



Review

Quantum dots processed by SILAR for solar cell applications

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ABSTRACT

Quantum dots (QDs) possess attractive optoelectronic properties and have been intensively researched for various applications. Interest in QDs has been driven by their tunable properties, low-cost processing techniques using low-cost materials, and the compatibility of the material for different purposes. A clear understanding of the different processing techniques used for QDs is required to efficiently explore their unique properties and further improve their performance. QDs can potentially improve the power conversion efficiency (PCE) of quantum dot sensitized solar cells (QDSSCs). However, surface phenomena arising from the use of non-uniform or poor deposition methods of QDs tend to impede the performance of QDSSCs. This review highlights the most frequently used processing techniques for QD materials. Specific focus is placed on the successive ionic layer adsorption and reaction (SILAR) method as the preferred processing method for QDs. The attractiveness of the SILAR method and the current performance of QDSSCs are discussed. The three main factors contributing to the performance of QDs processed by SILAR, namely the number of cycles used, the concentration of the precursor solution, and the dipping time reaction, are discussed. Optimization of QD films through precise deposition based on SILAR improves the surface quality and performance of QD-based devices.

1. Introduction

The incorporation of semiconductor quantum dots (QDs) in solar cells has transformed the processing techniques of materials and the tunability of light absorption over a wide range of spectral wavelength. The uniqueness of QDs for solar cell applications extends to their ability to be processed at relatively low temperature, sensitivity to diffused light, and compatibility for the design of flexible solar cells (Kamat, 2013). QDs are materials ranging between 2 and 10 nm in size and have perfect photo-stability as well as large extinction coefficients (Kouhnavard et al., 2014). Interestingly, QDs have received much attention in the development of solar cell technologies because of the quantum confinement effect that they exhibit as their exciton Bohr radius decreases. An exciton Bohr radius is the distance between an electron–hole pair, which is different for each QD material. A QD with a smaller size than its exciton Bohr radius is said to have strong confinement, whereas a QD with a larger size than its exciton Bohr radius is said to have a weak quantum confinement effect.

QDs absorb and emit precise color at a specific spectral wavelength corresponding to their particle sizes. Generally, the largest nano-sized QDs emit red light, while the smaller QDs emits blue light, with all the other colors appearing in between. This color-changing phenomenon indicates that QDs of a certain particle size possess specific

optoelectronic properties and differ in terms of their bandgap energies. The bandgap is the energy required for the electrons to travel and enter the excited state. Theoretically, small-sized dots have a larger bandgap than their bulk counterpart and require energy equal to or higher than their bandgap energy to enter an excited state. The tunability of QDs' particle size, energy level, and emission wavelength makes them extremely useful for optoelectronic applications such as photovoltaic cells (Kamat, 2013; Chang et al., 2012; Hod and Zaban, 2014), medical imaging (Wu et al., 2014), sensors (Li et al., 2015e; Mozafari and Moztarzadeh, 2011) and energy efficient lighting and displays (Sanchez et al., 2014; Song et al., 2012).

Among the widely used processing techniques for QDs, successive ionic layer adsorption and reaction (SILAR) is the preferred technique. An extensive survey of QD materials prepared during the past years has shown the versatility of the SILAR method. This review focuses on the processing of QDs based on the SILAR method. The microstructure and optoelectronic properties of QDs are discussed relative to their size-specific properties corresponding to their bandgap energy and spectral absorption. This review further highlights the recent performance of quantum dot sensitized solar cells (QDSSCs) based on SILAR and other deposition techniques and states their advantages and disadvantages.

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2. Characteristics and properties of QDSSCs

2.1. Quantum dots in sensitized solar cells

QD semiconductor materials absorb energetic photons of different wavelengths incident on their surface according to their specific particle sizes. This property makes them different from bulk semiconductors, which cannot generate photoelectrons at different spectral wavelengths due to their inability to absorb light at lower wavelength. Photon energy in bulk semiconductors produces an electron–hole pair and the excess energy is converted into heat (Kouhnavard et al., 2014). One possible way to overcome the loss of excessive and useful energy in the form of heat is by using QDs of different particle sizes to absorb different electromagnetic wavelengths. QDs have a size-dependent band gap and are tunable to a desired energy by controlling the particle size (Yue et al., 2014; Jara et al., 2014). Other unique optoelectronic property of QDs is the multiple exciton generation (MEG) effects which provide the opportunity to harvest energetic photons (Kouhnavard et al., 2014; Hod and Zaban, 2014; Beard et al., 2013; Semonin et al., 2011).

MEG is the main approach used to reduce heat loss in which the energy conversion controls the number of excitons produced by a single photon (Kouhnavard et al., 2014). Theoretically, the MEG phenomenon can only occur in the presence of a photon whose energy is at least double the bandgap of the QDs. The occurrence of MEG in QDs allows the generation of two or more electron–hole pairs upon the absorption of a single photon. In order words, QD materials can potentially generate two or multiple excitons upon the absorption of one photon, providing an opportunity to enhance the power conversion efficiency (PCE) of photovoltaic devices.

As mentioned earlier, tuning the particle size of QDs changes the bandgaps (Yuan et al., 2016; Zhang et al., 2016a; Zhang et al., 2014). QDs of various sizes are comparable with devices that incorporate different semiconductors because the specific particle sizes have different bandgap energies and absorb different spectral wavelengths. This indicates that QDs possess varying properties that enable them to absorb energy effectively at different solar spectrum, hence making the solar cell more efficient.

