	Heating up	320	838-918	25	CISe	Solar cells	99
$Cu(acac)_2$, $In(acac)_3$, Se powder, TOP ODE, OA	Solvothermal	170, 120			CISe	Solar cells	100
CuCl, $InCl_3$·$4H_2O$, Se powder, OLA	Solvothermal	220, 70		15	CISe	Photo catalyst	101
Cu powder, In powder, Se powder, DI water	Hydrothermal	180-220	863		CISe	photovoltaic devices	102
$CuCl_2$, $In(OH)_3$, Se powder, Gelatin	Heating up	120, 80	612-686	23.3	CISe/ZnS	LED	103
CI, In[illegible]e powder, OLA	Hot Injection	80-270		73	CISe	photovoltaic device	104
CuI, $(In(OAc)_3$, Se powder, $(Zn(OAc)_2$, S powder, OLA	Hot Injection	180	810		CISe/ZnS	photovoltaic device	105

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EG: Ethylene Glycol, DOP: dioctyl Phthalate, OA: oleic acid, OLA: oleylamine, TOP: trioctylphosphine, DDT: dodecanethiol, ODE: 1-octadecene, MA: myristic acid, MPA: Mercaptopropionic Acid, GSH: glutathione, DPP: Diphenylphosphine, TBP:Tributylphosphine, $(TMS)_2Se$: Bis(trimethylsilyl) selenide, TOPO: Trioctylphosphine oxide, HDA: hexadecylamine

3.1 Nucleation and Growth

The synthesis process of core/shell systems involves two steps. Initially the core QDs synthesis and subsequently followed by shell growth. During these growth of shells a few monolayers of a material is deposited on the surface of the core.

Basically according to model of Lamer,[106] with colloidal systems, QDs are synthesized via a three-stage process (Figure 5). In stage one, the precursor compounds rapidly mixed with mixture of solvents and organic ligands. The monomer concentration increases until critical supersaturation is reached. At this point, seed particles precipitate spontaneously from solution (nucleation, stage 2). This is followed by a period in which the newly formed seeds capture dissolved atoms or molecules from solution, and grow to form the desired QDs until complete depletion of monomers (growth, stage 3). However, further growth of the formed QDs may occur due to Ostwald ripening, where large nanoparticles compete with small nuclei during formation. Ostwald ripening is the mechanism of growth by which smaller particles dissolve and molecular species released for the formation of larger particles. This often leads to the dissolution of smaller particles at the expense of further growth of the larger ones. This process typically results to the formation of polydisperse samples. One can be notice that during the growth of the QDs there is formation of new nuclei, which may cause the spreading the distribution of sizes of the colloidal QDs.

During synthesis of colloidal QDs temperature plays key role. In fact, adequate amount of thermal energy, atoms need to rearrange in ordered structures for the formation of crystals. Fortunately, lower reaction temperatures are required consequently the melting temperature for a material as a function of thermodynamic size effect in respect to bulk systems. Capping ligands also have to be considered, since they can also form complexes with precursors used rather than binding the QDs. The capping ligands affinity to the surface and thermal stability associated to these complexes is strongly dependent on the reaction temperature too. A lower reaction temperature leads to stable complexes, lower reactivity of precursors (decrease diffusion rate) and strong binding of the ligand to surface of QDs. Nevertheless, working at higher temperature could lead to less control of size and shape or aggregated system. Consequently, suitable temperature is extremely important for control of size and shape of QDs.

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The type of capping ligands is another key parameter to adjust the synthesis of QDs. Weak capping ligands cannot avoid aggregation of the forming particles though strong coordinating ligands can hinder the nucleation and/or growth of QDs.

Generally, for the synthesis of semiconductor QDs there are several methods and some of them are discussed below accordingly depending on the solvent, reaction temperatures, the quality of products and etc. Varity of metal salt and sulfur sources along with their synthesis methods, reaction temperature and application is summarized in (Table 1) for CIS and CISe and (Table 2) for AIS and AISe QDs.

3.2 Hot injection method

The developments of colloidal chemistry enable low cost production of high quality QDs through wet chemistry process of QDs colloidal solution has attracted a great attention. In this method, precursors and surfactants react at high temperature reaction in the presence of stabilizers. Surfactants have a polar head group and one or more hydrophobic hydrocarbon chains. A mixture of coordinating solvents and surfactants heated in a reactor under argon or nitrogen flow, and precursors are quickly injected in the hot solution which leads to super saturation. The aggregation of precursors generates reactive species which induces nucleation rate followed by the growth of these nuclei. The size distribution of QDs is a kinetic process, can be controlled by fast and slow injection, driven by initial super saturation. Fast injection delivers narrow size distribution of QDs. In this approach, formation of a new phase during precipitation involves two distinct stages. The formation of crystallization (nucleation) and leaving a side the question of stability (growth). To control the growth of QDs, ligands and concentration of reactants have contribution to adjust the surface energy and chemical potential of the reaction respectively. Hot injection method produces a mono disperse-sized QDs. Organic amines and phosphine are most widely utilized ligands in this approach. Real break though come when Murray *et al.*[61] investigated a reaction mechanism for the synthesis of monodisperse CdS, CdSe and CdTe QDs by using a mixture of tri-n-octylphosphine (TOP) and trioctylphosphine oxide (TOPO) as high boiling point solvent/ligand. In continuation to this approach people successfully implemented to synthesize other QDs, such as CdSe and CdTe[61], ZnSe[107, 108], PbS [109], PbSe[110, 111], PbTe[112, 113], CIS[114-116], CISe[98] etc. Park *et al.* [117] synthesized CIS QDs having a florescent QY 8% and emission peak at 645 nm via hot injection approach. They added a ZnS shell by using zinc acetate for Zn source and it shows a blue shift by decreasing the size of core (Figure 6). In common condition, Zn or ZnS was used as combining agent on improving optical properties of QDs where hot-injection strategy was take apart. Allen *et al.*[79] recently demonstrated CISe QDs synthesis; using

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bis(trimethylsilyl)selenide as a chalcogenide precursor with good size control, but only the ordered vacancy chalcopyrite compounds using these approach. In 2011 Park *et al.* [118] demonstrated one pot synthesis of CISe core having emission peaks in the window of biomedical application. Latter they modify the band gap by using ZnS passivation layer, CISe/ZnS core/shell system shows blue shift for bio imaging application. Post synthetic treatment of I-III-VI QDs improve the optical properties and surface states which imparts good stability. Yarema *et al.* [94] synthesized luminescent CISe by using silylamide and controls the size of the QDs in between 3 and 5 nm by tuning the growth time, temperature, and amount of silylamide. The QDs growth temperature and time have influence on the size of particle size which in turn the absorption and emissions of QDs. In particular purpose, modification with ZnS (via ZnS coating, Zn diffusion and alloying with ZnS) to form AIS–ZnS (ZAIS) nanostructures is often done to enhance the PL properties of AIS. For instance, xiang *et al.*[119] have successfully prepare AIS and AZIS QDs with various stoichiometry. By varied Ag to Zn ratio, it was known that addition of Zn on the crystal system effect on absorption peaks that tend to blue-shifted (739 to 632 nm) and their emission wavelengths move to a higher energy accordingly, showing a quite tunable emission from red to green. Noteworthy, Zn on AIS can enhance QY up to 62% and be finely adjusted in the whole visible spectrum. Torimoto *et al.*[120] also proposed strategy optimizing QY of AIS. On the study, AIS QDs which prepared via pyrolysis process further coated with ZnS separately giving the highest quantum yield of *ca.* 80%. In our previous work, we try to develop ZnS coating onto AIS synthesis process via one-pot hot injection process.[121] By this simplified synthesis step, QY can be accelerate up to ca. 70% with slightly blue shift from 570 to 520 nm. However, increasing QY after ZnS coating has considered due to role of ZnS as passivizing layer which could remove non-radiative recombination sites on surface of AIS.

3.3 Non injection (heating up) approach

In this protocol reaction solution is prepared at low temperature, subsequently heated to generate the crystallization process which leads to the QDs growth at elevated temperature. Heating up method usually consists of a high temperature decomposition of metal salts in the presence of surfactant and high boiling point solvents. Crystallization process used to control the size distribution of the QDs. Hence the reaction temperature depends on the reactivity of the precursors. In 2004 Cao *et al.*[122] synthesized CdS by using a nucleation imitator compounds (tetraethylthiuram disulfides and 2,2′-dithiobisbenzothiazole) to isolate the nucleation and growth steps in homogeneous reaction systems. Recently in 2014 xia *et al.* [123] synthesized CIS via one step by adjusting kinetic variables and coordinating molecules like

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reaction temperature, time (Figure 7), stoichiometric ratio of precursors and stabilizing ligands. Unlike to hot injection approach, the system consists simultaneously two different starting reactants before the reaction starts at a certain temperature. As indicated in the hot injection approach, instantaneous supersaturation were induced and crystallization ways underlying the control of size are less understood in this approach. Due to characteristic limitations of injection method various research groups synthesized CIS by using heating up approach.[8, 35, 37, 70, 124] On the other hand, Li *et al.* [31] demonstrates the influence of temperature on the growth of CIS QDs as indicated in emission peak shift from 630 to 780 nm confirms bigger particle size. Increase in reaction temperature facilitates the growth of particle size, since to get desired size the reaction quenched by putting the flask in water bath.

