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"Green" Quantum Dots: Basics, Green Synthesis, and Nanotechnological Applications

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Abstract

Nanotechnological development of new materials involves the discovery or design of materials at small length scales with controlled physical and chemical properties than can be tuned or modified in function of their applications. One of the most suitable examples of nanoparticles used for this purpose are *quantum dots*, a type of colloidal fluorescent semiconducting nanocrystalline material that has the possibility, due to its unique optical and electronic properties, to be used in numerous technological applications such as biosensing, in vivo imaging techniques, photovoltaics, nanomedicine, molecular pathology, and drug delivery. Thus, there are almost endless possibilities for quantum dots materials. In spite of the fast advance in the search of quantum dots with better nanomaterial performance, environmentally benign and sustainable production is still lacking. Although the use of these materials is developing promptly, there is increasing concern that these materials might pose potential risks to human health. Herein, we discuss principal properties of quantum dots, including their functional architecture and toxicity, and review the main studies about "green" quantum dots synthesis to be aligned with green nanotechnology approach for nontoxic, cleaner, safer, and more responsible processes. The organometallic colloidal synthesis and the aqueous colloidal synthesis, as well as their drawbacks and benefits, are conferred. Recent advances in technological and biological quantum dots-based applications are also discussed in this chapter.

Keywords: nanoparticles, greener/quantum dots, fluorescence, "green" synthesis, in vivo/in vitro imaging, QDs-based solar cells

1. Introduction

Nanotechnology and nanomaterials, two closely related research fields, have become the central axis of world technological development [1, 2]. While nanosciences study the properties of

matter at nanoscale (in particular, size-dependent properties), nanotechnology has the ability to manipulate nanoparticles as building blocks for specific applications [3]. In the past 20 years, nanomaterials science had a rapid development, thereby opening up new opportunities for materials design in scientific, technological, and industrial applications [4, 5]. Such advance, a runaway race, can be counterproductive. It means that environmentally benign and sustainable process could be bypassed due to the almost endless possibilities of nanoscale materials. As consequence of this worldwide tendency, the “green nanotechnology” (GN) appears as a new promising research field. This concept seeks to provide energy, clean water, medical help, and a good environment in a sustainable way [6]. In this context, industrial revolution planted in the earth a notion about the unsustainable development, and nowadays the humankind is still suffering its legacy. Then, the so-called green process (synthesis, production, and disposition) represents an alternative for nongreen technologies, stating that it is possible to make it cleaner, safer, and faster with a neutral or positive balance for environment.

Currently, the huge challenge for new scientists is to reveal the nanoscale world discovering new knowledge, developing new characterization tools, and producing devices with great properties and applications. Importantly, a new generation of highly efficient technology is being developed employing quantum dots (QDs) as building block material [7–9]. Since their first discovery in glass crystals in 1980 by Russian physicist Alexey Ekimov [10], systematic progress has been achieved going from nanolithographic preparations to successful synthesis of colloidal QDs with size-dependent properties [11]. To understand the unique properties of QDs, we review in detail the following aspects: physicochemical properties, related toxicity, and recent technological applications, giving a special attention to the synthetic methods, including “green” approaches.

2. Physicochemical properties of QDs

Among all nanoparticles classified by their size, QDs arise as the key semiconductor material in the emerging nanomaterials area. QDs are luminescent solid-state, crystalline nanostructures composed of atoms of groups II–VI (CdSe, ZnS, and CdTe), groups III–V (InP and InAs), and groups IV–VI (PbSe and PbS) of the periodic table. Technically, these materials have structural features between the isolated atoms and the bulk macroscopic materials as a consequence of their nanoscale ranging from 1 to 10 nm. At this level, physical, chemical, and electronic properties change dramatically because of *quantum effects*, consequence of *quantum confinement*. This behavior is related to the electronic migration in semiconductor nanocrystals. Once the light absorption is over, electrons (e^-) and holes (h^*) generated perceive each other due to Coulomb attraction and an electron-hole pair called exciton is formed. The average physical separation between the electron and hole represents the *exciton Bohr radius*, which is typical for each material. If the size of semiconducting material is becoming increasingly smaller, it means when it is closer to the natural scale of its *exciton Bohr radius*, quantitation of states became present. In other words, continuous energy levels change into discrete ones (Figure 1 a).

