

Photovoltaic Properties and Solar Cell Applications of Colloidal Quantum Dots

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Abstract: As energy consumption increases across the globe, current energy supplies such as fossil fuel, natural gas, and coal are rapidly diminishing. Our current solar cell technologies are reaching all time high efficiencies, but our infrastructure and cost are still preventing expansion. Even though only 0.1% of our primary energy comes from sunlight (Raval and Gupta, 2015), colloidal quantum dot solar cells have properties that can be tuned and utilized to enhance energy conversion. This review article explores past research and analyzes the benefits and drawbacks of various synthesis, fabrication, and cell structures of colloidal quantum dots and their utilization in solar cells. In addition, further research on properties of CQDs, such as shape and multiple exciton generation, are discussed.

Introduction

One attractive option to help achieve high efficiency and affordable energy are quantum dot (QD) solar cells. QD solar cells have the ability to enhance light absorption, not only in visible light, but also the infrared light range. Because of this, they serve as an appealing alternative solar cell material. Due to their unique properties, QDs can be used for a wide variety of applications, including displays, sensors, batteries, and cancer treatment.

This review will focus on colloidal quantum dot (CQD) solar cells and their benefits. The quantum confinement effect will be discussed to demonstrate the photovoltaic benefits provided by the physics of CQDs. Additionally, synthesis, physical application methods, and solar cell structure will be reviewed to highlight benefits and disadvantages of each. Finally, the possibility of multiple exciton generation will be reviewed to illustrate promising characteristics of CQD solar cells.

Quantum Dots

QDs are very tiny semiconductors that are only nanometers in size. To put this into perspective, these particles are 10,000 times smaller than a human hair. Scientists have found that by reducing a particle to this level, its properties—that typically remain constant—can change drastically. The properties of QDs can be adjusted by their size, shape, and material. One characteristic property that is easily visualized is the photoactive nature of QDs.

A QD absorbs light and then re-emits light in pure colors when excited. The size of the dot determines the color of the light, such that smaller dots emit a higher energy light than larger dots. The size of the dots can be controlled through various synthesis methods and can be formed to produce nearly any color in the visible spectrum.

The ability to adjust the size and shape of QDs is a desirable characteristic (Carey et al., 2015; Kedera et al., 2008; Zhao & Rosei, 2017). The adjustable properties of QDs are entirely dependent upon their extremely small size. This can be described by the quantum confinement effect, which is a result of reducing a particle down to the nanometer scale. When a particle becomes this small, the energy level transitions from continuous to discrete energy levels. The idea of quantum confinement was first investigated in the early 1970s with Molecular Beam Epitaxy. Guyot-Sionnest (2008) states that “Quantum dots are the extension of quantum confinement ideas to three dimensions” (p. 778). This property plays an important role in the production of solar cell technology, as quantum confinement allows fine-tuning of specific optical properties such as absorption wavelength (Guyot-Sionnest, 2008; Zhao & Rosei, 2017) and bandgap (Xin, 2014). In comparison to other solar cells, QD solar cells have unique benefits and a bright future. Their potential for multiple exciton generation and narrow band-gap puts QD solar cells at a prospect of very high energy absorption and efficiency.

Literature Review

Synthesis - Colloidal Quantum Dots

The synthesis technique used to develop QDs is crucial to obtain specific desired properties. Colloidal quantum dots refer to dots that are made in a colloid, or mixture, where the particles are suspended throughout another substance. In recent years, CQDs have gained a lot of attention and research, especially pertaining to solar cell technology. In 2008, Guyot-Sionnest claimed that in the last five years (2004-2008), there have been five times more scientific publications on CQDs than the previous twenty years combined. Two key elements of CQDs are their high monodispersity and small size; this is important because properties that increase percent conversion of solar cells are size dependent. There are many different synthesis methods to produce CQDs. Four of the most common methods are solvothermal synthesis, aqueous media synthesis, ultrasonic synthesis, and hot injection synthesis.

Solvothermal Synthesis

Solvothermal synthesis uses a sealed vessel and an organic solvent as the reaction medium. One key advantage of this method is that it is heat promoted. Using heat increases the reaction and enhances the solubility of the reagents. Combining an appropriate organic solvent and a temperature higher than the normal solvent boiling point can be rewarding. This method allows raw materials which are poorly reactive to be utilized, such as Sulfur (S), Selenium (Se), and Tellurium (Te) (Barcelo et al., 2014). One disadvantage of this method is the use of toxic surfactants and organic solvents that require temperatures up to 300°C to decompose the precursor species (Zhao & Rosei, 2017). This is an environmental concern which must be considered when choosing between different synthesis methods.