Dai *et al.* and Kameyama *et al.* was reported utilization of non-injection or pyrolysis method on synthesis of AIS and AISe QDs.[125, 126] However, even prepared with precisely stoichiometric composition, difficultness to get QDs with single crystal structure commonly attributes on this type. For instance, synthesis of AIS proposed by Dai *et al.*[125] obtains the AIS QDs with tetragonal and orthorhombic crystal, additionally, cubic $AgIn_5S_8$ also produced as well (Figure 8). Heating up method is particularly advantageous for large scale synthesis of QDs for the reason it can be use large amounts of precursors in large volume of reactor.

3.4 Solvothermal approach

Solvothermal synthesis is a method similar to hydrothermal synthesis, but involves organic solvents instead of water. Compared to other methods, solvothermal synthesis has several advantages. First, solvothermal conditions permit rapid convection in solution. Comparably mild environment offers conditions to form crystals with few lattice defects and it allows for the precise control over the size, shape distribution, and crystallinity of nanoparticles.[127] Second, low boiling point of organic solvent involved can provide a higher reaction pressure when proceed at high temperatures, which will contribute to the procedure of crystallization. Third, because of the mild temperature, special structural features of precursors can be transferred to the products so that the morphology of products can be controlled. Solvents can also provide functional groups, which can further react with the precursors or the products to synthesize novel materials.[128, 129] Finally, for some reaction systems such as the one including toxic starting materials, solvothermal synthesis can reduce the releasing of harmful vapour during the reaction. Further the trend towards to greener technologies assets these approach, since it reduces consumption of energy and use of expensive solvents. It well documented that 1-dodecane (ODE) was a common solvent used on preparing both ternary I-III-VI QDs combined with several ligands like, oleic acid

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(OA),[114, 130, 131] 1-hexadecylamine (HDA),[132] oleylamine (OAM),[133-135] 1-dodecanethiol (DDT),[39, 40, 130, 136] and TOP[98, 114, 131]. Application of DDT on preparing CIS and AIS gave advantage only its potency as ligand but also as sulfur precursor on the QDs.[121, 137]

Nam *et.al* [138] synthesized CIS QDs solvothermally at a fixed temperature of 180 °C for different reaction times and the best result showed at 5 h 40 min with a QY 8.8%. Solvothermally synthesized QDs are mostly hydrophobic in nature, hence for biological application and to improve the stability they should be transferred to hydrophilic phase.

3.5 Hydrothermal approach

The principles of green chemistry attract many Scientists in the synthesis of nanomaterials. For example, the use of non-toxic reagents and solvents, increasing the product yield, simplicity of the purification steps, minimizing the amount of organic solvents will reduce the cost of synthesis and moderate environmental impacts.

Among tremendous ways of synthesis of colloidal QDs, aqueous synthesis employs environmentally friendly, biocompatibility and it is not restricted to inert atmosphere. The general synthetic approach mostly involves chemical reaction between metal precursors and surface ligands. As a metal precursor metal halide, nitrates, which are directly soluble in water and as a sulphur source Na_2S[53, 139] and sulfourea ($CS(NH_2)_2$)[140] is mostly used. It has some distinct advantages in addition to the features of solvothermal process. Key features of the hydrothermal approaches are facile preparation, direct water-solubility, good reproducibility, low costs, and improved biocompatibility.[141, 142] Rogach *et al.*[143] who demonstrate the aqueous phase synthesis approach of CdTe QDs at the first time.

Apparently, one pot direct aqueous synthesis of water-soluble CIS-based QDs is an effective way. Various hydrophilic short chain thiols (Figure 9) are usually utilized as the ligands, such as reduced glutathione (GSH), poly acrylic acid (PAA), and thioglycolic acid (TGA) etc., have been utilized to prepare water-soluble CIS and CISe-based QDs. The first study on applying hydrothermal approach on synthesis AIS proposed by Luo *et al.*[144], where they have synthesized AIS QDs capped with GSH directly in water for photo-catalytic application, but performing low QY (15%). However, to be effectively applied in both clinical and biological applications, it is necessary to make high QY of the QDs that water-dispersible and biocompatible. Based on this reason, several studies also using hydrothermal synthesis approach as direct way on obtaining bio-applicable QDs. Besides GSH, [27, 38] some hydrophilic ligand that also act as sulfur or selenium source like, diethyldithiocarbamate trihydrate, [145] Na_2S, [146, 147] L-cysteine, [148] NaHSe, [35,36] has used as responsible factor for producing water soluble ternary system QDs and has proven to applied on biological

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application. Hydrothermal method also open chance on alloying other elements into AIS system resulting more desired QDs. Doping Zn on to AIS system ($AgIn_5S_8$ QDs) was proposed by Song *et al.*[148] resulting enhancement QY of QDs up to 35 %. This study utilized L-cysteine as hydrophilic ligand and sulfur source. Separately, doping Ag in ZISe QDs system also investigated using hydrothermal synthesis process.[35,149]

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Table 2. Overview experimental synthesis procedures for AIS and AISe QDs.

Precursor	Synthesis method	Reaction temperature (°C)	PL emission (nm)	QY (%)	Material	Application	Ref.
$AgNO_3$, $InCl_3.4H_20$, DDT	Hot injection	170	639-732 at specific Ag/In	62	AIS	LED	119
$AgNO_3$, $In(NO_3)_3 \cdot xH_2O$, diethyldithiocarbamate trihydrate	Hydrothermal	60	480-700		AIS	Cellular Imaging and siRNA Delivery	145
$AgNO_3$, $In(NO_3)_3$, NaS_2	Hydrothermal	100	595	20	AIS	Bioimaging	146, 147
[Ag(HSal)], $InCl_3$, Sulfur	Microwave	350	653	14	AIS	Ion detection, bioimaging, solar cell	150-152
$AgNO_3$, $In(Ac)_3$, Sulfur	Hot injection	200	650-820		AIS	Bioimaging	153, 154
AgAc, $In(Ac)_3$, DDT	Hot injection	270, 210	670	28	AIS	Bioimaging	131, 136, 137, 155
$AgNO_3$, $InCl_3.4H_20$, N,N-diethyldithiocarbamate trihydrate	Heating up	180	580-750	70	AIS	Solar cell	120, 125, 156, 157
$AgNO_3$, $In(Ac)_3$, Sulfur	Hot injection	130	644		AIS	LED	132
$AgNO_3$, In(stearate), DDT	Hot injection	180	580	22	AIS	Bioimaging	121, 135
$AgNO_3$, $In(Ac)_3$, DDT	Hot injection	175,115	675	50	AIS	Solar cell	114, 130
$AgNO_3$, $In(Ac)_3$, L-cysteine	Hydrothermal	110	560	26	AIS	Bioimaging	148
AgI, InI_3, $(Me_3Si)_2Se$	Hot injection	280	650	15	AISe		98
$AgNO_3$, $In(Ac)_3$, Se powder	Hot injection	175	700-820	40	AISe	bioimaging	40
AgAc, $In(Ac)_3$, Selenourea	Heating up	250			AISe	Solar cell	126
$AgNO_3$, $In(Ac)_3$, Se powder	Hydrothermal	90	625-940	31	AISe	Bioimaging	158, 159
Ag_2O, $In(Ac)_3$, Se powder	Hot injection	230	800-1300	21	AISe	Bioimaging	39, 160
AgNO3, $In(NO_3)_3$, NaHSe	Hydrothermal	100	504-585	15	AISe	Bioimaging, LED, optical coding	149, 161

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3.6 Microwave irradiation approach

Synthesis of colloidal QDs using microwave heating is recently found a better approach as compared to other methods due to its numerous advantages. In microwave assisted reaction techniques; the reaction is conducted at the boiling point of the solvent, at normal pressure, small particle size QDs can be prepared,[162] short reaction time is required, purity of the product is good, reproducibility and product yield is better.[163]

In motivation to design faster, cleaner, and economically more viable synthesis method, some study use microwave heating. Utilization of microwave heating to conducting chemical reactions has considered due to its numerous effective applications in polymer synthesis,[164] material sciences,[165] nanotechnology[162] and biochemical processes.[166] In general, sometimes extreme temperature and the rapid heating in microwave chemistry leads to faster processes. Thermodynamic and kinetic barriers of the reaction are important factors for the growth of QDs. In ordinary thermolysis reaction, conduction of black body radiation is used to derive the reaction, using reaction vessel for transfer of energy. This cause sharp thermal gradients in reaction condition happens due to non-uniform nucleation and particle growth.