Figure 1. Schematic representation of energy levels in macroscopic, nanocrystal and atomic semiconducting materials (a), and related dimensions of exciton Bohr radius and particle size (b, c). Adapted with the permission from Alivisatos [12].

In this context, a discrete level refers to finite separation between energy levels due to the quantum confinement effects of electrons and holes in QDs with smaller sizes than its exciton Bohr radius (**Figure 1 b, c**). These QDs display physicochemical properties, such as high photostability, broad absorption spectra, narrow and symmetric emission spectra, slow excited state decay rates, and broad energy absorption cross sections. Their emission colors depend on their size, chemical composition, and surface chemistry and can be tuned from the ultra-violet to the visible wavelengths. QDs have nanoproperties in all three dimensions, whereas other nanoparticles as nanowire or single thin layers have ordinary properties along the wire and two dimensions, respectively.

On the other hand, respect to their functional architecture, QDs consist of an inorganic core responsible for the fundamental optical properties and semiconducting character, a layer or shell of another semiconductor material responsible for passivation of active QD-core surface and capping ligands. In almost all cases, the shell has a greater band gap than the core material. The growing of a very thick, defect-free shell is the best solution to render optical properties avoiding loss of quantum yield (QY), photobleaching, and blinking, which are typical drawbacks of QD-core material due to surface chemistry and chemical environment [13]. Additionally, the shell plays two crucial roles, one as physical barrier separating the core from its surrounding medium and other in the defect state saturation, a process related with dangling bonds at the core surface and crystalline defects suppression. Finally, capping agents or ligands are important components in nanomaterials, especially in QDs [14]. The nature of QDs' capping ligands is related with synthetic methods and final applications. For instance, long chain organophosphorates, primary amines, carboxylic acids, alcohols, and thiols are common ligands employed in QDs synthesis. Amines, alcohols, and carboxylic acids can offer the possibility of bioconjugation, a process that involves the linking of biomolecules (peptides, carbohydrates, virus, DNA fragments, and natural products) through electrostatic or hydrophobic interactions and covalent coupling [15]. In general, ligands provide colloidal stability, control particle morphology, and particle size distribution and stop uncontrolled growth and agglomeration. Nowadays, ligands are the key parameters in the design of QDs mainly because their electronic structure contributes to the final solubility, electronic and optical profiles of contemplated nanoparticle [16]. The physicochemical properties of designed QDs are directly related with nature and final assembly of core/shell/ligands, as depicted in **Figure 2**.

Figure 2. Basic architecture of core/shell/ligands in QDs.

In biomedical research, high fluorescence is the most attracting property of QDs [17]. This type of nanocrystals exhibits broad absorption spectrum; it extends in some cases up to the ultraviolet (UV) region. QDs have size-tunable fluorescence emission from visible to infrared in the electromagnetic spectrum. In other words, multiple QDs with same chemical composition can emit different colors depending on their size. Typically, smaller dots have larger energy band gap yielding a blue shifting of their absorption bands, so smaller QDs emit blue light. In contrast, bigger dots have smaller energy band gaps resulting in a red shifting and the emission of red light (**Figure 3**).

This is an important feature for biological applications because it allows simultaneous excitation of multicolor QDs with a single light source. Furthermore, high-quality QDs have large molar extinction coefficients ($0.5\text{--}5 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$) and narrow and symmetric emission spectra. These features are ideal qualities for ultrasensitive and multiplexing applications in biosensing [18].

Figure 3. Emission colors of ZnS-capped CdTe QDs excited under a UV lamp (365 nm).

