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Aqueous-Mediated Synthesis of Group IIB-VIA Semiconductor Quantum Dots: Challenges and Developments

Jejiron Maheswari Baruah and Jyoti Narayan

Abstract

Quantum dots (QDs) of group IIB-VIA are one of the most promising materials for various advanced technological applications in the field of optoelectronics, photovoltaic solar cells and biomedicine. Recent developments have suggested the incorporation of aqueous-mediated synthesis for the QDs, as it is greener, environment friendly, cost-effective and reproducible. However, the process involves several challenges, which ought to be met in order to produce stable, consistent and sustainable product formation. The present review discusses the significance of semiconducting QDs, their synthesis through various processes, their pros and cons, and above all the advantage of aqueous-mediated, atom economic and energy-saving methodologies.

Keywords: quantum dots, group IIB-VIA semiconductors, aqueous synthesis, luminescence properties, surface passivation, optoelectronics

1. Introduction

Nanoscience and nanotechnology is one of the highest potential applicative research fields in today's world. The current scenario of world depicts the valuation of nano sized materials (1–100 nm) [1] quite high in various areas of scientific applications, such as, photovoltaic solar cells [2–5], optoelectronics [6–10], biomedical [11–13], food and agriculture, industrial, textiles, etc. [14]. It has been observed that larger ratio of surface to volume of a catalyst would facilitate a better catalytic activity; therefore the size controlled synthesis of QDs to produce a larger ratio of surface to volume is of great importance. The enhanced surface to volume ratio would cause increase of surface states, which will change the activity of electrons and holes, thereby, affecting the chemical reaction dynamics as a whole. Studies reveal that the size quantization increases the band gap of photo catalysts to enhance the redox potential of conduction band electrons and valence band holes [15–17]. The resulting dominance of these tiny sized artificial atoms/molecules/materials reveals a prediction of market value of \$16.8 billion in upcoming future [18].

2. Classification of nanostructure materials

The nanomaterials can broadly be classified in four categories. They are (a) zero dimensional (0D), (b) one dimensional (1D), (c) two dimensional (2D) and (d) three dimensional (3D). (a) Zero dimensional nanostructures (e.g., quantum dots and nanoparticles) have all the dimensions within the nanoscale region. They are also addressed as artificial atoms as their size restriction, particularly quantum dots, can be found within a few nanometer ranges like atoms/molecules. They have grown themselves up in recent years as suitable applicant in the field of optoelectronics, biomedical, energy, textile industries, etc. (b) One dimensional nanostructure (e.g., nanowires, nanotubes, nanorods, etc.) have diameter/thickness in nanometer range, however its length to width ratio may be more than 1000 nm, i.e., several micrometers. It means that in this kind of material, one dimension of the nanostructure is not in the nanometer range. This specific class of nanomaterial has immense applications in electronics, in addition to other domains of applications like energy and environment [19]. (c) Two dimensional nano structures (e.g., nanofilms, nanosheets, nanowires, graphene, etc.) have two dimensions outside the nanometer range. It indicates that although the area (length and breadth) of these kinds of materials is more than nanometer scale, but the thickness is always within the nanoscale region. They are very useful in the applications of sensors, templates, photocatalysis, nanoreactors and nanocontainers. (d) Three dimensional nanostructures (e.g., bulk powders, nanocomposites, bundle of nanotubes/nanowires, multilayer films, nanotextured surfaces, etc.) are the nanomaterials in which, all the three dimensions of a material are not within nanoscale region. This class of materials has applications in all such fields where introduction of other dimensional nanomaterials is required in high scale, including the fields where electronics, optical, mechanical and magnetic properties are necessary.