Xiong *et al.*[152] synthesized AIS using microwave radiation approach and further coated with ZnS. Even using two step synthesis processes, each process was passed shortly and showed fluorescence, low toxicity and long PL lifetimes as good as its applicable on biodetecting and bioimaging. Further microwave synthesis technique was also developed by Mousavi-Kamazani *et al.*[150] as complementing new approach on simple producing composite of Ag_2S-AIS system QDs. This study showed that any relation between microwave power and irradiation time on obtained nanoparticles, where higher microwave power or longer irradiation time will increase particle size. However, most of synthesis process with microwave approach still remaining problem on low QY value and this problem become challenging aspect that must be solved on the next studies.

More recently our group, synthesized Gd-doped CIS/ZnS using a facile microwave assisted approach (Figure 10) which results enhanced photostability applicable for both fluorescence and magnetic resonance clinical applications.[167] We summarized the differences of the above mentioned synthesis protocols according to their advantages and disadvantage in Table 3.

3.6 Phase transfer strategies and bioconjugation

QDs are mostly synthesized in nonpolar organic solvents. Since their surface is hydrophobic aliphatic ligands such as alkyl phosphine oxides, aliphatic amines, alkyl phosphines, aliphatic carboxylic acids, which needs exact surface coating to disperse in

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aqueous solutions. However, solubilisation in aqueous systems and surface functionalization are important for many biological applications, but these process requires sophisticated surface chemistry, which is often significant challenge. Consequently, QDs require ligands that modify the surface defect sites, leading to bright, photostable QDs. As shown in schematic representations in Figure 11 various strategies have been developed to change the hydrophobic parts of QDs to hydrophilic in the past decades.[7, 168] These strategies generally can be grouped in two types. The first protocol is ligand exchange of the original surface ligands by hydrophilic molecules.[24] The most widely used ligands are monothiolated ligands like GSH and 3-Mercaptopropionic acid (MPA),[169, 170] mercaptoaetic acid,[171] bidentate thiols (dihydrolipoic acid derivatives),[172] alkyl thiol terminated DNA,[173] thioalkylated oligo ethyleneglycols.[174] In this strategy, as main concept, the molecules stabilizing QDs in the original first phase are changed by stronger new binding ligands and allow the transfer to the second phase which provide colloidal stability as well. The advantage of this method is small increase to the hydrodynamic radius of QDs since introduction of thin coating. This of a strong interest in QD based fluorescence resonance energy transfer (FRET) investigation[175, 176] and for some biological application which require high diffusional motilities.[177, 178] Though there are limitations of this method, the stability of the thin surface ligand is often affected by local conditions, such as concentration, pH, and temperature.[172] Such conditions are unable to disperse in the cytosol of cells. Recently, some new approaches by using similar thiol-containing molecules as L-cysteine,[179] poly (ethylene glycols)-terminated dihydrolipoic acid (PEG-DHLA)[180] have been developed for solubilisation and functionalization of QDs and achieved significant *in vitro* and *in vivo* stability.[181-184] PEG-DHLA ligand have advantage to provide QDs small hydrodynamic size, low non-specific binding and high QY and show good solubility with a wide range of pH. Li *et al.*[8] synthesized CIS/ZnS core/shell QDs initially capped with DDT surface ligand, transferred to the aqueous phase using surface ligand exchange with DHLA and the functionalized QDs were used for *in vivo* imaging. Subramaniam *et al.*[185] have utilized MPA as new binding ligand for Dodecylamine-capped ZnS-AIS following by polymer coating to functionalize and loading siRNA. The resulted water soluble QDs has been proven has low toxicity and facile to be applied on brain tumor staining and delivery of siRNA *in vitro*. However, a considerable issue on phase transfer via ligand exchange is the stability and the optical properties in the case of QDs' fluorescence. In the aqueous phase, both the QDs surface and probably the thiol groups of the ligands are disposed to oxidation. In this situation, the fluorescence QY is reduced and desorption of the capping ligands can eventually lead to aggregation.

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The second strategy is based on encapsulation into a layer of amphiphilic diblock[186] or triblock copolymers,[187] phospholipid micelles,[154, 188, 189] silica shells,[190] dendrimers,[191] or amphiphilic polysaccharides,[192] polymer shells,[185, 193-195] oligomeric phosphine coating,[196] or by phytochelatin-peptides coating,[197] or histidine-rich proteins,[198] fatty acids.[199] This strategy was developed to overcome decreasing optical properties of QDs as the limitation of ligand exchange method. Formation multilayer ligand allows transfer process from organic phase to water phase. On this strategy, the molecules that act as phase-transfer agents have to perform amphiphilic feature comprising a hydrophobic and a hydrophilic part. For instance, a study on phase transfer strategy of CIS/ZnS and AIS/ZnS was conjugated by Liu *et al.*[86] via micelle-encapsulated QDs formulation. On the process, the Pluronics F127 block copolymer was used as micelles precursor, which drives organic soluble QDs to water phase with good optical and colloidal stability for more than 2 to 3 weeks. Previously, Tang *et al.*[200] also proposed Pluronics F127 as transferring polymer of AIS/ZnS and applied transferred QDs as staining agent on tumor cell. He claims that, by this phase transferring process, the resulted QDs still maintain original optical properties and easily concentrated by slight heating to get desired concentration. It was well-known that application of synthetic polymer or macromolecule material on biological application was favorable based on its durability and simplicity in preparation. However, in the cases of safety and easiness for further modification, natural polymers or biomacromolecules are better choice. These materials offered the improvement of having the intrinsic property of environmental responsiveness as well as non-toxic, even at high concentrations. Based on this consideration, formation of micelle also proposed by Deng *et al.*[201] for transferring hydrophobic Zn doped AISe. The micelle was prepared via amphiphilic modification of chitosan by tagging with succinic anhydride. Interestingly, at this study micelle was firstly attributed with RGD as tumor targeting agent before the QDs insertion (Figure 12). Owing this way, the hydrophobic QDs can be effectively loaded and simultaneously transferred to water, in which crystal structure, the shape, and optical and electronic properties of initial QDs were kept. Foda *et al.*[202] synthesized CIS/ZnS QDs in organic solvents at elevated temperature and uses lipophilic silane encapsulation to make it hydrophilic for cancer cell imaging. Such encapsulated QDs have advantages, high PL efficiency and improved stability, but the thick overcoating produces large hydrodynamic diameters in the range of 20-30 nm for a 4-6 nm core/shell QD. This is limiting for biological application since much larger than the cellular receptor. These group also controls the size in the range of 17-25 nm by controlling the silica shell and shows good bio functionalization in cell imaging. As alternative, Sheng *et al.*[203] proposed phase

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transfer strategy of organic soluble Zn doped AIS via a template coating route with formatting silica layer on the QDs surface. The silica as shell of QDs can maintain QDs inside from extremely environmental damage such as oxidation and dissolution.

In our previous work, we also proposed phase transferring strategy of organic soluble AIS/ZnS by utilizing protein macromolecule, namely bovine serum albumin (BSA) with sonication treatment.[204] In this work, the BSA can accommodate organic soluble QDs by physical interaction on "hydrophobic pocket" on the part of BSA covering with the other hydrophilic part. This situation makes QDs can be stable existing on water. We also proved that BSA is a versatile material due to perform many active site that ability to be attributed with many proposed molecules like folic acid and doxorubicin that conjugated via both covalent and non-covalent, respectively (Figure 13). Beside big molecules, phase transfer of organic soluble AIS QDs was also performed with small molecules. Before, we also proposed the smart strategy on facile phase transfer of QDs by utilizing small amphiphilic molecules, like some kind of fatty acid, OAM, DDT and dosecanediol.[137] On ultasonication treatment, hydrocarbon part of the amphiphilic molecules can make van der Waals interaction with hydrocarbon part of QDs, which resulting transferring process. By this approach, we can show that the transferred QDs still maintain their size and optical properties as well.

Recently several review on methods of synthesis, water solubilazation and functionalization and applications of QDs was published.[14, 17, 25, 205-211] To become applicable to biological systems certain biological molecules should be attached to the surface of QDs without changing their properties. As illustrated in schematic representation in Figure 14 Such biological molecules attached to the surface of QDs via cross linking molecules hydrophobic surfactant with reactive functional groups. Various crosslinking molecules like 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and 4-(Nmaleimidomethyl)-cyclohexane carboxlic acid N-hydroxyl succinimide ester (SMCC) are the commonly used which is attached by adsorption, covalent linkage, and electrostatic interaction fashion. These are few imitations from the enormous choice of phase transfer strategies and functionalization QDs.

To summarize surface engineering required to adjust the fundamental properties of QDs, to make stable, soluble in different solvents and to create QD-biomolecule hybrids which enhances the capability of participating in biological processes. However, depending on the type of QDs and its respective biological application design of surface of QDs is based on its optical properties, stability, size, solubility, biodegradability and biocompatibility. So as to improve the problems associated for example the size of QDs is smaller nanometer, the

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attachments of such molecules with biomolecules might affect the properties by steric effects, affect enzymatic activities and molecular recognition depending of the type of biomolecules used for surface engineering of QDs. Hence, for design of specific applications, modification and improvement of bioconjugation and water-solubilisation methods remain as active area of research including for bioimaging, detection and therapeutics. More complex research seeks to reduce QDs contact with normal tissue. This situation requires a specific protein binding to the tumor tissue that exist. Membrane proteins/receptors in living cells can be labeled either directly with QD-antibody or QD-ligand conjugates.

