

Research Article

Enhanced Device Performance of Bulk Heterojunction (BHJ) Hybrid Solar Cells Based on Colloidal CdSe Quantum Dots (QDs) via Optimized Hexanoic Acid-Assisted Washing Treatment

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As-synthesized colloidal quantum dots (QDs) are usually covered by an organic capping ligand. These ligands provide colloidal stability by preventing QDs agglomeration. However, their inherent electrical insulation properties deliver a problem for hybrid solar cell application, disrupting charge transfer, and electron transport in conjugated polymer/QDs photoactive blends. Therefore, a surface modification of QDs is crucial before QDs are integrated into solar cell fabrication. In this work, enhancement of power conversion efficiency (PCE) in bulk heterojunction (BHJ) hybrid solar cells based on hexadecylamine- (HDA-) capped CdSe quantum dots (QDs) has been achieved via a postsynthetic hexanoic acid washing treatment. The investigation of the surface modification was performed to find the optimum of washing time and their effect on solar cell devices performance. Variation of washing time between 16 and 30 min has been conducted, and an optimum washing time was found at 22 min, resulting in a high PCE of 2.81%. The efficiency enhancement indicates improved electron transport, contributing in an increased short-circuit current density of solar cell devices.

1. Introduction

Bulk heterojunction (BHJ) solar cells based on organic-inorganic hybrid materials have been developed significantly due to the possibilities for low-cost fabrication of high-efficiency solar cells in flexible large-area devices [1]. In principle, they are analogous to organic solar cells (OSCs); the dissimilarity is that they utilized inorganic semiconductors such as quantum dots (QDs) as electron acceptors, while OSCs is still dominated by fullerene derivatives [2]. Various types of QDs, namely, TiO₂, ZnO, CdS, CdSe, and PbS, have been utilized so far as electron acceptors [3]. In 1996, the first polymer QDs hybrid solar cells that use CdSe QDs as the acceptor was reported, achieving a PCE of about 0.1% [4]. It was observed that a resulted PCE of their device was attributed to low charge transport and electron transfer of CdSe QDs in the photoactive layer. Afterward, many

works have been focused on addressing this problem, which includes controlling the blends nanomorphology and tuning dots into various shapes such as rods and tetrapods [5]. These works have contributed to the significant enhancement in the solar cell devices performance, with a recent PCE reaching 4% [6].

One of the crucial keys of the QDs-based solar cell to be addressed carefully is the surface of QDs itself. The stability of colloidal CdSe QDs is helped by the existence of surface ligands such as stearic acid, trioctylphosphine (TOP), and hexadecylamine (HDA) [7]. The long aliphatic tails of ligands provide steric stabilization and hydrophobic surface, hence hindering nanoparticle agglomeration [8, 9]. However, at the same time, they also perform as an electrically insulating layer, which has undesirable properties for the photoactive layer in hybrid solar cells application. The ligand layer affects the percolation network by inhibiting charge

transfer from conjugated polymer to QDs and also electron transfer within neighboring QDs [10]. Therefore, these as-synthesized colloidal QDs should be modified before they are utilized in highly efficient hybrid solar cells fabrication.

One simple method that can be used effectively to reduce the ligand layer is hexanoic acid-assisted washing treatment [11]. In this washing treatment, the reaction between a hexanoic acid (HA) and ligand produces salt that then is separated from QDs. Moreover, another benefit of this treatment is its capability to maintain dispersibility of QDs, hence allowing a well distribution of the CdSe QDs in the photoactive blends. The optimum loading and distribution of the CdSe QDs are crucial in percolation network formation of the photoactive composite film [12, 13]. However, an optimized HA washing treatment duration should be found before QDs will be utilized in the photoactive layer of solar cells. Therefore, this work is focused on investigating the HA washing treatment duration and their effect on the device performance of BHJ hybrid solar cells.