2.1 Defining QDs: physical and quantum mechanical concept

QDs are having quite resemblance with the atomic confinements. Basically, they are the nanoparticles of bulk semiconductors and their average size range lies within 1–10 nm. The physics behind the size of a QD is the exciton Bohr radius. It states that if the size of a particle is less than twice the size of the exciton Bohr radius of a specific material, then, the particle behaves as a quantum confined matter. At this point, the particle acts as a particle within a box of quantum mechanics. Brus et al. were the first to use the term ‘Quantum Dot’ [20]. They defined these artificial atoms’ behavior as molecule like. They realized that this particular class of particle has discrete and quantized energy states, due to which their electronic properties possess resemblance with atoms/molecules. Although, nanoparticles of the semiconductor materials are found to be within the quantum confined region, it is quite obvious to achieve bigger particles during the process of synthesis within the same solution of nanoparticles, than, the Bohr exciton radius. But, people are focusing on the production of smaller size, i.e., within quantum region. The idea behind targeting quantum confinement is their dramatic change in electronic properties within the quantum dimension, which cannot be achieved beyond that size. Hence, nanoparticles of semiconductors are synthesized within that confinement precisely. One of the primary reasons behind occasional achievement of bigger particles is the aggregation of individual particles. This can be overcome by effective encapsulation with suitable capping agents during the course of various physical and chemical synthesis processes.

2.2 Semiconductors: introduction and utility

Semiconductors are well known class of compounds, whose properties are considered to be between metals and insulators. The fundamental expression of this idea is the band gap energy, generated due to the presence of distinct valence band, VB (HOMO) and conduction band, CB (LUMO). The overlapping of both VB and CB is very much absent in semiconductors; instead they are differing by ‘specific amount’ of energy. However, there is a provision for the electrons in the VB to jump into CB by absorbing that particular ‘specific amount’ of energy. The required threshold energy to overcome the VB-CB difference is termed as ‘Band Gap Energy’. Since the QDs are the diminutive form of the bulk semiconductors, hence they also follow the band gap theory. In QDs, the transition of electrons from the HOMO to LUMO, primarily, depends on the size of the individual particles. Smaller the size of the particle, higher energy is required for an electron to jump to conduction band and vice versa. Therefore, smaller particles show more blue shift from the bulk in both absorption and luminescence spectra than the bigger particles (**Figure 1**). Interestingly, in a solution, the particle size of QDs of a particular material is never homogeneous, i.e., the size of each dot cannot be exactly the same. Therefore, when absorption spectrum of QDs in a solution is recorded, due to the merging of peaks for each and every particle (responsible for individual electronic transition of individual particle), the absorption maximum is always broad, sometime edge only [21]. That is why, these QDs can cover a wide range of light spectrum to excite its electrons as per the requirement of energy. The broader excitation spectra of the QDs also help them in the illumination of multicolored QDs through the excitation of single light. The high stoke shift finds the QDs resistant toward the auto fluorescence, hence their sensitivity is enhanced drastically. These metamaterials are synthesized in laboratories according to their requirement in a specific application. A very interesting and important factor behind the utility of these nano materials is their tunability in size and shape. Different sized particles of different materials within the same