The bioconjugated surface of QDs, able to adsorb, bind and transport biomolecules such as drugs, probes and proteins. Hence they have the potential to increase the sensitivity of imaging at cellular level including progression and treatment,[212] cancer detection,[154] radio- and chemo-sensitizing agents,[213] electron and x-ray contrast agent and targeted drug delivery.[214]

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4 I-III-VI QDs biomedical applications

In recent years, advances in nanotechnology, biology, chemistry, physics and imaging resulted in the emergence of theranostic nanomedicines as capable agents to bring modified medicine for disease and patient-specific diagnosis and treatment. A huge number of researches have been published over the last decade and many of them are reviewed in review articles.[15, 19, 205, 215, 216] Herein we try to give interesting and advantageous overview about I-II-VI QDs in different biomedical applications to provide a good beginning point for interested readers to carry on their research for retrieving more enthusiastic works.

Due to broad range of absorption in the NIR region and narrow emission, photophysical properties, large stocks shift, resistance to photobleaching, higher QYs become more attractive for *in vitro* and *in vivo* targeting, detection/imaging and therapy of cancer cells and tissues. More specifically, functionalized I-III-VI QDs become a part of bioengineering for biosensors, imaging, drug delivery, PTT and PDT applications. Selected biomedical applications for this review are explained in the following sections.

4.1 Biosensors

To screen the physiological activities of cells, that lead to a range of intercellular diagnostics for diseases outlining on cellular level, fluorescent-based biosensors have been implemented. Among fluorescent-based biosensors, QDs display unique photo-physical and photo-chemical properties over organic dyes and protein fluorophores, thus can be remain as a great fluorescence probes in sensitive biosensor applications. The developments of fluorescence and fluorescence resonance energy transfer QD-based biosensors for the detection of biomolecules such as sugars, nucleic acids, antibody, antigens, enzymes, proteins, pathogens, small molecules, cancer biomarkers and cancer cells are widely explored.[217, 218] The advances of surface engineering and bioconjugation in addition to unique properties such as narrow emission bands, photostability against photobleaching, single light source for simultaneous multi-colour excitation and single-dot sensitivity of QDs allows to be active complement and alternative choice for biological labelling. More specifically cadmium free I-III-VI ternary QDs are less coast to fabricate, better stability, low toxicity and its sensitivity makes interminable candidate for biosensor applications. Su *et al.*[219] integrated fibrinogen with fluorescent CIS QDs as a biosensing probe for selective and sensitive detection of thrombin which is found in the blood and causing blood clotting. In their study, opens a great potential for diagnosis of diseases related to coagulation abnormalities.

For clinical tests, diagnosis and other biomedical applications immunoassay is a valuable tool. The recent developments of QD-based sensing immunoassay demonstrated

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multichannel detection of toxins, drug residues, chemical residues, and biomarkers. For example, Speranskaya *et al.* [220] reported the use of CIS/ZnS QDs for fluorescent label for immunoassay quantitative analysis of the mycotoxin aflatoxin B1. Their report shows QD-based immunoassay displays enhanced sensitivity compared to enzyme-based immunoassay. Recently, Kang, Pan and their co-workers[221] reported synthesis of a gram scale polyethylenimine coated AIS QDs, and applied for glucose detection and luminescence properties of AIS QDs used for optical imaging. The PL-intensity change of AIS QDs was used to detect the glucose to recognise peroxides. Dmitry S. Koktysh and Sharon M. Weiss *et al.*[222] reported detection of biotin conjugated AIS/ZnS QDs for reflectance and fluorescence measurements. Here the QDs serve as refractive index signal amplifier and as fluorescent emitter. The other useful area QDs application is QDs-based detection of nucleic acids. For genetic target analysis on the surface of QDs, DNA or RNA groups conjugated to form fluorescent probes. After conjugation with QDs with DNA, QDs with different emission colors can be applied to multiplexed detection of corresponding sequences that are immobilized in microarray platform.[14] Organic fluorescent labels for DNA detection have problems like decomposition of DNA molecule and forms free radicals due to photobleaching, further the interaction between DNA and proteins disturbed. QDs avoid such problems and permit color determination of orientations of a single DNA molecule.[223]

Generally, QDs conjugated with numerous anticancer antibodies can be applied for the detection of cancer biomarkers in immmuno-chromatographs and immune-microchannels. For FRET- based detection organic dye labelled strands, QDs conjugated with oligonucleic acids are prevailing platforms. QDs are greatly resistant to metabolic degradation and retain fluorescence after modification. In addition, as compared to Cadmium based QDs, there is a real need to address the applications of copper and silver based ternary QDs have to continue to explore better applications in live cells for future. However, the toxicity, monodispersed and specificity of QDs remain a pressing issue for the broader community interested in using QDs live cells will have to explore and try to understand.

4.2 Optical imaging

Optical imaging is a fundamental tool that provide high resolution *in vitro* and *in vivo* information for biological researches. It has a number of advantages including low cost, easy portability, and potential for multiple imaging. This uses allows one can employ optical imaging techniques during surgery and endoscopic processes. Optical imaging is advantageous for imaging guided surgical resection of tumors and primary detection of cancer cells. For both *in vitro* and *in vivo* purposes cells or tissues can be labelled with QDs.

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Since copper /silver based QDs have high QY, nontoxicity, aqueous dispersibility, resistance to photobleaching, large surface area, long luminescence life times and rich in surface chemistry for targeted imaging applications. I-III-VI QDs with these unique features can be applied to fluorescent imaging, multicolor imaging and in confocal imaging systems. Li *et al.*[8] synthesized luminescent CIS/ZnS QDs and make it water-dispersible through ligand-exchange method using DHLA. Further used as a fluorescent label for *in vivo* imaging in mice. Deng *et al.* [224] synthesized NIR –emitting AISe/ZnS QDs (with a QY of 40%) and encapsulated with poly(acrylic acid)–octylamine (PAA-based) amphiphilic polymer micelles to make them water-soluble. The AISe/ZnS QDs functioned as luminescent probes for *in vitro* and *in vivo* targeted cell-imaging. For *in vitro* and *in vivo* RGD peptide surface modification of polymer-wrapped AISe/ZnS QDs enhance the targeting capability of the tumor as a versatile fluorescent probes. Wang *et al.*[225] demonstrated surface modification of CIS/ZnS with trimethyl(tetradecyl)ammonium bromide (TTAB) for *in vitro* labeling HepG2 , Hela and MCF-7 cells. The fluorescence signal has observed in cytoplasm. The increasing time of incubation CIS/ZnS -TTAB can penetrate nucleus. Because the small size of CIS/ZnS -TTAB particles less than 10 nm and the cationic surface charge introduced by TTAB modification as main driving force for the nuclear selectivity, CIS/ZnS -TTAB have ability to pass into nucleus through the nuclear pores. Zhao, Bai and their co-worker [170] reported that GSH and MPA as ligand exchange can provide CIS/ZnS QDs a better performance in solubility, stability and imaging breast tumor cells. Even, fluorescence of CIS/ZnS – (GSH, MPA) QDs only stay in cytoplasm but their QYs better than another capping ligand such as 11-Mercaptoundecanoic acid (MUA), cetyltrimethylammonium bromide (CTAB) and F127 at the same condition. Lee *et al.*[226] employed folic acid receptor as tumor targeting ligand. The injected CIS/ZnS QDs were efficiently directed to the tumor tissue. The fluorescence signal in the tumor is the highest. It means that CIS/ZnS QDs with folic acid receptor successfully stayed at specific target. CISe/ZnS QDs conjugated with tumor targeting peptides and to obtain a strong tumor-targeting imaging probes.[97]

Until now, there are handful research articles demonstrating CIS/ZnS, CISe/ZnS, AIS/ZnS and AISe/ZnS QDs effectively used for *in vitro* and *in vivo* imaging application.[227-229] Developments of technology and instrumentations related to different imaging modalities there is no perfect imaging method and suffer from limitations. Some of the limitations can be eradicated by advancements of technology, but others are a function of basic biology and chemistry, making it complicated to find a solution even impossible in some occasions. Moreover, each modality delivers information about the patient. In recent advances of QDs

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technology, numerous research groups are developing multifunctional or multimodal QDs that enable to imaging more than a single modality, enabling to exploit the advantages of each and to obtain much information about the patient while reducing the limiting factors.