3. Toxicity of QDs

We now describe the task that must be overcome in QDs research to advance toward mainstream environmental and biological applications: QDs' toxicity. Cadmium-based QDs are the most studied nanoparticles in biosensing and intracellular or in vivo applications showing remarkable results [15]. CdSe and CdTe are the two of the most extensively studied QDs. However, several research groups have demonstrated the extremely toxic profile of Cd and other heavy metals such as In, Hg, and Pb, even under extended periods of time [19, 20]. This

toxicity is related to the leaching of Cd from the core into the cellular environment, resulting cellular death due to the DNA damaging properties of components in mention (**Figure 4**).

Figure 4. Schematic representation of cytotoxicity—DNA damage—due to the leaching of Cd from the core into the cellular environment.

Neurological and genitourinary toxicities are also related with Cd leaching. Moreover, previous studies showed that ultimate destination of QDs' decomposition final products remains unclear. In particular, careful methods are being developed for cytotoxicity assessment of nanoparticles, especially QDs [21]. Conventional methods used for drugs or chemicals, in some cases, are inappropriate because they obviate physicochemical characteristics, such as size, color, superficial defects, nature of capping ligand, and intracellular associations. Nowadays, one of the most promising in vivo model systems for toxicity studies, *Danio rerio* or zebrafish, has been used as evaluating biomaterial for nanotoxicity assessment in QDs [22].

A special condition of QDs in cell culture is associated with cytotoxicity assessment. An increase of QDs' toxicity is detected when UV illumination is used for their location; this condition is related with UV irradiation energy, which is close to that of a covalent chemical bond and promotes the dissolution of semiconductor particles in a process known as photolysis [23]. In contrast, under absence of UV irradiation, QDs with stable capping ligands (e.g., polymeric coating) seem to be nontoxic to cells and animals [24]. Among all physical and chemical properties of QDs, the hydrodynamic diameter (hd) define in vivo behavior of these nanocrystals [25]. Particles with hd smaller than <5.5 nm are rapidly and efficiently eliminated from the mice through renal clearance. This hd value suggests a limit to be considered in property-based design QDs to achieve an acceptable biocompatibility. In environmental applications, acute toxicity has been found as the main drawback due to the formation of reactive oxygen species (ROS) [26].

Although, several efforts have been made to reduce QDs' toxicity keeping optical and physical properties unaltered. Basically, QDs' core protection can, to some degree, control the toxicity related to metal ions leakage. Shell growth (ZnS, CdS, or polymeric capping) is the most applied alternative to largely alleviated cellular damage. Enhancing stability and surface modification are other approaches in the challenge to overcome QDs toxicity. One of the most promising superficial modifications is the coating with suitable water-soluble organic ligand/biomolecules, such as biotin, folic acid, peptides, bovine serum albumin, antibodies, and DNA [27].

These biomolecules act like biorecognition agents in the cellular media—promoting biocompatibility. With difficult cellular recognition and continuing demand for more biocompatible QDs as the signal reporter in biosensing, new emerging alternatives known as “greener” QDs are in the spotlight of current biological research. This current research field has shifted its emphasis toward the fabrication of cadmium-free QDs, such as silicon, carbon/graphene, Ag_2Se , and Ag_2S QDs (**Figure 5**) [28, 29].

Figure 5. Emerging QDs in response to the constant demand of more stable and less toxic nanoparticles.

With the possibility that GN offers to design/make and build “green” from the beginning, there is no doubt that there will be more “greener” QDs available in the future.