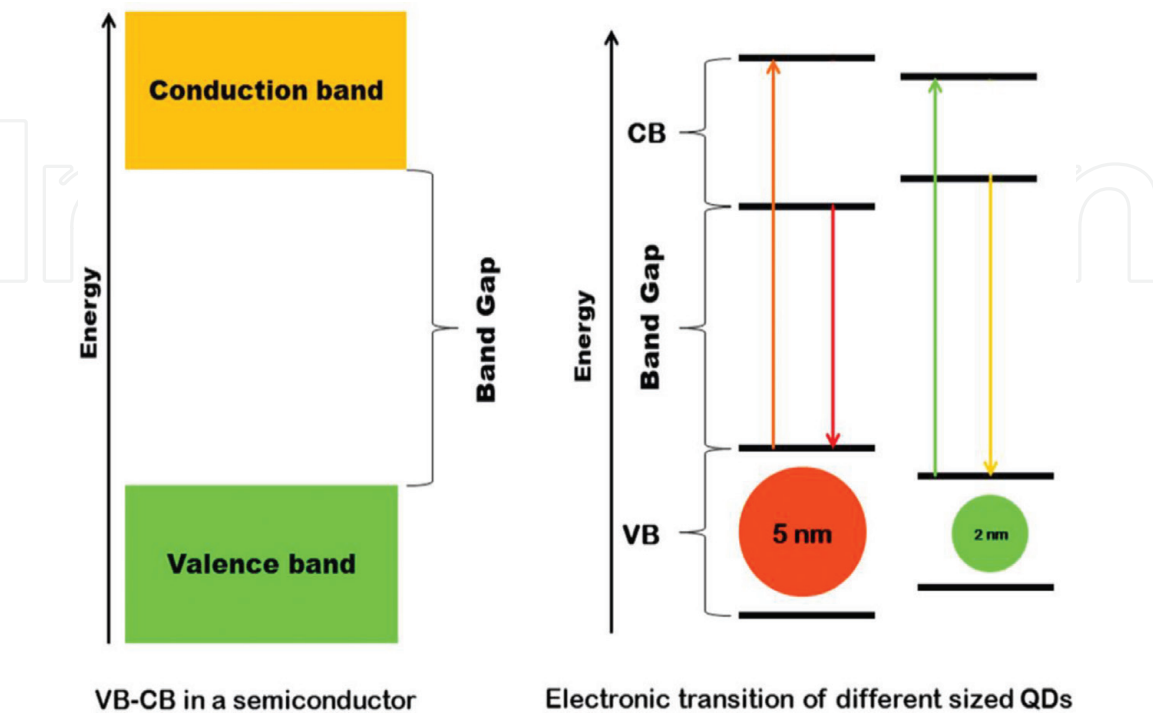


Figure 1.
Effect of size of QDs on electronic properties.

Materials	ZnS	ZnSe	ZnTe	CdS	CdSe	CdTe
Band gap (eV)	3.61	2.69	2.39	2.49	1.74	1.44
Wavelength (nm)	343.2	460.5	518.4	497.5	712.1	860.3

Table 1.
Band gap and excitonic wavelength of group IIB-VIA semiconductors revealing the capacity of accessing the visible light spectrum, thereby exhibiting their potential applications in optical and electronic devices.

application are essential for providing improved efficacy of the device, e.g., quantum dot sensitized solar cells. Researchers around the world have reported various shapes of nanoparticles, viz., spherical, cubic, hexagonal, triangular, wire, ball, necklace, etc. They deliver different properties and can be utilized for different applications.

Among various semiconductors, the QDs of group IIB-VIA [zinc sulfide (ZnS), cadmium sulfide (CdS), zinc selenide (ZnSe), cadmium selenide (CdSe), zinc telluride (ZnTe) and cadmium telluride (CdTe)] are potential candidates in various applications, primarily in optoelectronics due to their wide and direct band gap (**Table 1**).

Chemistry of these semiconductors suggests that the formation of variable strong bonding between these molecules is responsible for their differences in band gap and absorption maxima. The covalency of the molecules from Sulfur to Tellurium is different in these hybrid molecules, so as their electronic transition properties are varied and hence the band gap.

3. Synthesis of QDs: aqueous route and mechanism

The effective synthesis of QDs is a challenging task. Research is warranted in the mechanism of synthesis, leading to the reproducibility of size and shape of QDs, so that the growth of QDs at the time of nucleation can be controlled effectively [22–26]. There are several methods of synthesis of QDs: molecular beam epitaxy (MBE), vapor phase epitaxy (VPE), metal organic chemical vapor deposition (MOCVD), radio frequency sputtering (RFS), electron beam lithography (EBL), optical ablation, Ball milling, quenching methods, reduction with microorganisms or plants [14] and chemical method [27–34]. Among all, chemical method is the most widely used method for the synthesis of QDs due to its better accuracy and large scale production [35–56]. Various reducing agents such as sodium borohydride, hydrazine hydrate, etc. are used during the chemical reduction synthesis. These methods are broadly divided into non-aqueous and aqueous-mediated reactions. Non-aqueous method have received first remarkable development from Bawendi, Alivisatos and Peng [57–62], popularly known as TOP-TOPO (trioctylphosphine for TOP and TOP oxide) or hot injection method in 1990s. Although the reaction developed by Murray et al. [57] for the synthesis of cadmium chalcogenides is probably the first ever controlled synthesis of semiconducting CdE (E = S, Se, Te) QDs. However, due to the highly toxic, pyrophoric and unstable nature of main precursor dimethyl cadmium [(CH₃)₂Cd] at room temperature, the method was not preferred [63–67]. Peng et al. [68, 69] contributed a comparatively greener method for the synthesis of CdE, as the first most efficient process of synthesizing highly fluorescent QDs with excellent morphological uniformity. The formed QDs in this high temperature method involved long chain organic solvents with high value of boiling point. Resultant QDs were found to be less defective due to effective surface passivation by TOP/TOPO. Both, the choice of ligand as well