Aqueous Synthesis

In contrast to the solvothermal method, synthesizing CQDs with aqueous media is considered an environmentally conscious choice due to the low synthetic temperature, which is less than 100°C. This application, however, has consequences in performance. It exhibits a lower photoluminescence quantum yield (PLQY) (Zhao & Rosei, 2017), which is the ratio of photons absorbed

to the photons emitted. A precipitation reaction is utilized to collect the CQDs formed by this method. Thiols are added as stabilizing agents and play an important role by preventing uncontrollable growth as they actively absorb on the surface of the nanocrystal (Barcelo et al., 2014). The components of thiol-capping molecules allow the ability to obtain CQDs with a functional shell (Barcelo et al., 2014; Zhao & Rosei, 2017). While the other synthesis methods are typically capped with an inert organic molecule, obtaining a functional shell allows more adjustment to specific properties and characteristics, such as solubility in water.

Ultrasonic Synthesis

The ultrasonic method is a low temperature synthesis which contributes to a much lower cost to produce QDs. Chen et al. (2017) used ultrasonic synthesis and its ligand-assisted re-precipitation to provide up to 70% PLQY at room temperature. This is an excellent improvement for low temperature production, in comparison to the aqueous method. The ultrasonic method can also produce high-quality dots that absorb a wide range of colors from blue to near infrared wavelengths. Other advantages include reduced particle size and the ability to produce different shapes (Chen, 2017), including spheres, rods, wires, and rings. Some researchers suggest that controlling the shape of the CQDs can influence their quantum confinement (Carey et al., 2015), absorption properties (Barcelo et al., 2014), and optical transitions of energy (Zhao & Rosei, 2017). However, Bagher (2016) states that there is insufficient evidence to support any effect that shape has on optical properties. By continuing research on shape and determining how to fine tune these characteristics, CQD solar cells could potentially reach record efficiencies.

Hot Injection Synthesis

One of the most discussed and widely used methods in forming CQDs is hot injection synthesis. By mixing highly reactive precursors at a high temperature, a rapid nucleation is followed by slow growth. High temperature causes a burst nucleation that produces monodisperse nuclei that will continue to grow homogeneously. Such nucleation is typically controlled by temperature, supersaturation, and

interfacial tension (Carey et al., 2015). One side effect of this method is the high surface-to-volume ratio, which can be compensated by surface-passivating reagents or ligands (Carey et al., 2015; Kedera et al., 2008), which is similar to the ultrasonic method. With hot injection synthesis, products can be formed with 5-10% standard deviation from the average size without post-preparative size fractionation (Reiss, 2008).

In addition to size control, the optical properties can be tuned based on the choice of ligand attached. Controlling the size of CQDs is relatively easy because it is a simple time dependent reaction. The time of the reaction and the size of the CQD are correlated—as time increases, size increases. When using hot injection synthesis, controlling the size of the dot also allows the bandgap and optical absorption to be easily tuned. The ability to adjust these properties increases percent conversion of sunlight into energy.

Batch vs. Continuous Synthesis

Traditionally, CQDs are synthesized in a laboratory setting using benchtop glassware that produce high percent yields but can only be produced in small batches. Small batch synthesis works well because it is much easier to control the temperature and monitor the progress of the reactions. When trying to produce CQDs with large batch synthesis, the batch-to-batch products lack consistency and fine control over their properties (Jeong et al., 2016). Most importantly, when these production procedures are scaled-up, the quality of the CQDs are compromised. This limits the commercialization of QD-based devices (Jeong et al., 2016). Therefore, an alternative production method must be employed to promote large scale production. Microfluidic reactors are one solution to this problem, offering complete automation of the process as well as excellent consistency. In comparison to the small batch reactions, the microfluidic reactors also can be tuned to control the reaction time and flow rates of precursor solutions (Jeong et al., 2016). This enables quality CQDs to be produced continuously, which can be applied to create solar cells. In 2016, with the use of microfluidic reactors and their ability to control flow rates, Jeong et al. were able to tune the spectral range and PLQY of CQDs. They were also

able to increase the efficiency of the solar cells by 19% when using the enhanced QDs from the microfluidic reactors (Jeong et al., 2016).