4. “Green” synthesis of QDs

The search for environmentally friendly and reliable processes for nanomaterials production is an active topic in GN. Synthesis of nanomaterials with highly monodispersion, crystallinity, shape control, and narrow size distribution plays a critical role in QD-based applications. In the beginning of QDs’ nanotechnology era, preparation was based mainly on physical methods, and the main goal was high-purity products. After 20 years, essential studies about the mechanisms of QDs formation have improved current synthetic methods, encouraging innovative routes for the synthesis of nanocrystals with controlled size and shape. Currently, there are two synthetic procedures (others use minor variations of these two methods) to produce QDs (**Figure 6**). Each method exploits different aspects of chemistry to produce QDs with the desired optical properties like high QY, narrow fluorescence emission, broad absorption profile, and stability against photobleaching [30].

The first procedure is an organometallic colloidal synthesis (OCS; **Figure 6a**) at high temperature (HT), which makes use of high boiling point organic solvents, such as tri-*n*-octylphosphine oxide (TOPO), trioctylphosphine (TOP), or hexadecyl amine (HAD), three of which are

containing long alkyl chains. OCS was developed by Murray's et al. in the early 1980s and rapidly become in a seminal work [11]. In a typical synthesis for high-quality QDs, elevated temperatures ($\approx 300^\circ\text{C}$) are used in junction with coordinating solvents (TOPO or HAD) and metal/chalcogenide precursors (OCS; **Figure 6a**). Basically, coordinating solvent serves as a solvent and as a ligand and is commonly a mixture of surfactants such as TOP/TOP and HAD. During synthesis process, these ligands attach their terminal functional groups (phosphines, phosphine oxides, and amines) to the QDs surface leaving the ligand alkyl chains directed away from the surface. As consequence, a long alkyl chain monolayer is formed resulting in QDs highly hydrophobic and only soluble in nonpolar solvents, such as toluene, chloroform, and hexane. A deep look into OCS reveals the thermic decomposition at HT of organometallic precursors (TOPO-Cd and TOP-Se, in CdSe synthesis) previously formed in a process known as pyrolysis [31]. An experimental requirement for this method is related with the need to be carried out in an inert atmosphere together with quick hot injection of metallic precursors. Discussions about the influence of hot injection in OCS have been reported recently [32], it is concluded that QDs prepared through hot injection had higher QY but poor sensing attributes compared to QDs synthesized at room temperature.

Despite great performance of QDs prepared by OCS, these syntheses involve the use of nongreen conditions, hazardous chemicals, and high energy requirements. As example, extremely toxic/pyrophoric/volatile metallic precursor, dimethylcadmium ($\text{Cd}(\text{Me})_2$), and chalcogenides vapor phase compounds, such as H_2Te , are employed in these syntheses. In this field, the only way to develop process as "green" synthesis is to adapt benign synthesis approaches that use mild reaction condition and nontoxic reaction precursors or reaction media, achieving the desired product in the highest yield possible and preventing unwanted waste. In response to this trend, easier and greener approaches have been developed for OCS replacing the highly toxic and volatile Cd precursor for a cheaper and more stable cadmium sources, such as $\text{Cd}(\text{Ac})_2$ [33], CdO [34], and CdCl_2 [35]. Additionally, solvents such as glycerol and paraffin have been shown to decrease nanoparticle toxicity when are used in OCS [36, 37].

Moreover, the greenest approach for OCS includes the use of environmentally renewable raw materials as solvents and coordinating agents, such as oleic acid [38], castor [39], and olive oil [40]. These are three remarkable green alternatives of renewable materials employed in QD synthesis avoiding the need for the use of air-sensitive, toxic, and expensive chemicals, such as TOP, TOPO, or HDA.

The second procedure is an aqueous colloidal synthesis (ACS; **Figure 6b**). ACS appears in response to the needs of TOP/TOPO-QDs solubilization for biological applications. Usually, the hydrophobic layer in TOP/TOP-QDs is substituted by hydrophilic molecules, such as amines, polyhydroxy alcohols, and especially thiols, through cap exchange in liquid phase. This superficial modification brings in most cases significant decrease in QDs' photoluminescence [41]. To overcome this problem, ACS involves the direct aqueous synthesis of QDs using the less toxic and most biocompatible solvent—water. In a typical ACS, heavy metal precursor (e.g., CdCl_2 , $\text{Cd}(\text{NO}_3)_2$, and $\text{Cd}(\text{CH}_3\text{COO})_2$) is easily dissolved in water and coordinated by the hydrophilic agents such as thioglycolic acid (TGA), mercaptosuccinic acid (MPA), glutathione

(GSH), and L-cysteine (L-Cys). A basic version of ACS was first investigated by Gao and co-workers [42].