2. Experimental Method

Firstly, the colloidal CdSe QDs were synthesized by the hot injection method; the detail procedure is described elsewhere [14]. The as-synthesized colloidal CdSe QDs were washed with HA [15]. In brief, 5 ml HA is mixed with 1.6 mg CdSe QDs and then stirred for 16 min at 110°C to bind the ligands [11]. Afterward, 10 ml methanol was injected into the solution and stirred for another 10 min. The following step was carried out by adding methanol and chloroform with a ratio of 3:1 and stirred for 10 min to precipitate the QDs and remove the residual hexanoic acid. The dispersion is centrifuged for 1 min at 14.5 krpm to separate CdSe QDs from the solvent. Finally, the washed CdSe QDs product was dispersed in chlorobenzene (CB) forming a solution with a concentration of 20 mg/mL. Afterward, CdSe QDs solution is blended with 20 mg/mL of PCPDTBT. These steps are also applied for 22 min and 30 min of HA washing time.

The devices were fabricated on the top of a structured ITO substrate with a sheet sensitivity of about $\leq 10 \Omega\text{sq}$. The first layer is a hole transport layer, and PEDOT:PSS was spin coated at 3000 rpm for 30 s. Afterward, the photoactive blend solution was spin coated at 1100 rpm for 30 s and followed by a 1 min drying at 3000 rpm, resulting in a thick film of about 80 nm. The last deposition step is thermal evaporation of 80 nm aluminum cathode layer. Devices performance are individually measured using the sun simulator illumination (LS0400 LOT-Oriel) with an AM 1.5 G filter, inside a nitrogen-filled glovebox at temperature 25°C.

3. Results and Discussion

The structure of fabricated solar cells devices is depicted in Figure 1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level of PCPDTBT were adapted from the literature and about -5.3 eV and -3.6 eV , respectively [17]. From the TEM image, average size of CdSe QDs is found at about 6 nm.

Based on this size, the valence and conduction band of CdSe QDs are about -6.3 eV and -4.0 eV , respectively [18].

All of the fabricated devices utilized the same batch of CdSe QDs. The J-V curves of best devices performance based on the variation of HA washing treatment duration are displayed in Figure 2. In Figure 3, it can be seen clearly that HA washing duration influenced devices performance of PCPDTBT/CdSe QD hybrid solar cell. Table 1 summarizes the performance changes based on the variation of HA washing duration.

According to the results value of devices performance summarized in Table 1, the duration of HA washing treatment affects the performance of solar cells devices significantly. The washing duration of 16 min contributed to short-circuit currents (J_{SC}) of about $5.11 \pm 0.20 \text{ mA/cm}^2$. The higher J_{SC} of about $8.05 \pm 0.30 \text{ mA/cm}^2$ is donated by the duration of 22 min. However, a longer washing duration of 30 min resulted in J_{SC} and dropped significantly to $6.73 \pm 0.20 \text{ mA/cm}^2$. It can be concluded that when the optimum duration of HA washing treatment is not reached or already exceeded, a lower J_{SC} is shown as displayed by the duration of 16 min and 30 min.

The phenomenon of improved performance can be reasonably explained as a result of the reducing ligand. As schematically illustrated in Figure 4, the organic ligands consist of two insulating layers: inner layers that are firmly attached to the CdSe QDs surface and the outer layers that are weakly bound [9]. The inner layers provide stability for the CdSe QDs and are formed during their synthesis at elevated temperatures. In contrast, the outer layer is formed during the crystallization of CdSe QDs. This outer layer of ligands is detached from CdSe QDs via protonation of HA and formed a free-ligand salt, which is later removed by methanol solvation. The longer the duration of HA washing, the more the removed ligands. To our knowledge, it is difficult to observe clearly the washing effect on inner layer morphology of CdSe QDs with HRTEM. A recent work has reported that a high dose of beam is strongly required for this purpose; on the contrary, it can damage the material [19]. The morphology of CdSe QDs and their PL intensity is generally utilized to confirm the reducing ligands effect, which we have discussed elsewhere [20]. In this work, the effect of the reduced ligand can be dominantly observed from its J_{SC} and resistant values [21, 22].

The removed ligand leads to the higher conductivity of QDs, which contributed to the increased J_{SC} overall. However, if the washing treatment duration is exceptionally long, it will attack the inner layer parts and cause the surface defects of QDs which form a trap for the electron [23–25]. Once the electrons fall into the traps, the electron will recombine with holes and hence more energy losses [26]. Furthermore, too long washing time resulted in strong reduced ligand which also affects the stability and solubility of CdSe QDs itself. It leads to the agglomeration of QDs in the PCPDTBT polymer matrix [27]. The agglomeration affects the stability of the internal structure of the photoactive layer by disrupting the QDs distribution, and consequently, an ineffective charge extraction, as well as low charge mobility, resulted in decrease in J_{SC} [28].