4.3 Magnetic resonance imaging (MRI)

MRI is widely used technique in clinic for high resolution imaging. MRI is regarded as one of leading diagnosis tool due to its unique features including, friendly to humans and environment since non-invasive with no exposure to radiation, low coast, and easy implementation, high spatial resolution, strong soft tissue contrast. Exploring the above qualities, MRI is a capable for precise diagnosis of cancer. However, recently multiple modalities have gained in acceptance and simplified coupling the complimentary abilities of different imaging modalities in tandem. MRI images generally can be classified into two different imaging modes longitudinal (T_1)-weighed and transverse (T_2) weighed images. MRI allows the imaging in deep areas of the body which is not restricted by the tissue. However, targeted contrast agent required to achieve molecular imaging, since the sensitivity is somewhat low. Magnetic QDs have displayed great promise for targeted molecular imaging using MRI techniques. Contrast agent can accelerate the T_1 and T_2 relaxation rate in the tumor cell and are used to increase contrast between the normal cell and cancer cell. Positive contrast agents are most particularly selected from paramagnetic metal ions, consisting of unpaired electrons such as Mn^{2+}, Gd^{3+} and Fe^{3+}. [56, 230-232] However, negative contrast agents most normally employ super-paramagnetic iron oxide nanoparticles, due to biocompatibility such as, Fe_2O_3 and Fe_3O_4.[233-235]

In most MRI techniques magnetic QDs are used as contrast agents. However, to explore the advantages of absorption in the biological windows and florescent transition magnetic metal doped I-III-VI type QDs are used for this application. Researchers have already developed combination of magnetic nanoparticles and QDs for MRI. In a work by Lin *et al.*[236] CIS-$Zn_{1-x}Mn_xS$ QDs were prepared by doping Mn used for optical and T_1 weighed MRI contrast agent. The encapsulation of CTAB solution aid magnetic QDs soluble in water. The results showed that the fluorescence of human pancreatic cancer cell line BXPC-3 were observed clearly by confocal microscopy and were imaged by MRI. Furthermore, The feasibility of the Gd-Labeled Fe_3O_4 construction and CIS QDs conjugated with arginine-glycine-aspartic acid (RGD) was investigated by Shen *et al.*[237] Silica coating was used to modify the $CuInS_2$ and Fe_3O_4 surface to achieve water dispersibility. Subsequently, the conjugation of the Gd-diethylenetriaminepentaacetic acid (Gd-DTPA) and RGD Peptides direct modified QDs@SiO_2 to form Fe_3O_4/CIS@SiO_2(Gd-DTPA)-RGD nanoparticles. The ability of

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multimodal probes for *in vitro* and *in vivo* human pancreatic cancer BXPC-3 cells was observed. The result showed that the fluorescence emission from QDs was bright and the significant signal was detected in MRI targeted T_1 and T_2 signal enhancing effects for the treatment of cancer cell. Ding *et al.*[238] synthesized PEGylated CIS@ZnS:Mn QDs which is applied for *in vivo* fluorescence and MR imaging. Biodistribution of injected QDs in the mouse the main organs such as heart, liver, spleen, kidney and others general, liver present the strongest fluorescence. This is due to liver function to clean the blood of foreign objects and harmful substances.

Most recently, our group reported amphiphilic poly (maleic anhydridealt-1-octadecene) stabilized Gadolinium (Gd) based CIS/ZnS QDs modified with carbodiimide chemistry for a dual-modality nanoprobe magnetic resonance and optical imaging. These material also used as specific targeting via folate receptor mediated targeted receptor.[239]

4.4 Drug Delivery

The surface chemistry of QDs enables connection of numerous ligands for different functionalities and loading of both hydrophobic and hydrophilic therapeutics. Moreover, there physical and chemical stabilities can give long systemic circulation times in the cell. With the utility various coupling strategies, the QDs can be functionalized by a range of cancer-targeting moieties (e.g. Aptamers, anti-cancer drugs and folic acids). QD-based drug delivery paths must be capable to carry and release the drug to a specific location. Drug delivery systems may be covalent and noncovalent systems and it needs a specific careful about temperature, pH, and biological reactions. Covalent systems involve a covalent linkage between the drug and QD while which requires breaking of the bond between the QD and the drug may also decrease the specific release. Careful design of this linker can give exact cleavage based on thermal, enzymatic or pH tempted release. Noncovalent drug delivery is any form of drug carrier that does not exist any form of chemical bond i.e. the QDs involve encapsulating ways or as stabilizing pockets for the drug until released. Extensive reports have been made about drug delivery systems using QDs. [204, 214, 240, 241]

Previously our group reported AIS/ZnS QDs, by conjugating with anticancer drug methotrexate possess dual-functionality, for optical imaging and drug delivery.[242] The anticancer drug covalently bonded on the surface of QDs showed effective carrier for anticancer drug.

4.5. Photo-therapeutic applications

Biological researches has also relied on developing alternative cancer cell treatment modalities that are safe, powerful and cost effective. Near infrared (NIR) light mediated

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photo-therapeutic methods with QDs, such as PTT and PDT has been show a great advantage including better spatiotemporal selectivity, avoiding surgery, noninvasive, effective and fast treatment, reduce cost and side effects.

PTT is therapeutic strategy, which involves the NIR photoabsorbers to generate hyperthermia for thermal ablation of cancer cells up on exposure NIR laser irradiation. It can eradicate the cancer cell in primary tumor and can be combined with other therapeutic modalities to treat cancer cell.[243, 244] Up to now, a numerous types of phtothermal therapeutics including plasmonic nanoparticles,[243, 245] transition metal sulfide/oxides,[246-249] organic nanoagents,[250-252] nanocarbons[253] and QDs.[254] On the other hand, PDT involves a photosensitizer which can change triplet oxygen ($^3O_2$) molecule to the reactive oxygen species (such as: singlet oxygen, hydroxyl radical, peroxides) up on exposure to a single wave length light, which causes death of nearby malignant cancer cells. To know further about the details of PDT we recommend to read the review reported by Lucky *et al*.[255] Wu *et al.* [254] synthesized CIS/ZnS QDs and used for PTT and PDT by conjugating with reduced graphene oxide nanosheets and linked by liposomes, which improves the medical therapy of these toxic element free I-III-VI band QDs. Ghosh *et al.* [256] synthesized $CuFeS_2$ QDs by substituting the conventional In atom and applied for PTT. The report shows that Fe can create an intermediate band to be suitable for light-to-heat conversion.

Recently, Guoxian Lv *et al.* [257] demonstrated the *in vitro* and *in vivo* theranostic applications of CIS/ZnS which packages the imaging and therapeutic nanomedicines. Such "all in one" nanomedicines are attractive for particular diagnosis and effective destruction of tumor. The simultaneous, PTT and PDT upon a single wavelength laser irradiation (Figure 15), application of these materials reported as effective synergistic phototherapy against tumors with negligible toxicity.

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5 Toxicity and biocompatibility

Biocompatibility of QDs is related to the reply of immune system following its administration and intrinsic toxicity due to biodegradation metabolites. In general, most of QDs are found in organic solvents, a phase change, surface functionalization and bioconjugation is usually needed before applying them for biomedical application. The cytotoxicity issue is to some degree challenging. It is due to the intrinsic toxic nature QDs themselves, size and structure effects, surface modification, solubility, stability of ligands, charge, delivery methods and dosage injected, biodegradability, biodistribution, and pharmacokinetics are significant and should be carefully considered. Furthermore, QDs must be eliminated from the body in shortest possible time. Despite to all the inspiring progress of QDs, the cytotoxic actions are not entirely anticipated, since the *in vitro* and animal studies consists of varied range of QDs concentration, size and structure, surface modifications, exposure time, and delivery methods etc. making them challenging to forecast the cytotoxicity of QDs for new design.[239, 232, 56, 167, 214, 227] However, compared to cadmium based QDs, I-III-VI QDs have lower cytotoxicity. Furthermore, higher PLQY, size tunable photoluminescence, high photo and chemical stability and broad absorption spectra gives wider research topics to be addressed to eliminate cytotoxicity related issues.

Clearance of QDs from the body is a key factor for clinical application of any in vivo diagnosis and therapeutic agents. It was previously reported that the smaller QDs (<5 nm) can be removed, by renal pathways, from the blood which protects QDs accumulation on the cancer cells. QDs from 10-20 nm size can be consumed by the liver, and larger QDs (>200 nm) size filtered by spleen or reticulo-endothelial system.[258-260] Once the QDs transported to the cancer cell, it should be spread to the cancer cell, consumed by cancer cell, and localize to their intracellular cell to execute therapeutic action. Thomas Pons *et al.*[73] reported that shell growth and monitored dosage of CIS/ZnS QDs have much reduced in vivo local acute toxicity. To evaluate the *in vivo* clearance process and bio distribution, adult zebrafishes were exposed to a solution of the as-prepared *q*-dots. For example, S. Shashank Chetty *et al.*[261] uses zebrafishes embryos to check the toxicities of CIS/ZnS QDs. As reported up to a minimal dosage it shows minimal toxicity and acute teratogenic consequences. In summary, still a lengthy path from understanding the application of QDs in bioapplications though researchers realised to advance understanding about toxicity. From the aspect, experimental conditions, dosage, experimental cell lines for *in vitro*, animal models for *in vivo* will bring different result and leads to diverse understanding to toxicity. *In vitro* experiments are valuable to investigate new QDs at the early stages for quantitative measurements of toxicity.