Fabrication for Solar Cell Application

Processing CQDs for solar cell application requires two steps, depositing solution and solvent evaporation. After a small volume of the solution is deposited onto a substrate, the solvent evaporates, leaving behind immobile QDs (Carey et al., 2015; Kedera et al., 2008). Various methods have been used to apply the CQDs to a substrate, which allows them to be used within solar cells.

Spin Coating

The method of spin coating requires a rotating vacuum stage upon which the substrate is mounted. Once the CQD solution is deposited, the stage is rotated at speeds between 1000-5000 rpm. The spinning spreads the solution and shearing occurs to produce an even layer of deposited CQDs. Dispersing the CQDs via spin coating creates consistency and high-quality film morphology (Carey et al., 2015). Past research suggests that this application method can be successfully utilized. However, this method is primarily used for research and testing solar cell properties. The inability to be used in scaled-up or continuous large-scale fabrication prevents spin coating from becoming an industrial application method. Also, spin coating wastes much of the QD solution and is a sensitive procedure where spin speed, humidity, and temperature must be considered and observed (Carey et al., 2015).

Dip Coating

Much like spin coating, dip coating is a process that is not compatible with continuous processing, but it has potential to be scaled-up. Dip coating involves dipping the substrate directly into the CQD solution. This process is typically automated to help maintain a consistent dip and removal rate. Despite its scalability, dip coating does not produce uniform films and is sensitive to changes in processing conditions. Another hindrance of dip coating is the necessity of using a lower boiling point solvent to ensure correct deposition of the liquid onto the substrate (Carey et al., 2015).

Spray Coating

Contrary to both spin and dip coating, spray coating has shown to be successful with scale-up manufacturing (Carey et al., 2015; Kramer et al., 2014; Lin, 2014). Spray coating applies the colloidal solution through a nozzle to spray the solution onto the substrate. An air-injection mechanism is typically added to aid in prevention of particles accumulating in the nozzle (Lin, 2014). This method can apply ultrathin layers of CQDs that are almost a monolayer (Kramer et al., 2014). Spray coating can also be used to cover almost any surface, shape, and size, including curved surfaces. Kramer et al. (2014) found that their spray coating method, termed “sprayLD,” could achieve superior performance when applied to a flexed surface. With the ability to apply CQDs to any shape and surface, the cost of production can be minimized by reducing the cost of the solar cells themselves. Solar cells can be created using flexible and economical materials and can be easily coated with the CQDs. Another benefit to this method is the simplicity in layering the CQDs. The layers can be sprayed directly on top of previous layers. Kramer et al. (2014) achieved a 33% enhancement in percent conversion efficiency when layering was applied via spray coating. One disadvantage to this method is the need to be considerate of the viscosity of the CQD solution.

Solar Cell Structure

Cell structure for solar cells is an important consideration when developing CQD solar cells. Advances have been made to the performance of solar cells by improving the design of solar cell structure. This section will explore two of the architectural and device concepts discussed throughout the research of CQD solar cells.

Schottky Cells

The Schottky CQD solar cell was developed after the first thin film CQD solar cell employed CQDs for absorption and charge transport. This elementary structure utilizes an ultrathin film of CQDs sandwiched between two contacts (Barcelo et al., 2014). Taking advantage of a work function difference between the top metal contact and conductive oxide, this model generates a built-in field which produces a photocurrent through the

sandwich layers. The charge transfer between the metal contact and CQDs generates band bending between themselves and Schottky metal, which makes the contact selective (Barcelo et al., 2014). Advantages of this model include its simplicity and its ease of fabrication (Carey et al., 2015; Barcelo et al., 2014). The cells have limited number of interfaces and impressive photocurrents which have led to their use in testing different properties of CQD films. These properties include size-tuned band positions, drift, depletion, and diffusion. These simple models also come with their drawbacks. Fermi level pinning at the metal-QD connection creates an upper bound on open-circuit voltage (Barcelo et al., 2014), which is relatively low considering the CQD band gap (Carey et al., 2015). Finally, these cells require the non-rectifying side of the junction to be illuminated due to the low electrical characteristics of the Schottky design.