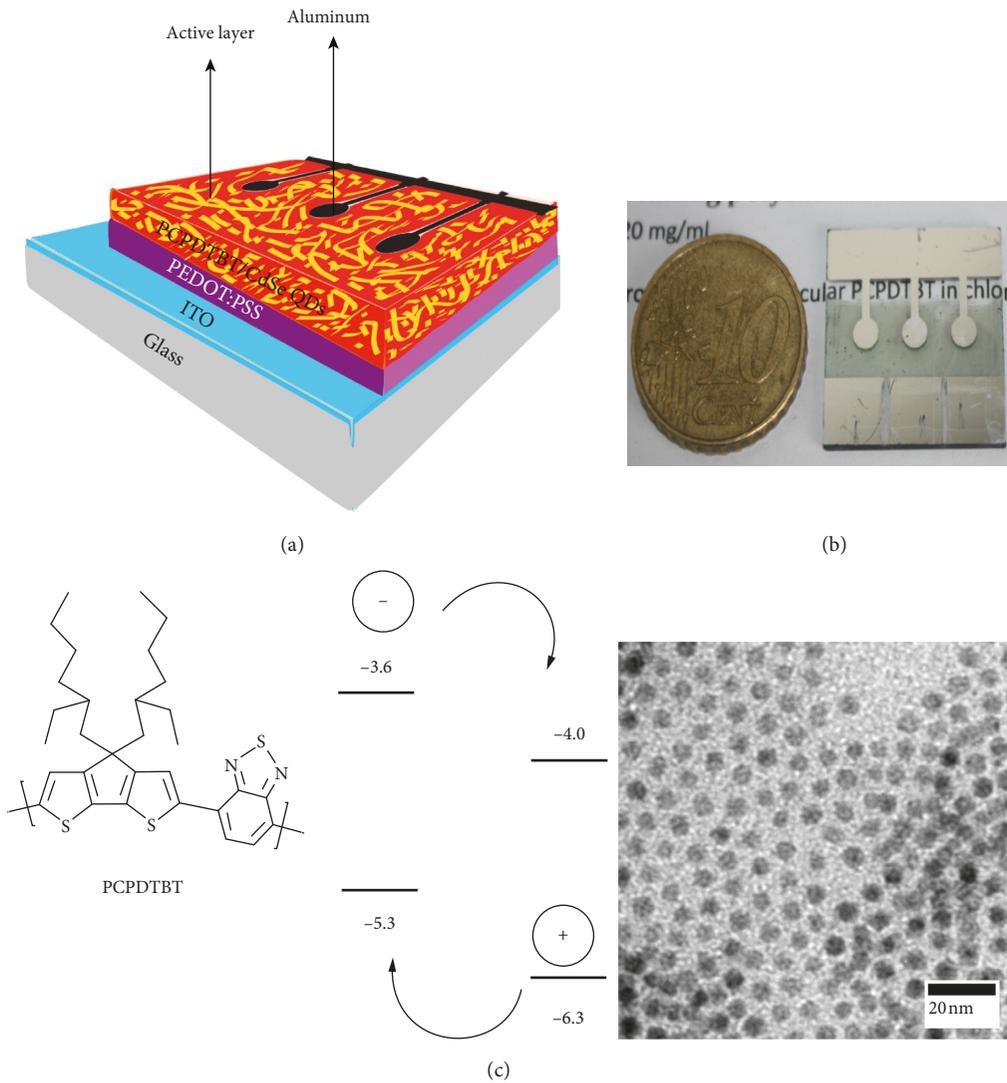


FIGURE 1: (a) Design structure, (b) photograph of fabricated solar cell devices, (c) chemical structure of PCPDTBT, and a TEM image of CdSe QDs as well as their energy level diagram in the photoactive layer. The image was adapted from [16].