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Whereas, *in vivo* experiments are used to evaluate neurological, cardiovascular, immunological, reproductive and developmental related toxicity to assess chronic systemic toxicity of QDs.

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5 Conclusions and outlook

Bioconjugated QDs widely used as nanoplatforms for several biomedical applications, such as biosensing, imaging, diagnosis and therapy. In a more specific summery the mixture of careful material composition and engineer with versatile surface molecules of biological conjugation can tip very advantageous and multifunctional I-III-VI QD-based for advanced theranostics. In this review, we discussed recent advances of I-III-VI QDs for various biological applications. QD-based nanoprobes has been considered as effective for biosensor, optical imaging, MRI, drug carriers, therapy and great achievements in multimodal nanomedicines. We have included a brief introductory about the optical properties, synthesis protocols, and surface modification strategies as well as bioconjugation. Furthermore, the ultimate optical properties of I-III-VI QDs display certain common features that are essential for biosensor, imaging, PTT and PDT. For example, the tunable photoluminescence, a broad absorption spectra spanning from UV to NIR, higher QY and large stocks shift. In addition to this, the availability of various surface chemistry and low toxicity of such QDs boosted novel applications towards biomedical.

Despite extensive reports on the area, the synthesis of doped ternary systems in the core and shell, the proportion and location of the incoming atom should be carefully considered during reporting of novel synthesis methods. The other challenge needs to be address is rendition to, QD probes and issues biocompatibility, targeting efficacy, noninvasiveness and long-term stability, and clinical applications. Pointing at expanding QDs usage even further, early steps have been made headed to design of multifunctional nanomedicines, that promise to combine the advantages of multiple imaging modalities, contrast agent together with chemotherapy and phototherapy. Prior to biological application with these I-III-VI QDs, we should reduce the toxicity of these materials by using appropriate surface modification such as biocompatible polymer, DNA/RNA, peptide etc. After improve their biocompatibility, in future, research development could focus on the QD-based biomedical imaging, and therapeutic intervention techniques implementation on demand of monitoring and therapy of malignant.

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Conflict of interest

The authors declare no conflict of interest.

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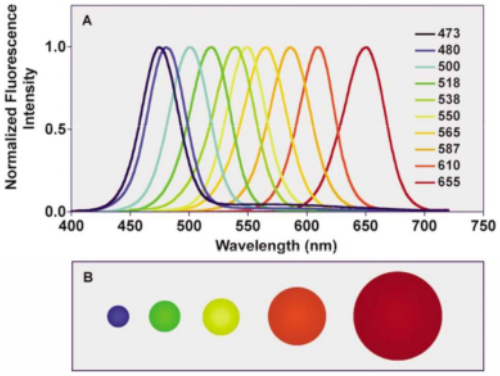

Figure 1. A) Size dependent fluorescence spectra of quantum dots, B) Different relative particle sizes with diameters between 2.1 - 7.5 nm (Reproduced from Ref. 24 with the permission from the Royal Society of Chemistry)

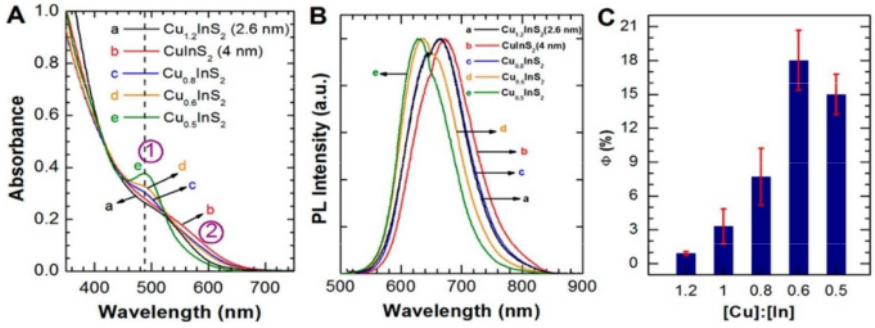

Figure 2. A) Different [Cu]:[In] Cu_xInS_2 QDs B) Absorption spectra emission spectra and C) Emission quantum yield (Reproduced from Ref. 42 with the permission from the American Chemical Society)

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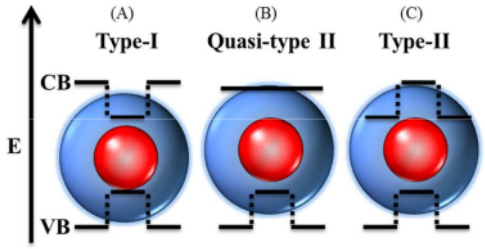

Figure 3. Schematic band alignments; A) Type-I B) Quasi-type-II C) type-II at the hetero interface between two semiconductors of core/shell QDs.

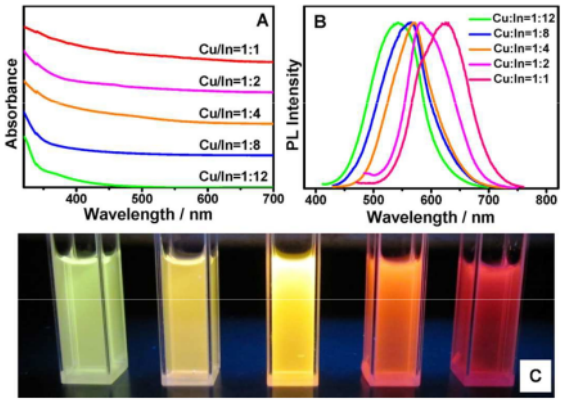

Figure 4. A) Absorption spectra B) PL spectra of CIS/ZnS QDs with different Cu/In ratios in the cores; C) Corresponding digital pictures of CIS/ZnS QDs under UV-light irradiation. (Reproduced from Ref. 53 with the permission from the American Chemical Society)

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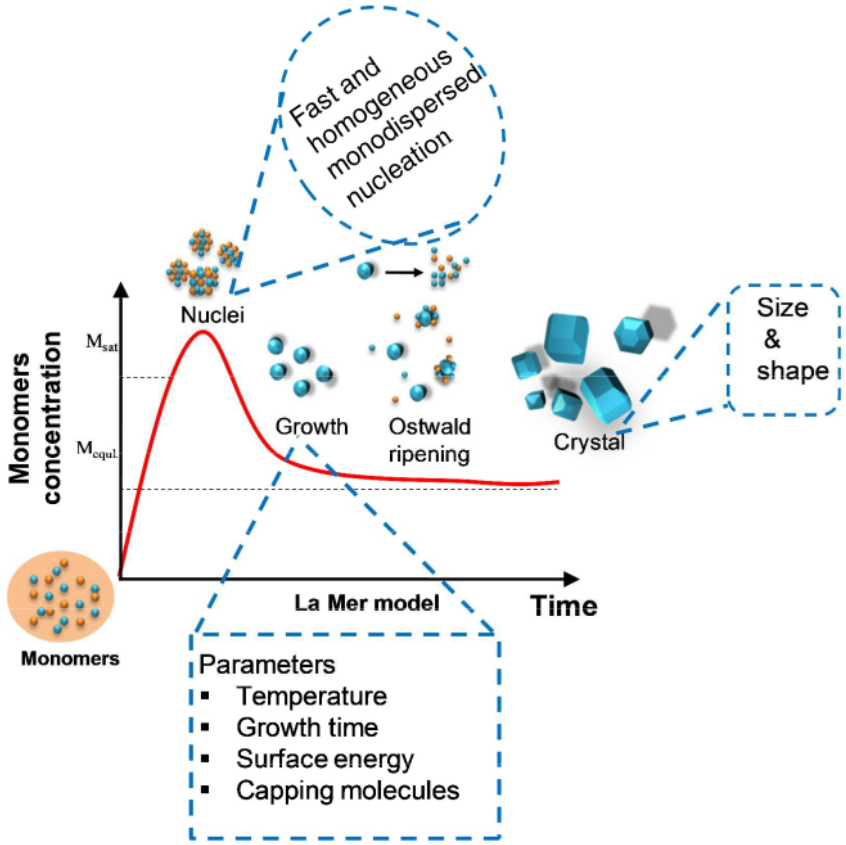

Figure 5. Schematic representation of nucleation and growth of nanocrystals and illustration of steps in synthesis of colloidal QDs.