Figure 6. Schematic representation for two main QD synthesis methods, OCS (a) and ACS (b) in CdSe QD preparation.

In ACS, chalcogen precursor can be freshly prepared in aqueous medium before using in the reaction. NaHE ($E = \text{Se, Te}$) produced from the chemical reduction of selenium (Se) or tellurium (Te) in presence of sodium borohydride (NaBH_4), and Na_2SeO_3 from the reaction of Na_2SO_3 solution with Se are common sources employed in QDs ACS. Rigorous inert atmosphere is not necessary because precursors like Na_2SeO_3 are stable at open-air conditions [43]. After precursor injection or addition, crude reaction is refluxed ($92\text{--}95^\circ\text{C}$) to promote QD growth. This is an example of low operating temperatures compared with the necessary 300°C for OCS; there are even reports for ACS at room or freezing temperature [44, 45]. During synthesis process, thiol-type capping agents attach their functional group $-\text{SH}$ to the QD surface leaving the hydrophilic groups available for subsequent bioconjugation processes [46]. Additionally, compared with the organic-based synthesis, ACS is preferred as key procedure for QD preparation in biological studies as they exhibit good reproducibility and low toxicity and are less expensive and environment friendly, resembling many of the goals pursued by GN [47]. Initially, quality of QDs prepared by ACS was relatively low (low QY and large size distribution) compared to OCS. Nevertheless, continuous efforts and experimental improvements in the field allowed the discovering QDs with equal or better properties than organic-based synthesized QDs [48]. Parameters such as type of capping agent, precursor's source, heavy metal/chalcogenide/capping agent molar ratio, and shells thickness define final properties of QDs [49].

The reaction medium, a crucial feature that in most cases determines the quality of QDs, has been subjected to a green approach; alternatives, such as micellar synthesis and green solvents, have been investigated achieving outstanding results [50]. The energy input for QD synthesis, commonly used over years, was direct thermal energy; despite this, the successful synthesis of widespread nanomaterials using microwave [51], ultrasound [52], and hydrothermal [53]/mechanical [54, 55]/electrochemical [56] energy has increased particular attention. The utilization of these techniques allows the preparation of high quality and nearly monodispersed QDs from appropriate molecular precursors. In particular, microwave chemistry offers unique opportunities to significantly increase the rate of nanoparticle formation, while not compromising on the high-quality and narrow-size distributions needed for these nanomaterials to be further used in other areas.

Nowadays, the greenest approach in nanoparticle preparation is plant/microorganism-mediated biosynthesis, a field of recent development able to produce highly fluorescent QDs at ambient conditions by biological organism like plants and fungus in the presence of appropriated substrates [57]. A heavy metal concentration in plants and microorganisms affects their growth, morphology, membranes, enzymes, and DNA, and in most cases high concentration causes cellular death. In spite of effects in mention, biological organisms exposed to toxic concentrations of heavy metals such as Cd, In, or Pb have developed tolerance mechanism through detoxification by enzymatic oxidation or reduction of heavy metals to less toxic forms or covalent modifications [58].

An efficient and environmentally friendly method of plant-based biosynthesis of CdS QDs using hairy root culture of the flowering plant *Linaria maroccana* L. has been developed [59]. Several studies suggest that the broad range of natural products, such as alkaloids, terpenoids, phenols, flavanoids, tannins, and quinines, are involved in redox process and could mediate the synthesis of nanoparticles [60]. Microorganisms such as fungi (*Fusarium oxysporum* [61] and *Saccharomyces cerevisiae*) [62] or bacteria (*Escherichia coli*) [63] have been employed to synthesize CdSe, CdTe, and CdS QDs, respectively.