as the growth temperature, allowed the lattice morphology to be modified in a better way toward the synthesis of QDs. Hot injection method processes through two steps, i.e., rapid nucleation, while the reaction is heated up to the utmost temperature, followed by slow growth of colloidal nano crystals (CNCs) due to the addition of another precursor, with much lowered temperature. Though this method was observed to be suitable for the synthesis of the CNCs/QDs, there are some unexpected drawbacks, which lead the scientists to rethink about this particular process, before they could propose this method for the up gradation of the end products at the industrial level. The primary issues with this method are (a) use of non-ecofriendly organic solvents, (b) cannot be scaled up for mass production, which require several and repetitive reactions to achieve the desired amount of product, (c) non-biocompatibility, as water is not a suitable solvent for them to get solubilized, (d) difficult purification and extraction methods of the QDs from its mother liquor, (e) high cost of solvents as well as the process and (f) non-cooperation of green chemistry principles, which leads the whole process of synthesis into an environmentally challenging problem. Adoption of non-water soluble surface passivators (i.e., TOP/TOPO) confirms the non-biocompatibility mode for these high temperature synthesis methods; therefore the concept of biocompatible aqueous phase QDs synthesis is warranted. Aqueous route of synthesis have all the positive aspects and most importantly, they are easy to carry out and are environmentally benign. Additionally, one can use high fluorescent nature of QDs in various bio-medications due to their water solubility. One can modify the surface of the QDs as required, with the help of water soluble chiral capping molecules to make the dots size dependent chiral optical property enhancer [70, 71]. Moreover, utilization of short water soluble ligands boost the optoelectronic applications (including photodetectors, solar cells and photocatalysis) too, by reducing dielectric barrier and inter dot separation distances in a solid QD film. Hence the objective of preparation of QDs reach to another domain of methodology, i.e., water-mediated or water soluble routes of synthesis. In early 1980s, Brus [72] and Henglein [3] and their co-workers first pioneered the aqueous synthesis route. They reported the change of band gap of QDs with their size. Vossmeier et al. presented their work on CdS QDs. They reported the variation of UV-vis absorption spectrum with the change of size of CdS QDs. However, none of them discussed the photoluminescence property. First aqueous based synthesis with fluorescence properties of QDs was introduced by Weller et al. [73]. They have reported the water based synthesis of CdTe QDs under reflux condition at 96°C for prolonged hours, to obtain photoluminescence emission. After that, several approaches have been made toward the aqueous synthesis of CdSe and CdTe QDs. Although, they have achieved a mile stone, but as the research progressed, researchers tried to find the best route of synthesis in which they were able to synthesize the same or better quality CNCs. In the way of harvesting betterment and refinement of the existing methodologies, present day world scientists are trying to reach to a mile stone, in which the QDs are prepared as multiuse molecules. Hence, the aqueous synthesis method is still under investigation and modification. Therefore warrants systematic studies under variable conditions. Presently, global scenario speaks about the understanding of the reaction mechanisms and the suitable greener conditions involved during the synthesis of better quality QDs with easy, cost effective and most importantly greener technological way. However, achievement is still under the margin.