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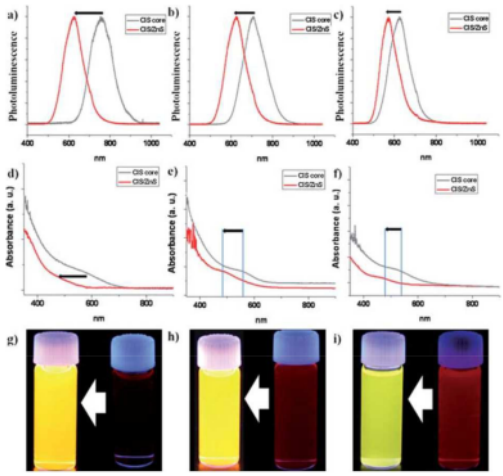

Figure 6. The emission (A-C) and absorption (D-F) spectra of different size CIS core QDs before and after formation of ZnS shell. (G-I) Pictures of the corresponding core and core/shell under UV-irradiation. (Reproduced from Ref. 117 with the permission from the Royal Society of Chemistry)

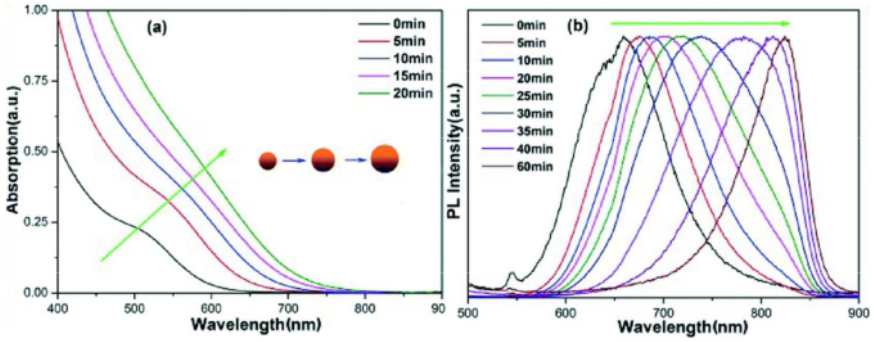

Figure 7. A) The absorption and B) Emission of CIS at different synthesis time and same temperature. (Reproduced from Ref. 123 with the permission from the Royal Society of Chemistry)

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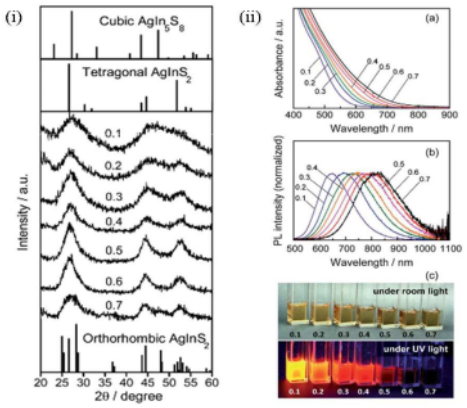

Figure 8. (i) XRD patterns of AIS nanoparticles prepared from pyrolysis synthesis process. (ii) A) UV spectra B) PL spectra and C) Photograph of AIS. (Reproduced from Ref. 125 with the permission from the Royal Society of Chemistry)

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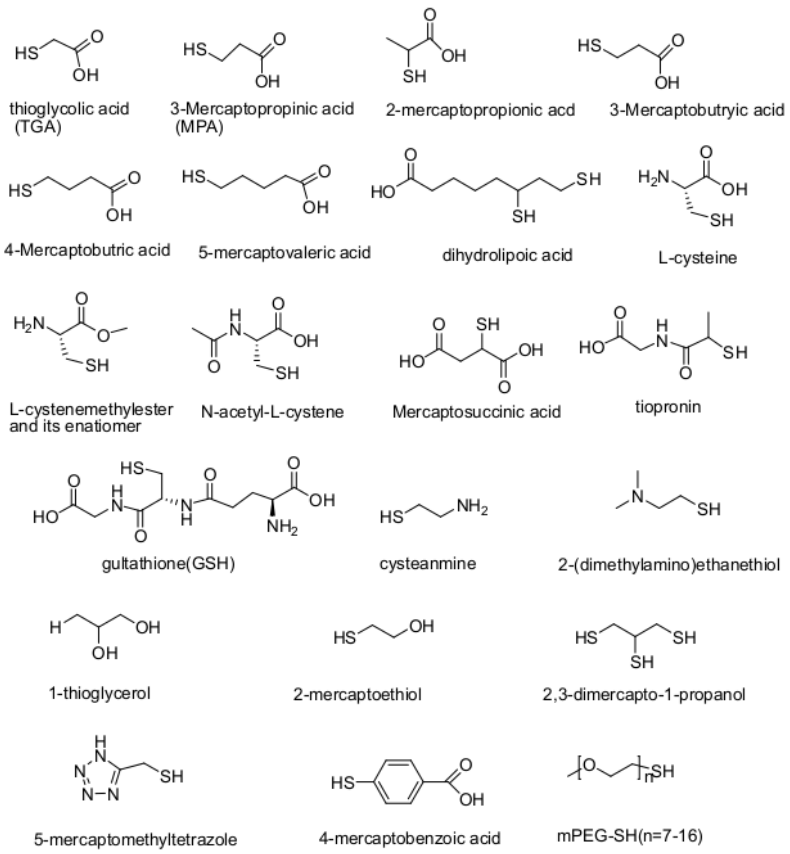

Figure 9. Chemical structure of different possible capping ligands involved in aqueous synthesis of I-III-VI QDs.

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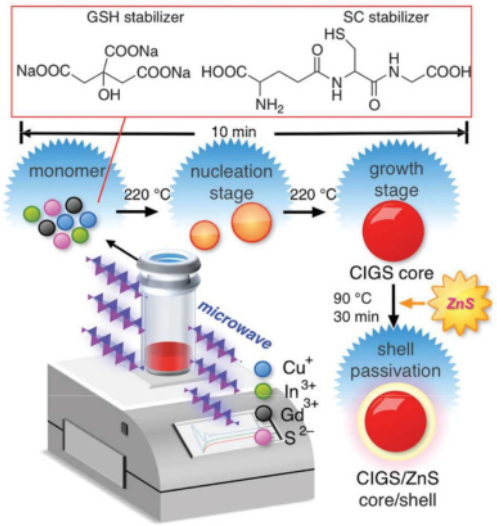

Figure 10. Schematic of the formation of the Gd:CIS core and Gd:CIS/ZnS core/shell QDs using microwave irradiation synthesis approach. (Reproduced from Ref. 167 with the permission from the Royal Society of Chemistry)

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Table 3. Summary of features of different selected synthetic methods of ternary I-III-VI QDs.

Synthesis Method	Advantage	Disadvantage
Hot- Injection	Size control, higher quantum yield.	High temperature, difficult for large scale production, use of organic solvents, use of inert atmosphere, reproducibility, reagent mixing time, cooling time
Heating up	Easy large scale production, reproducibility	High temperature, use of organic solvents
Solvothermal	Size control, shape distribution, crystallinity of NCs, morphology , and reduce the release of harmful vapors.	Use of organic solvents
Hydrothermal	Nontoxic solvent, cost effective, biocompatible, direct water solubility, reproducibility	Poor size control, lower PL QY
Microwave irradiation	Rapid, highly pure product, environmentally friendliness, low energy consumption, easy control of pressure and temperature profile, reproducibility, initiate rapid homogeneous nucleation, reduce crystallization time, narrow size distribution	Lower PL QY

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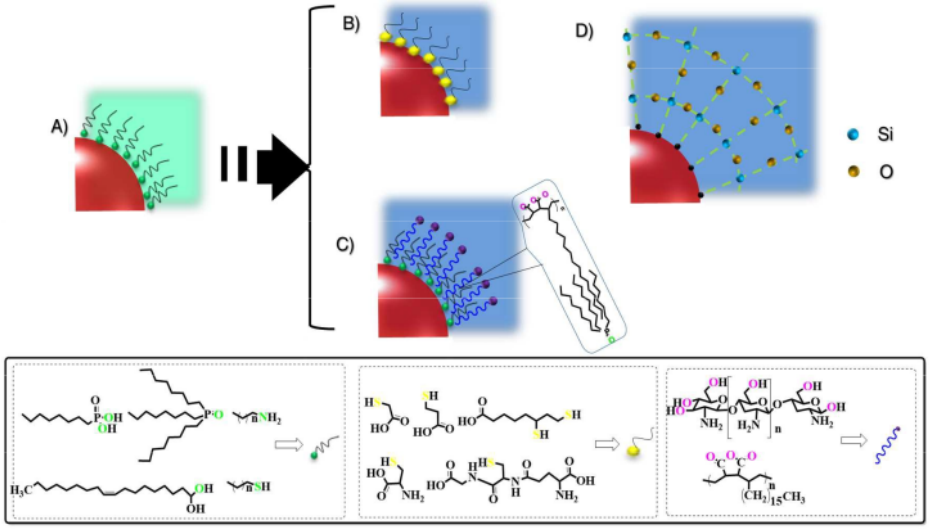

Figure 11. Schematic representation of some phase transfer strategies A) QDs capped with hydrophobic ligands B) QDs ligand exchanged with water soluble thiols C) QDs encapsulated with long chain polymers and chitin molecules with hydrophobic interaction D) QDs encapsulated silica shells.