There are three important components in the basic structure of a QDSSC, namely a photoelectrode sensitized with QDs, an electrolyte with a redox couple, and a counter electrode, as shown in Fig. 1 (Jun et al., 2013). The photoelectrode consists of a mesoporous wide-bandgap semiconductor layer that is attached to the transparent conducting glass. Most studies used titanium dioxide (TiO_2) as the photoelectrode in preference to other transparent oxides such as zinc oxide (ZnO) and niobium pentoxide (Nb_2O_5) (Vogel et al., 1994). This could be because TiO_2 is abundant in nature and delivers the highest photo-

conversion efficiency compared to other alternative oxides. The mesoporous TiO_2 film particles are coated with a QD sensitizer layer to absorb and convert photons into excited electrons. Between the photoelectrode and the counter electrode, mesoscopic pores are filled with a conducting medium such as an electrolyte. Under illumination by sunlight, charge injection from the excited QDs into the TiO_2 nanoparticles is followed by the collection of charges at the electrode surface. The electrolyte scavenges the holes and ensures the regeneration of the QDs (Yi, 2013). The front and back parts are encapsulated to protect the device and prevent leakage of the electrolyte.

2.2. Advantages and disadvantages of different QDs deposition methods

QD particles are solution-processed, which usually involves the chemical reaction of a non-coordinating high boiling point solvent, which reduces the melting point of the semiconductor materials (Kale et al., 2006). The choice of the technique used for the fabrication of the QDSSC is very important and has a significant effect on the PCE of the device. The common processing methods used by most researchers for QDs are the hydrothermal or solvothermal, SILAR, chemical bath deposition (CBD), hot injection, and molecule linker attachment (MLA) methods. However, as stated in Table 1, the SILAR method has advantages over other methods, which could certainly help in improving the performance of QDSSCs.

2.3. Performance and efficiency of QDSSCs

Theoretically, QDSSCs can boost the power conversion efficiency up to 66% or above 80% with the occurrence of the MEG phenomenon (Halim, 2012). To date, the highest PCE of 11.16% was achieved by using a $\text{CdSe}_{0.65}\text{Te}_{0.35}$ QD-sensitized photoanode with the presence of Ti-mesh-supported mesoporous carbon as the counter electrode (Du et al., 2016). In the studies, a carbon-based counter electrode with a carbon film having an optimum thickness of $\sim 294 \mu\text{m}$ was attained by screen-printing the paste on Ti mesh in a certain number of screen printing cycles. During the device fabrication, CdSeTe QDs were prepared by using a non-injection high-temperature pyrolysis route, which has the advantages of synthetic reproducibility and large-scale capability. The QDs were then deposited onto the TiO_2 substrate via a capping ligand-induced self-assembly approach and used as a sensitizer in the solar device. This high-quality QDSSC has opened up a new strategy for better device performance with high catalytic capacity as well as providing an efficient three-dimensional electrical tunnel with better conductivity. However, the best performance reported for QDSSCs is still far behind their theoretical efficiency. Further researches with different aspects are still required to improve the conversion efficiencies of QDSSCs.

Comparing the quality of QD deposition with the device conversion efficiency, it is noticeable that the performance of QDSSCs is strongly dependent on the sensitizer used and the QD synthesis method. As mentioned previously, the technique used for the fabrication of QDSSCs is very important. Different methods lead to different quality levels of QD deposition, which is one factor that contributes to the improvement of solar performance. According to More et al. (2013), the quality of QD deposition can be determined by the size of the crystallites, morphology, and chemical environment. Tables 2 and 3 shows the recent performance of solar devices with various QD synthesis methods for both toxic and non-toxic QD materials, respectively.

To the best of the author's knowledge, the highest efficiency achieved by the SILAR method for QDSSC application was 6.4% (Huang et al., 2016b). Based on the studies, the optimum performance was achieved with five SILAR cycles of toxic Cd-based QDs. Using three SILAR cycles; ZnSe was then deposited on the QD layer as the passivation layer, which reduced the lattice mismatch between the QDs and passivation layer, thus improving the stability of the solar device. As reported by Zhang et al. (2015a), Cd-based QDs can also be synthesized

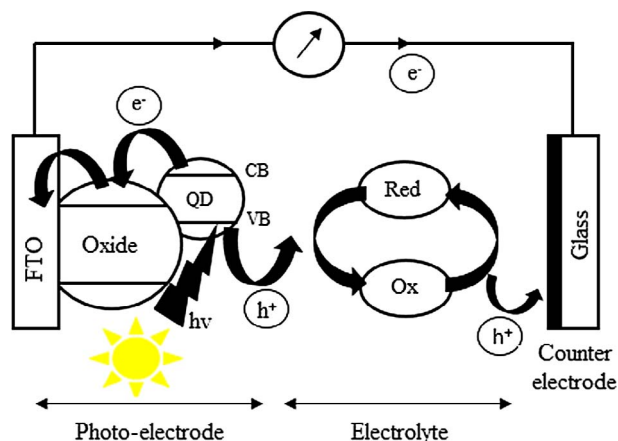


Fig. 1. Operating principle of a typical QDSSC.

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