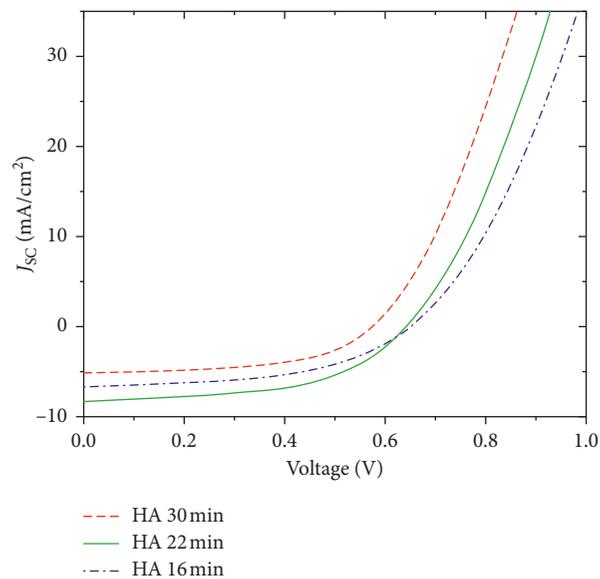


FIGURE 2: J-V curves of solar cell devices based on HA washing treatment duration.

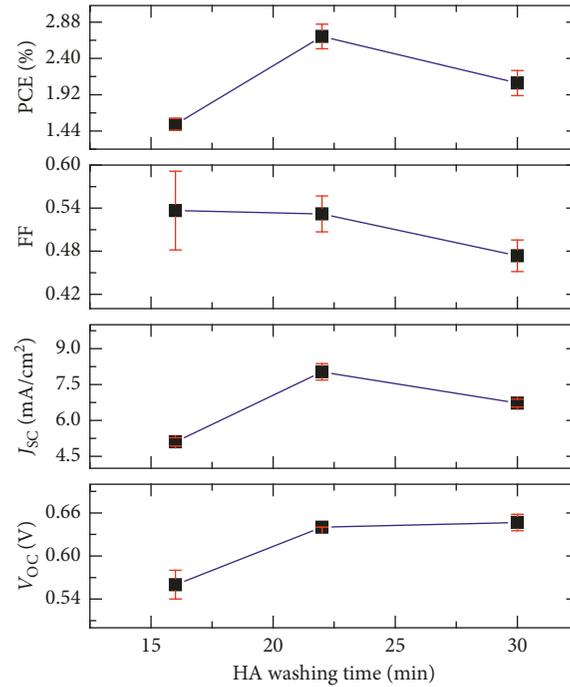


FIGURE 3: Effect of HA washing duration on the device performance parameters.

TABLE 1: Summary of the device performance based on HA washing treatment duration.

Duration (min)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ωcm^2)	R_{sh} (Ωcm^2)
16	0.57 ± 0.01	5.11 ± 0.20	0.55 ± 0.10	1.54 ± 0.10	509	13.3
22	0.63 ± 0.00	8.05 ± 0.30	0.54 ± 0.02	2.71 ± 0.20	551	9.6
30	0.64 ± 0.01	6.73 ± 0.20	0.48 ± 0.03	2.08 ± 0.20	527	12.2

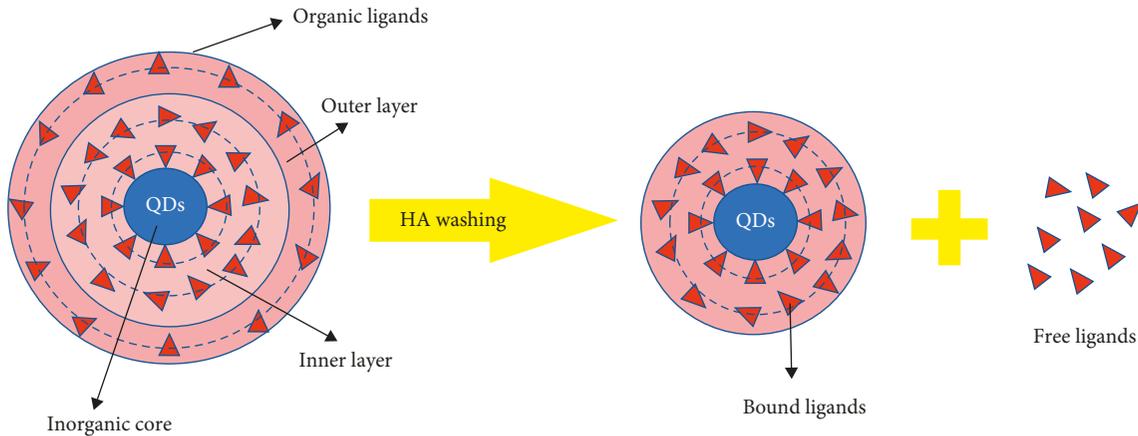


FIGURE 4: Schematic illustration of the ligands bound to the CdSe QDs and free ligands after HA washing.