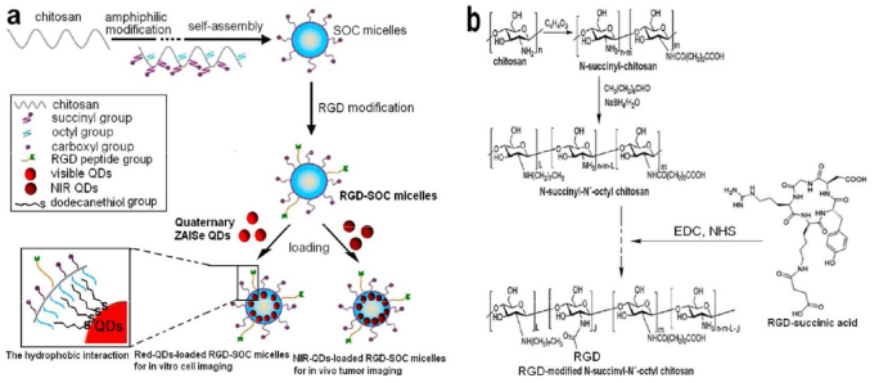

Figure 12. A) Overall synthetic scheme for the QD-loaded RGD-SOC micelles. B) Synthetic scheme for RGD-modified N-succinyl-N'-octylchitosan (SOC). (Reproduced from Ref. 201 with the permission from the American Chemical Society)

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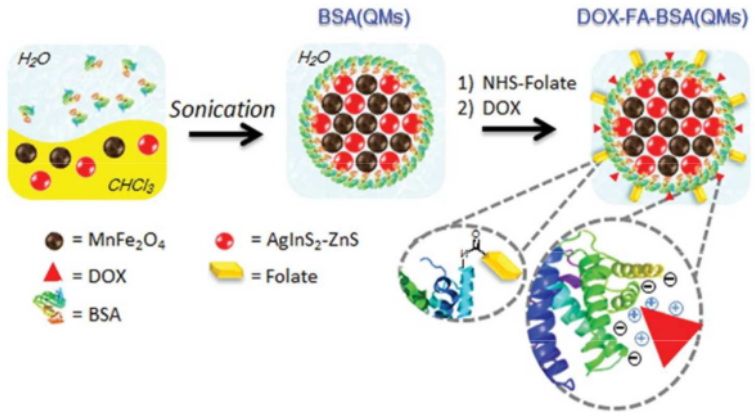

Figure 13. Schematic route for preparing DOX–FA–BSA(QMs) (Reproduced from Ref. 204 with the permission from the Royal Society of Chemistry)

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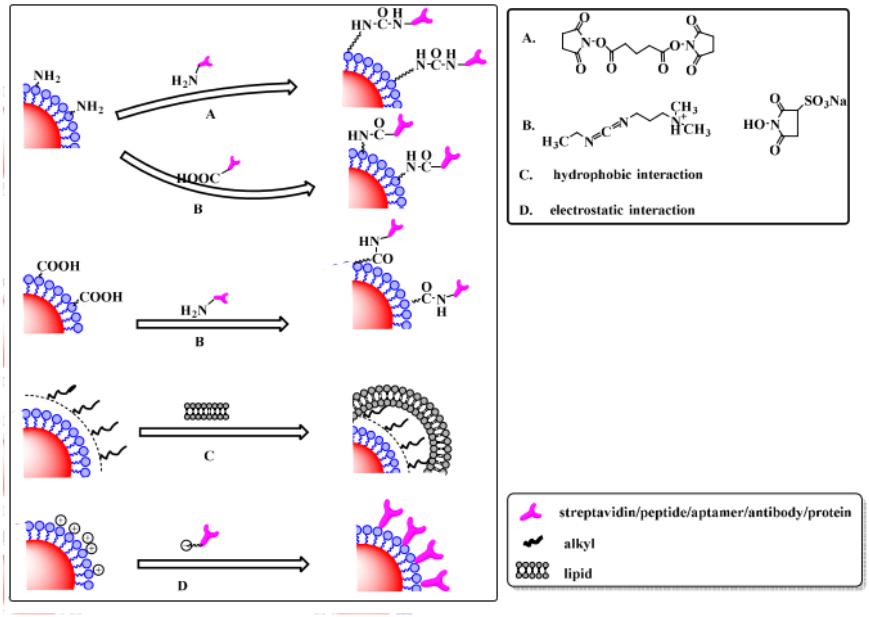

Figure 14. Schematic presentation of QDs bioconjugation using various methods of coupling reactions and interactions.

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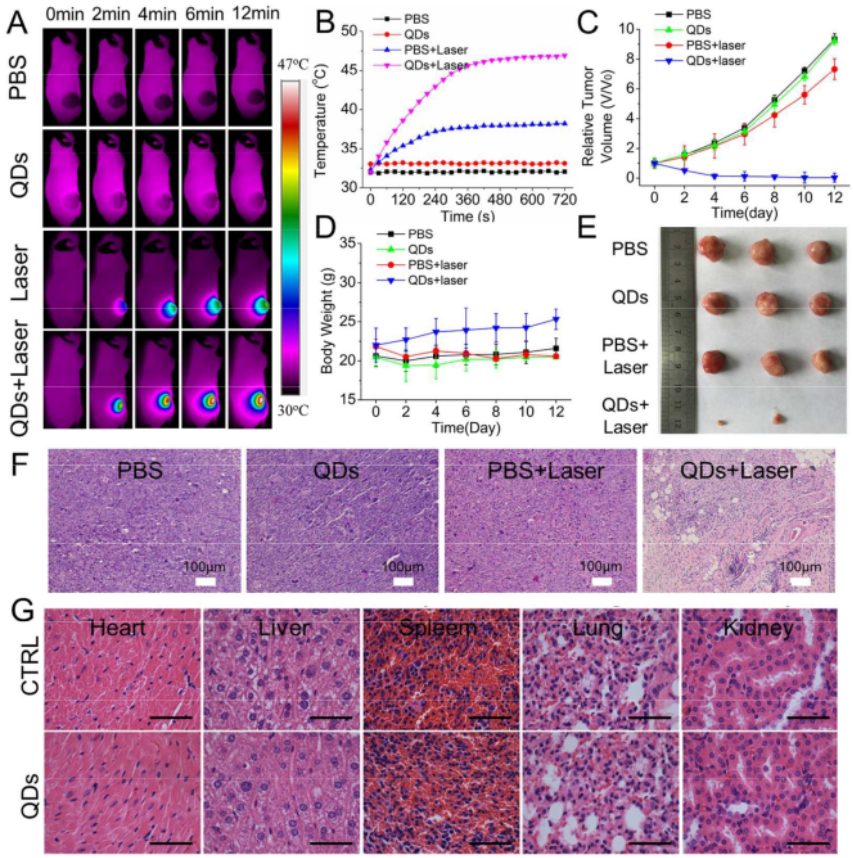

Figure 15. *In vivo* thermal imaging and PTT. A) Thermal IR imaging of 4T1 tumor-bearing mice after i.v. injection of ZCIS NMs-25 and exposure to 660 nm laser irradiation. B) Temperature change curves of 4T1 tumors in mice treated with or without ZCIS NMs-25 and laser irradiation as a function of irradiation time. C) Growth curves of tumors in mice from the different treatment groups. Tumor volumes were normalized to their initial sizes. Error bars represent the standard deviations of 3 mice per group. D) Body weight curves of mice in the

different treatment groups. E) Digital photos and F) H&E staining of tumor tissues collected from mice in the different groups at the end of treatment. G) H&E-stained slices of the heart, liver, spleen, lung, and kidney in mice without and with PTT treatment. Scale bar = 50 μm. (Reproduced from Ref. 257 with the permission from the American Chemical Society)

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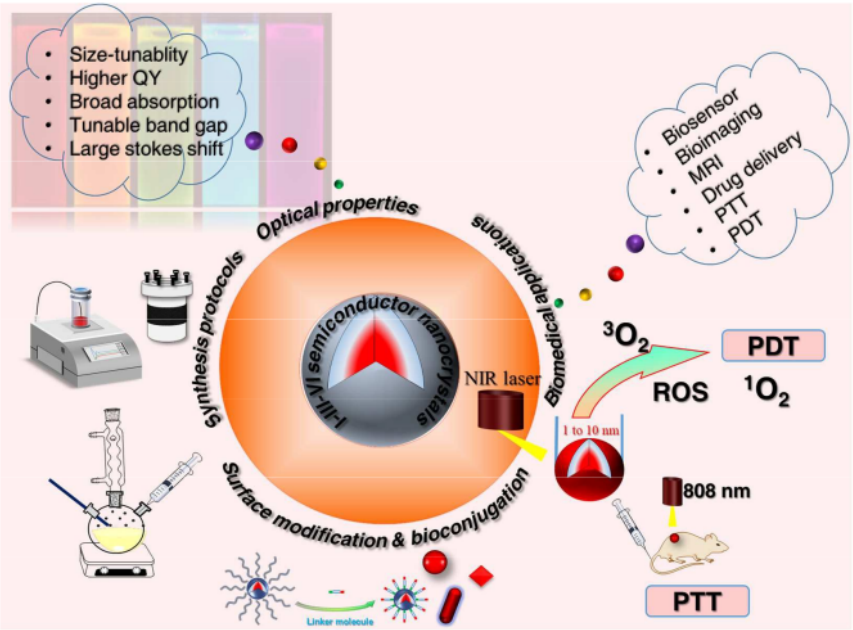

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