4. Factors responsible in aqueous synthesis of QDs

There are four major parameters which are primarily responsible for precision of the end product during aqueous synthesis route. They are (a) the solubility product

of the semiconductor compounds in water, (b) binding affinity of the capping agent molecules toward the metal atom, (c) binding affinity of water and hydroxyl atom for the metal atoms and (d) pH of the reaction medium [74–81]. These enlisted thermodynamic parameters can be understood with the help of HSAB (hard and soft acids and bases) theory. HSAB states that hard-hard or soft-soft interactions are expected to have lower water solubility [82, 83]. Since chalcogenides ions (S^{-2} , Se^{-2} and Te^{-2}) are soft bases and (Cd^{+2} and Zn^{+2}) are borderline soft acids, it is expected that they readily form insoluble compounds. Soft-soft interaction leading to the low solubility of these compounds is the basis of their semiconducting nature. Their covalent nature increases in comparison to the hard-hard interactions. The pH of the medium also effects the formation of the desired compounds in a dramatic way. Since we know that $-OH$ (hydroxyl) ion is a hard base, therefore its binding affinity toward hard metal cations is more and hence $-OH$ can easily form bonds with Zn^{+2} than Cd^{+2} in basic conditions, thus effecting their solubility product constant (K_{sp}). Therefore, careful pH management is very necessary for Zn chalcogenide than Cd chalcogenide compounds to prevent formation of metal hydroxide compounds. Because Cd can tolerate more basic condition than Zn due to its comparative more softness. Thus, one can understand that acidic condition may be more suitable for Zn chalcogenide compounds than Cd compounds, which can accommodate basicity up to $pH = 12.5$. Beyond this, Cd metal atoms will form $Cd(OH)_2$ compounds. Hence, the conclusion can be drawn that, acidic condition is more suitable for the synthesis of these compounds. Another very important positive concept of utilization of acidic condition is that, it enhances the formation of smaller QDs than basic condition. The presence of $-OH$ radical in the medium is found to be responsible for this, due to the bigger size of the hydroxyl group than H^+ in acidic medium. The chemistry of the group IIB-VIA compounds overall reveals that aqueous medium is very easy and effective way of production of the QDs of those bulk compounds due to their solubility factor in water. We can easily extract them from the medium as after formation they show poor solubility in water. The band gap energy of these compounds can also be understood from the covalent nature of the bonding between the metal atom and the chalcogenide. It is observed that the pattern of band gap energy of metal (M) chalcogenides (S, Se and Te) is $MS > MSe > MTe$. The fact behind this order is the electronegativity of the anions. Since, the bigger sized anion (lower electronegative chalcogenides) does not hold their outermost electrons as strongly as the anions of their group possessing higher electronegativity, therefore covalent character is enhanced in these compounds. As a result, their bulk band gap (BG) gets decreased in a group with the same metal atom ($CdS_{BG} > CdSe_{BG} > CdTe_{BG}$).

5. Surface chemistry of QDs: role of capping agent in aqueous synthesis

The surface chemistry of the CNCs is very interesting, as well as challenging one to achieve. Due to the presence of high surface to volume ratio, the surface of the QDs generates dangling bonds of both cationic and anionic substituents. Noteworthy, the dangling bonds in a QD are generated due to the unsaturated surface level atoms of the QD, which may alter the electronic transition by introducing new electronic states. The primary strategy to satisfy these surface defects is by using more cationic precursor to satisfy the anionic part, while the stabilizing agent, has to satisfy the dangling bonds formed from the cationic part. In most of the reactions, the presence of a stabilizing agent is very necessary to overcome the instability factor in the colloidal solution. In colloidal synthesis method, it is almost

