Further Improvement in Efficiency of ZnO Nanorod Based Solar Cells Using ZnS Quantum Dots as Light Harvester and Blocking Layer Material

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Abstract

Zinc oxide nanorod arrays (ZnO NRs) were grown on the ZnO seed layers via an aqueous solution using hydrothermal method and their photovoltaic properties were investigated. It was found that the growth period of 20 minutes is the optimum condition for ZnO nanorods growth, the cell containing these nanorods was considered as a reference cell. In order to further increase the cell performance, ZnS quantum dots (QDs) were fabricated on the ZnO NRs (reference cell) by SILAR technique with different number of cycles. The effect of the number of SILAR cycle (n) on structural and photovoltaic properties was studied. The optimum number of SILAR cycles for ZnS QDs was obtained (n=4). Experimental results showed that using ZnS QDs as light absorber material is an effective way to improve device performance. Morphology, crystalline structure and optical absorption of layers were analyzed by a scanning electron microscope (SEM), X-ray diffraction (XRD) and UV-Visible absorption spectra, respectively. The maximum power conversion efficiency of 3.59% in the inverted configuration of ITO/ZnO film/ZnO NR(20)/ZnS(n) QDs/P3HT:PCBM/Ag hybrid solar cell was achieved for a device based on ZnS(4) under an illumination of one Sun (AM 1.5G, 100 mW/cm²).

Keywords: ZnO nanorods, ZnS quantum dots, hydrothermal method, growth period, Spin-assisted SILAR technique, Solar cell

1. INTRODUCTION

Photovoltaic (PV) devices attract great attention owing to the growing demands for clean and renewable energy. Low-cost fabrication methods are of the major interest to reduce production costs of PV devices. Recently, using nanostructures (such as nanowires and nanorods) has extensively been studied for solar cells applications [1-7].

Different wide band gap metal oxides, such as TiO₂, ZnO, SnO₂, and Nb₂O₅ have been frequently tested for photovoltaic properties [8-10]. Among these materials, ZnO has attracted much attention in fabrication of solar cells due to its excellent properties such as low cost, direct band gap (3.37 eV), high exciton energy (60 m eV), high electron mobility (200 cm² V⁻¹ s⁻¹), non toxicity and good air stability [11-13]. Environmentally friendly and low-cost ZnO nanorod array is particularly well suited for solar cell application as they can be easily grown on different substrates by different physical and chemical techniques, such as metal–organic, chemical vapor deposition, magnetron sputtering, vapor liquid solid, chemical vapor deposition, and hydrothermal method [14-19].

Among these methods, the hydrothermal technique is the best one due to its simplicity, low temperature, low cost, reproducible and able to control the length and diameter of nanorods by varying experiment conditions such as time and concentration of precursors. In addition to an increased charge carrier collection in 1-dimensional structures of ZnO (e.g. nanorods), they possess the potential of enhanced light absorption [20, 21].

It has been reported that ZnO nanorods in solar cells improve light absorption and charge carrier collection [22-26]. Employing semiconductor nanoparticles (or quantum dots) as sensitizers in solar cells has two special advantages. First and foremost, the size quantization effect allows one to tune the band energy and visible response by simply varying the QD size [27, 28]. Another advantage is that QDs open new ways to utilize hot electrons or generate multiple electron–hole pairs with one single proton through the impact ionization effect [29].

Zinc sulfide (ZnS) is an important II-VI semiconductor inorganic compound which exists in two main crystalline forms (cubic and hexagonal). It has a direct band gap of 3.6 eV (bulk) at 300 K [30, 31]. ZnS is a
promising material for optoelectronic device applications such as blue light emitting diodes, modulators, electroluminescent devices and photovoltaic cells. It has been extensively studied and most importantly, it is a nontoxic and is more environmentally friendly material [32-34]. ZnS QDs can be fabricated by using various techniques such as spray pyrolysis, chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR) and so on. SILAR method which is known as modified version of chemical bath deposition (CBD) is a simple, low cost, versatile, less time-consuming and large-scale production technique for the deposition of quantum dots. A variety of substrates such as insulators, semiconductors, metals and temperature sensitive substrates (like polyester) can be used since the deposition is carried out at or near to room temperature [35]. SILAR method can be done during either spin-coating or dip-coating processes. The process based on spin-coating is denoted spin-SILAR to distinguish it from the conventional SILAR method based on dip-coating (dip-SILAR). The spin- SILAR or spin-assisted SILAR method involves the layer-by-layer build up of a quantum dot film via the successive adsorption and reaction of anions and cations by spin-coating. Because the adsorption, reaction, and rinsing steps occur simultaneously during spin coating, spin-SILAR does not require rinsing steps, making the growth process simpler and faster than in the dip-SILAR technique [36]. In present work, ZnO nanorod arrays (ZnO NRs) were synthesized using a hydrothermal method and in order to further increase the cell performance, ZnS QDs as light absorber material were synthesized on these nanorods via spin assisted SILAR technique. The spin-assisted SILAR process eliminates the rinsing of excessive precursors and the additional drying process in conventional SILAR methods. The influence of number of SILAR cycles on the photovoltaic properties of fabricated solar cells with structure of ITO/ZnO film/ZnO NRs/P3HT/PCBM/Ag was investigated.