5. Nanotechnological applications of QDs

Nanotechnological applications of QDs represent one of the most important challenges in nanomaterial science. The exploitation of unique QD properties opens the door for endless applications [64]. The primary applications of QDs are in energy-efficient lighting [65], solar photovoltaic [66], and biological imaging [67, 68].

In recent years, energy-efficient lighting has been enthusiastically investigated in regard to the unique properties of colloidal QDs, positioning it as one of the most promising emitters for next-generation displays and lighting devices [69]. As a demonstration of nanotechnological development, light emitting diode (LED) technology has been a breakthrough innovation in this lighting revolution, enabling efficient and high-power devices with prolonged lifetimes. The first demonstration of QDs-based LEDs (QDsLEDs) by Alivisatos et al. in 1994 opened the door to a continuous development improving step-by-step the structure of ideal device [70]. The performance of QDsLED devices has been rapidly improved, as a result of technological

development and the accumulation of fundamental knowledge [71]. Compared with conventional LED and organic LED (OLEDs) technologies, QDsLEDs may offer many advantages in terms of color purity, stability, and production cost while still achieving similar levels of efficiency. Emission from the QDsLEDs can be easily tuned by varying the size of the QDs without changing their processing properties; this feature allows producing different QDs emissions over a broad wavelength range replaying the device fabrication procedure, covering the visible and near-infrared regions. Recently, deep-blue [72], green [73], and red [74] QDsLEDs have shown maximum external quantum efficiency (η_{EQE}) of 7.1, 12.6, and 18–20%, respectively (**Figure 7**); these are performance values comparable to those of OLEDs. However, to reduce the manufacture complexity in the synthesis (one-pot or two-pot synthesis approaches) and device architecture (conventional/inverted assembly or solution/vacuum deposition), unification of the total procedure is needed to achieve full-color displays with the highest efficiency for each color.

Figure 7. Photograph of (a) deep-blue, (b) green, and (c) red QDsLED devices. Adapted with the permission from Colvin et al. [71], Ki Bae et al. [72], and Yang et al. [73], respectively.

Keeping in mind the GN alignments, QDsLED devices for light harvesting have significant potential in terms of saving energy with a projected reduction of 50% in the electricity consumption occurring due to lighting [75].

In solar photovoltaics, several characteristics make QDs an attractive option for the development of QDs-based solar cells (QDsSCs) [76]. In QDs, the band gap can be tailored to absorb light in the whole solar spectrum, which is a crucial feature for solar applications. Also, the enhanced impact ionization leads to multiple exciton generation for each photon absorbed, characteristic that favors high and stable photocurrent generation [77]. Works by Kamat and Bawendi are the two of the most important sources of experimental and technological improvements; these groups have developed a deep knowledge in the field for nearly 10 years of continuous research. In 2014, Kamat [78] reported a detailed and concise review of QDsSCs, which highlighted the recent advances in size- and shape-selective synthesis and design of QDsSCs with photoconversion efficiencies greater than 5% (**Figure 8**). However, it was recalled that to make QDsSCs competitive with other existing thin film or polycrystalline photovoltaic technologies; it is important to overcome kinetic barriers for charge transfer at semiconductor interfaces.

Figure 8. Example of QDSCs developed in Professor Kamat's group (for more information visit: <http://chemistry.nd.edu/people/prashant-kamat/>).