mandatory to use a capping agent [2, 37, 84] as a capping agent does not allow the QDs to grow, after reaching a certain size depending upon the capacity of the agent. On the other hand, in an appropriate solvent, a stabilizing agent, not only caps the QD, but also offers stability to it to retain its size in the solution. The terminology of stabilizing agents is slightly different from surface capping agents. But efforts have been made by researchers to put both the surface modifying agents within a single umbrella by trying to use the same molecule for both the purposes. These molecules attach with the surface of the NCs by dative, covalent or ionic bond and provide them electrostatic stabilization as well as surface passivation. These agents are often called as surface ligands, due to their capacity to act as ligands in a coordination complex, which attach to the metal ion by exchanging electrons. The molecular structure of a stabilizing agent/surface capping agent is very much different in aqueous medium than non-aqueous medium. In non-aqueous solvents, these molecules are normally water insoluble long chain hydrocarbons, whereas in aqueous media the capping agents have short hydrocarbon chain and a polar group at one end. The polar group can provide stabilization to the QD as well as passivation to the surface. But, importantly the ratio of capping agent with the precursor also plays an important role in the nature of the solubility and formation of the QDs. It is because, higher concentration of these molecules may not allow the metal atom to form the semiconducting NCs and lower concentration may lead to the instability of the QD in the medium due to weak interaction between the capping molecule and the metal ion. In this context, till date thiol or carboxyl or phosphate group holding polymers and macromolecules have been tried to achieve better surface stability. However, at the same time, ligands capable of binding with more than one binding site are also drawing tremendous attention of the researchers due to the probability of fetching aspired product. Selecting effective surface modifying agents and optimization of the added amount of them are at utmost importance to develop better synthesis route to achieve desired QDs. Another aspect of choosing an effective surface capping agent is the biocompatibility and thus, their application in biomedical sectors [85–87]. The advantageous positions of these inorganic artificial atoms as fluorophores over organic dyes is due to their bright (10–20 times more than organic dyes) and narrow fluorescent and less photo bleaching (up to 30–40 ns) nature than the traditional dyes. The primary issues regarding the use of these QDs in biological application are non-biocompatibility, ineffective coating and the use of hazardous capping agent. It is well understood that although the synthesis of QDs are performed in water medium, it may not offer the biocompatible nature to the dots and hence they can undergo oxidative degradation inside the cell and harm the same. Moreover, non-functionalization may lead to unspecified exit route of these drugs from the treated organism, hence the treated organism may become intoxicated. Therefore, surface functionalization of these dots is the most important part if we want to cast them inside the body of an organism. Secondly, capping agent has to be a perfect surface passivator, which will act as inhibitor to the surface trap states in the QDs. Thirdly, it is also observed that many a times the capping agent/stabilizer/surface passivating agent itself act as a harmful material toward to treated organism. Hence, selection has to be made on this scenario too. Overall, the research of biologically active and applicative QDs demands the production of such engineered QDs, which can answer all the three major problems. At the same time, the role of capping agent/stabilizer/surface passivator has to be restricted to only one molecule, which can act as capping agent, stabilizer and surface passivator in parallel. Therefore, the quest of potential multiuse QDs with multiuse surface modifying agents is still going on around the globe and warrants a thorough investigation.

6. Challenges of aqueous synthesis of group IIB-VIA QDs

The process of synthesizing all the QDs of the mentioned semiconductors in aqueous media is a challenging task. Literature [88, 89] to some extent reveals that the anionic/chalcogenide portion of the semiconductors plays the key role in the synthesis. It is because the reduction of sulfur (S), selenium (Se) and tellurium (Te) is very much different from each other due to the difference in their reduction potential, i.e., -0.467 , -0.924 and -1.143 respectively. Reduction of S is relatively easier in comparison to Se and Te in water, because it easily dissociates into S^{-2} from its available metallic salt. But strong reducing reagents are required to reduce Se and Te in room temperature. Moreover, they are not stable in the solution and can readily form Se^0 and Te^0 once the effect of reducing agent is finished. Proper precaution has to be taken. In case of Te, reduction has to be carried out under inert atmosphere (nitrogen/argon atmosphere) as it readily converts to Te^0 in non-inert condition [90]. During the addition to the metal precursor, one has to be delicate and calculated enough, or else, Te^{-2} will be readily converted to Te^0 . Hence, performing the synthesis in the aqueous medium at room temperature is a challenging task; however, the successful completion of this challenge may lead the world into different class of environmentally benign, easy and cost effective synthesis route for QDs.