2. EXPERIMENTAL DETAILS

2.1. Deposition of ZnO seed layer All devices were prepared on ITO-patterned glass substrates. Prior to depositing ZnO seed layer, these substrates were ZnS QDs and fabricated photovoltaic devices containing ZnO NRs covered by ZnS QDs.

3. RESULTS AND DISCUSSION

3.1. Optimizing the growth period of ZnO NRs without ZnS QDs (the reference cell) To optimize the growth period of ZnO nanorods, first of all and in the absence of ZnS QDs, the growth period of NRs were varied, and the photovoltaic properties of devices with structure of ITO/ZnO film/ZnO NRs/P3HT/PCBM/Ag were recorded. The relationship between growth period of ZnO NRs and cell efficiency is shown if Figure 2(a).

Figure 1. Schematic view of a (a) reference cell and (b) solar cells containing ZnS QDs.

Figure 2. (a) The variation of cell efficiency with growth time, (b) SEM image of ZnO nanorods grown for 20 min (NR20).

As it can be seen from Figure 2(a), the maximum power conversion efficiency of 3.33% was obtained for a cell containing ZnO nanorods grown for 20 min which will be considered as the reference cell. The cross sectional image of these nanorods with an average length of 120 nm is shown in Figure 2(b).

3.1.1. Characterization of ZnO seed layer and nanorod arrays The photovoltaic (PV) properties of reference cell with structure of ITO/ZnO film/ZnO NR20/P3HT/PCBM/Ag were investigated. In Figure 3(a), the J–V characteristic of this solar cell is shown. The active area of device was 6 mm². The XRD spectra of the ZnO seed layer and ZnO nanorod arrays are shown in Figure 3(b).

Figure 3. (a) J–V characteristics of reference solar cell based on ZnO NR(20), (b) XRD patterns of ZnO seed layer and ZnO nanorod arrays.

The crystalline nature of ZnO nanorods can be well indexed to known structures of hexagonal (wurtzite)
ZnO, with lattice constants $a=0.32498$ nm, $b=0.32498$ nm and $c=5.2066$ nm [JCPDS cardno.36-1451]. Five significant wurtzite ZnO diffraction peaks, (100), (002), (101), (102) and (103) appear at $2\theta=31.8^\circ$, $34.4^\circ$, $36.2^\circ$, $47.6^\circ$ and $62.7^\circ$, respectively. These results are in agreement with those of other authors [38].

It is evident that the (002) peak intensity of ZnO seed layer is lower than that of NRs. This strongly enhanced (002) diffraction peak in Figure 3(b), at about $34.4^\circ$ indicates preferential growth of ZnO NRs along the c-axis [18, 39]. Moreover, the growth rate of ZnO along c-axis is faster than those of other orientations because the basal plane (001) has the highest surface energy [40, 41].

3.2 Further increasing the cell performance
To promote the cell performance, ZnS quantum dots (QDs) were used as light harvester and blocking layer material in device. Such structure can be called a quantum dot sensitized solar cell (QDSSC).

The application of QDs in solar cells may help to develop solar cells with energy conversion efficiencies above the Shockley–Queisser [42] limit (for solar cells with a single band gap). The high potential of QDs for large solar energy conversion efficiency as well as possible configurations of QD solar cells were discussed by Nozik [43].

The function of a QDSSC is based on the formation of electron-hole pair (exciton) in nanoparticle semiconductor by absorbing the incident light. Figure 4 shows the schematic diagram of exciton generation and charge transfers to different layers and corresponding energy level diagram for (a) reference cell and (b) other cells in our experiment. The situation of electronic energy levels is the most important factor governing efficient electron transfer between two semiconductors (and, consequently, photocurrent generation) [44].

Devices are irradiated from ITO side. In the reference cell, the P3HT absorbs light and electron-hole pairs are generated over this layer (Figure 4(a)). To extract the electric energy, these excitons must be dissociated at interfaces and generated electrons have to be transferred to (ZnO layer) an electron conducting layer in a properly way before they recombine with holes (the arrow shown in Figure 4). While the photo-generated holes must be extracted by (P3HT/PCBM), a hole conducting layer, toward silver contact. The strategy to separate electron and hole pairs into the neighboring layers can be achieved by choosing materials with appropriate energy levels [45].