On the other hand, Bawendi [79] reported a room temperature solution process for high efficiency, low-temperature fabrication, and good atmospheric stability of SCs composed of ZnO/PbS QDs. These improvements were possible through delicate band alignment engineering of the QD layers through the use of different ligand treatments achieving a photoconversion efficiency of 8.55%. Greener approaches, such as CuInE₂ (E=S, Se) QDs, have been reported, in spite of high absorbing capacity and low toxicity, this SCs have shown lower efficiencies (<6.79 %) [80]. Photovoltaic applications of QDs open the possibility of development of light-harvesting structures, one of the most important fields in GN. Actually, the maximum efficiency theoretically predicted for QDs-sensitized solar cells (QDs-SSCs) is 44%, this value is higher than that for dye-sensitized solar cells (DSSC) using organic sensitizers (33.5 %) and for traditional Si solar cells (35%) [81].

Finally, in the biological imaging field, QDs can act as exogenous probes in the study of biological samples, cells culture, and animal models. Due to the high stability as fluorophore and long fluorescence lifetime, QDs are used in *in vivo* imaging, *in vitro* diagnostics, drug delivery, and photodynamic therapy [68]. Fluorescence imaging technology is well established in research and medicine for biological imaging and clinical diagnostics; however, the nanotechnological improvement that QDs offer may help to overcome the persistent limitations of traditional organic dyes and genetically engineered fluorescent proteins, such as narrow excitation spectrum, broad and asymmetrical emission spectra, low photobleaching threshold, rapid lifetime decay, and low QY [82]. As we described in previous sections, QDs can be conjugated to biological molecules retaining their photophysical properties without alteration of the function of these biomolecules itself. Among bioconjugation methods, adsorption, electrostatic interaction, and covalent linkage are the most commonly used [83]. After bioconjugation process, modified QDs are used as fluorescent biological labels for cellular and molecular imaging. Basically, the main studies can be separated into *in vitro* and *in vivo* imaging. For *in vitro* imaging, fixed and living cells cultures are employed to the specific

labeling of proteins and structures [84]. These techniques are helpful to understand the process in molecular cell biology associated with the protein and gene expression in cells. Also, immunohistochemical detection of single or various molecules of interest can be accomplished using primary and secondary antibodies. DNA and RNA mapping can be developed in cellular environment with QDs using the well-established fluorescent *in situ* hybridization [85]. In living cells culture, QDs are able to help in the understanding of dynamic cellular (*e.g.*, cell tracking) and *in vivo* molecular interactions over prolonged periods at high resolution. For *in vivo* imaging, ideal coating for QDs must be designed and applied to mitigate or nullify the toxic profile of the core. One of the most interesting *in vivo* studies is cancer studies [86, 87]. Generally, QDs are attached to tumor-specific antibodies acting as cell marker in preliminary ultrasensitive cancer diagnosis. Promising studies are being developed using QDs in photodynamic therapy, a therapy that uses a photosensitizer or photosensitizing agents (like QDs) and a particular type of light to generate ROS that kills nearby cells [88].

6. Conclusions

Nanotechnology offers the opportunity to find solutions to global issues that affect society at all levels, such as disease recognition, cleaner water, and sustainable energy needs. Through continue research and development of deep knowledge in the field of nanosciences and nanotechnology, the problems and processes of life are now being revealed step by step. However, findings, improvements, and joint efforts will have a realistic impact on everyone's life if we are able to make it *green*. It means, stops being *potential* and develop complete eco-friendly process applying sustainable technologies, a responsibility that lies on the hands and minds of scientist and engineers today. QD-related nanomaterials should be produced and applied more efficiently to exploit all their unique properties in chemistry, biology, and physics.

Actually, the aqueous colloidal synthesis and organisms-mediated synthesis are considered "greener" methods of QD production; they offer appropriated materials with tailored properties for specific applications. In the near future, there is no doubt that scientists and engineers will provide a sustainable and economical approach for production of QDs, avoiding the use of *quotes* in the word "*green*" to make it completely *green*.

Additionally, the on-going fruitful collaborations between several disciplines involving biotechnology, photonics, nanomedicine, toxicology, physics, engineering, and others may place QDs' development as a breakthrough in this worldwide nanorevolution. QDs, with their intense luminosity and high photostability, are the best candidate for these types of research.

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