The values of series resistant (R_s) and shunt/parallel resistant (R_{sh}) can also be used to analyze the device performance. R_{sh} is an important parameter which is determined by the quality of the photoactive layer and interfaces, while R_s is attributed to the low conductivity of the semiconducting materials [29]. Low values of R_{sh} are a result of the loss of carriers via leakage paths; these may include pinholes in the photoactive film and the recombination and trapping of the carriers during their transit

through the cell [30]. Therefore, the ideal solar cell devices should have zero R_s and infinity R_{sh} . It was reported that increasing R_s is usually accompanied by a decreasing R_{sh} , and vice versa [15, 31–33]. In addition, many reports have concluded that R_s plays dominant roles in determining the efficiency of solar cells [34]. As can be observed in Figure 5, the washing duration significantly affects R_s values of the devices. The short duration of 16 min displayed the highest R_s and lowest R_{sh} of about $13.3 \Omega\text{cm}^2$ and $509 \Omega\text{cm}^2$,

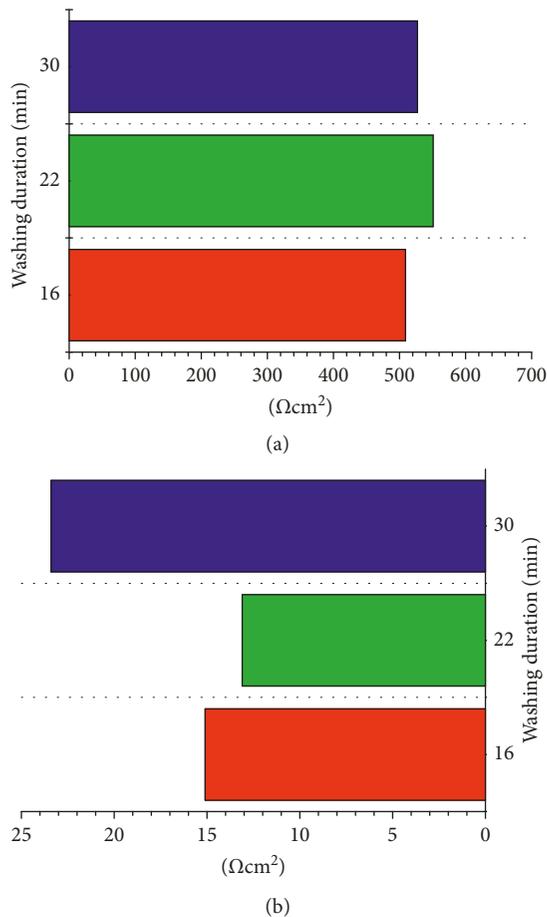


FIGURE 5: Summary of absolute values of shunt resistance (R_{sh}) (a) and specific series resistance (R_s) (b).

respectively, which can be attributed to the high amount of its ligands. Washing duration of 22 min showed the lowest R_s and highest R_{sh} of about 9.6 Ωcm^2 and 551 Ωcm^2 , respectively, resulting in a highest J_{SC} . Compared to these resistivity values of 22 min duration, washing duration of 30 min contributed to a slightly higher R_s and lower R_{sh} of about 12.2 Ωcm^2 and 527 Ωcm^2 , respectively, leading to lower efficiency. Therefore, an investigation to find an optimum washing treatment duration of CdSe QDs is imperative for highly efficient BHJ hybrid solar cells application.

4. Conclusion

The crucial factor dictating the performance of BHJ hybrid solar cell devices which is caused by the electrically insulating layer of organic ligands in as-synthesized colloidal CdSe QDs is overcome by an optimized of hexanoic acid washing treatment. The washing procedure was conducted before CdSe QDs integration in the photoactive blend. The investigation has been performed to find the optimum HA washing treatment duration. Best device performance has been achieved by the washing duration of about 22 min and resulted in an effective way to enhance device performances.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest, regarding the publication of this manuscript.

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