Heterojunction Cells

The depleted heterojunction cell was developed specifically to overcome the limitations of the previously discussed Schottky cell. Taking inspiration from another solar cell known as a sensitized solar cell, the heterojunction design uses a nanostructured wide band gap oxide that is supported on conducting glass (Carey et al., 2015; Barcelo et al., 2014). The CQDs are then multilayered, followed by a metal oxide which is deposited on top. Finishing the layers is a back reflective contact constructed with a deep work functioning metal such as gold (Barcelo et al., 2014), followed by silver or aluminum (Carey et al., 2015). These cells are then used to develop the bulk heterojunction cell. Creating a bulk heterojunction cell helped combat the limitations of planar device structures. A three-dimensional interpenetrating network ensures that no photogenerated exciton is farther than one diffusion length away from a charge separating interface. The bulk concept also fixes a problem with minority carrier transport of CQD solar cells (Carey et al., 2015). The electron accepting phase is now substituted, and the CQDs act as both the hole transporting phase and the light absorber (Barcelo et al., 2014). The wide band gap semiconductor and CQD film form an interpenetrating layer. This allows the depletion region to be extended and more CQD material to improve absorption and carrier collection.

However, this design introduces the drawback of bi-molecular recombination, which can be attributed to the increased interfacial area.

To prevent the back recombination, the need to manage the CQD metal oxide conduction band also lowers the device's built-in voltage. Important considerations for this cell type include the need to prevent shunting in highly structured devices (Carey et al., 2015). So far, these cells have seen very low conversion rates. They have the potential to be efficient with the tuning of the CQDs previously discussed, but currently optimization of the solar cell design is in its infancy. In particular, the lack of pathways for the transport of charge need immediate attention (Barcelo et al., 2014). Continued research on the surface quality of CQDs will also play an important role in producing greater efficiency in bulk heterojunction solar cells.

Multiple Exciton Generation

Multiple Exciton Generation (MEG) is one property of CQDs with the most promising potential to increase solar cell efficiency. In a traditional solar cell, one photon from the sun's light excites one electron across the band gap of the semiconductor, where any additional energy in excess of the bandgap is lost as heat. Within conventional solar cells, up to 47% of the solar energy can be lost to heat (McElroy et al., 2014), making heat the largest source of energy loss. MEG is the ability for a CQD to take the excess energy and produce additional electron hole pairs which in turn will increase the efficiency of the solar cell. Carey et al. (2015) found MEG has been shown to double the efficiency of isolated quantum dots compared to the bulk material. This illustrates that MEG may have the potential to greatly increase solar cell efficiency.

One difficulty working with MEG is how quickly the excess charges that are created disappear. However, Xiong et al. (2018) has indicated the possibility to extract the additional charges well within the multi-exciton's lifetime. The potential of MEG has not been fully utilized within CQD solar cells. This is because the mechanism of MEG is not fully understood. To help achieve the full potential of MEG, McElroy et al. (2014) suggests controlling structure, composition, and size could be beneficial. Furthermore, analyzing occurrence, dynamics, and

size will help with understanding the mechanism of MEG. Optimizing these characteristics could drastically increase the percent conversion of CQD solar cells. Schaller et al.'s (2006) experiment clearly demonstrates the potential to maximize solar cell efficiency using MEG. Schaller et al. (2006) were able to generate seven excitons from a single photon. This corresponds to an energy loss around 10%, where traditionally 90% of the photon energy would be dissipated as heat. This provides a photon-to-exciton conversion efficiency of up to 700%, which exhibits the potential to extremely enhance solar cell technologies.

Conclusions and Future Study

The photovoltaic properties of quantum dots have shown their potential to be improved and produce high quality and efficient solar cells. With the energy challenge presented to this generation, quantum dots will likely find their place in providing the world with renewable energy. The ability for colloidal synthesis to provide monodisperse and smaller QDs at a flexible and lower cost is promising a wide range of applications in many fields of technology. If the issues with solar cell structure can be reduced, CQD solar cells will be able to rely on their fine tuning to expand their percent conversion efficiency. By using lower cost synthesis methods, solar cell cost could be reduced to expand the infrastructure of solar capture worldwide. In addition, further research on shape and MEG could provide uncontested benefits and maximize overall efficiency. CQDs remain a relevant and promising opportunity to grow within the solar cell industry.

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