7. Application of group IIB-VIA semiconductor QDs

Most essential part of these QDs is their application in optoelectronics such as light emitting diodes [91–99], photodetectors [100] and photovoltaic solar cells or quantum dot sensitized solar cells (QDSSC) [101–105]. Colvin and his associates had first designed QD-LED (1994) [91] and this invention was a milestone in optoelectronics. The quantum efficiency of first CdSe QDs was 0.01%, which was a better result in that time, although much lesser than today's QD-LEDs. The reason behind fast development of efficiency of the QDs in LEDs is the report of newer developments in synthesis methodologies and their quality along with that. Recently, impressive development has been made by Samsung electronics in the form of quantum dot televisions. The manufacturing authority claims that the color intensity is much more intense than an ordinary TV and it happens due to the incorporation of QDs. The greatest potential of colloidal QDs in optoelectronics lies in their humongous flexibility of semiconducting and optical nature over wide range of light spectrum, which allows the tailoring of QDs according to their desired applications. In addition to that, the low cost production and effective charge transfer capability also offers these dots the suitability in optoelectronic appliances. The utility of the QDs in LEDs or QDSSCs can be consolidated by fabricating the thin films of them. Thin films are the easiest but effective support as well as cost effective solution to incorporate the highly luminescent QDs in a device. In thin film science, a thickness range of nanometers to a few micrometers of the synthesized QDs is spread over suitable templates (commonly used glass, ITO, FTO, mica, etc.) by various methods (e.g., chemical vapor deposition, electron beam deposition, spin coating, dipping, etc.). First generation silicon solar cells were the first thin film solar cells, however, slowly 3rd generation thin film solar cell has been replacing them. In the preparation of a thin film, the suitable roughness according to their thickness has to be maintained to receive desired optical luminescence. In the fabrication of thin films, the methodology to prepare them is very important. It is because during the process of fabrication, the characteristics of the synthesized QDs must not change, as making of thin films may undergo different rigorous

treatment including heating too. Therefore, to find a valid and effective method of thin film fabrication is very important. Simultaneously, the cost of production of the thin films also has to be minimal so that the product will be a cheaper one. Hence, research is undergoing intense investigation to find a low cost and effective way of production of QD thin films, which can necessarily, fulfill the demand of industry as well as global market. Although having tremendous potential utility of these QDs in various application fields of science and technology, their high production cost (~\$10,000 per gram of QDs) makes it difficult to raise them as a part of our day to day life [106, 107]. Unless scientists develop some sort of easier and cost effective way to produce and fabricate specific shape and sized QDs in mass scale, we cannot understand their broad application [108]. Therefore, chemical engineering of QDs has begun to solve these two major following issues: (a) use of eco-friendly inexpensive starting material for synthesis of QDs and (b) development of green synthesis routes with the optimization of all the reaction parameters [62]. Therefore, it is become mandatory for the research community to design newer and greener optimized synthesis processes, so that in near future these QDs can become leader in every aspects of mankind.

8. Future work

Semiconductor QDs are advanced materials for various applications which have been discussed elaborately. Their unique physico-chemical properties make them suitable for applications in energy conservation, imaging devices, non-linear optics, nano electronics, nano photonics, solar cells, miniaturized sensors, photography and bio-medical domains. Material preparation and physico-chemical characterization of group IIB-VIA QDs should be further modified in order to fabricate smart devices. The future work toward the greener synthesis of binary and multicomponent nanocomposites is warranted as doping with suitable metal and metal alloys enhances the optoelectronic and optoelectrical properties of these QDs.

Conflict of interest

The authors declare that there is no conflict of interest.

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Author details

Jejiron Maheswari Baruah and Jyoti Narayan*
Synthetic Nanochemistry Laboratory, Department of Basic Sciences and Social
Sciences, School of Technology, North Eastern Hill University, Shillong, India

*Address all correspondence to: jnarayan.nehu@gmail.com

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