To prevent the recombination (electrons in ZnO with holes in P3HT/PCBM), a blocking layer of ZnS QD was deposited between ZnO and P3HT/PCBM (Figure 4(b)). As it can be seen from Figure 4(b), in this situation, the energy levels of components [46, 47] create a cascade structure between ITO/ZnO/ZnS/P3HT/PCBM which facilitates charge transfer from ZnS QDs to ITO contact. In this structure, ZnS QD layer absorbs the light and blocks the recombination in the ZnO & P3HT/PCBM interface.

3.3 Absorption spectra
To investigate the quantum confinement effect of ZnS QDs, the optical absorption spectra of ZnS QD with various SILAR cycles (n) over the range of 0.32–0.40 μm are shown in Figure 5. The spectra exhibit a peak in the short-wavelength region (350-370 nm) for each sample. The intensities of the absorption peak increases with the SILAR cycle (n). These absorption peaks can be attributed to the excitonic excitations associated with the band structure of ZnS. The increasing absorption suggests the increased number of QDs deposited on the substrate.

![Figure 4. Energy levels and charge transport mechanism in (a) reference cell and (b) other cells containing ZnS QDs.](image)

![Figure 5. Absorption spectra of ZnS QDs on glass substrates. The labels beside the curves indicate the number SILAR cycles (n).](image)

Band gap energy of the ZnS(n) can be calculated by plotting $(\alpha h\nu)^2$ versus $h\nu$, as shown in Figure 6. It is clear that by increasing (n), the band-gap energy of the ZnS quantum dots slightly decreases from 3.70 eV (for n=2) to 3.38 eV (for n=12). Extrapolations in Figure 6 show a reduction in the band-gap energy (red-shift), which suggest that more number of ZnS nanoparticles are gathered on substrate,
their aspect ratio increases, and this leads to a red shift of the absorption peak [48].

Figure 6. Optical band-gap energy ($E_g$) of the ZnS QDs with various SILAR cycles (n).

3. 4. Characterization of ZnS QDs

Diffraction patterns of ZnS QDs are shown in Figure 7. All the diffraction peaks from (111), (200), (220) and (311) respectively at 20 = 28.9°, 33.5°, 48.1° and 57.1° are associated with reflections of the cubic zinc blende phase ( sphalerite) of ZnS and are in agreement with other reports [49, 50]. These peaks were identified by using JCPDS (reference code: 01-080-0020) data for ZnS. The central broad hump is due to the amorphous glass substrate. The lattice parameters of the cubic structure are equal to $a = b = c = 5.345 \text{ Å}$. The presence of broad peaks in XRD implies presence of smaller particles [52].

Figure 7. XRD patterns of ZnS quantum dots deposited on bare glass substrate.

3. 5. Surface morphology

The surface morphology of ZnO NRs grown for 20 min (NR20) on the ZnO layer without ZnS QDs (reference cell) and ZnO NR20 covered with ZnS QDs with different cycles (n) are shown in Figure 8.

It is clear from Figure 8. that in reference cell (Figure 8. (a)), there are void spaces between ZnO nanorods and the tip of nanorods are separated. But deposition of ZnS QD layer on top of nanorods gradually fills these void spaces. On the other hand, repeating the number of cycles in spin assisted SILAR technique leads to change in size, density and morphology of deposited ZnS QDs. So that for n=2 (Figure 8(b), thickness ~ 16 nm), ZnS particles are deposited separately in the space of between nanorods, and no aggregation is observed. For n=4 (Figure 8(c)), the average thickness of ZnS QDs is 24 nm and ZnS QDs can still penetrate in the space between NRs. But for n>4, the whole area of nanorods are covered by ZnS QDs (Figure 8(e, f)). QDs are stacked on each other and make a nearly smooth and compact layer. These images suggest that ZnS QD (n=4) provides optimal surface morphology and device performance.

Figure 8. Plan-view FE-SEM images of ZnO NRs grown for 20 min (a) without ZnS QD (reference cell), covered by ZnS QDs with (b) 2, (c) 4, (d) 6, (e) 8 and (f) 10 SILAR cycles. Scale bar: 500 nm.

3. 6. Photovoltaic properties of samples

The photovoltaic (PV) properties of samples were investigated. In Figure 9, the J–V characteristics of solar cells based on ZnO nanorods grown for 20 min and cover by ZnS QDs for different number of SILAR cycles are compared. All the devices are fabricated with the same active area of 6 mm².

Figure 9. J–V characteristics of solar cells based on ZnO nanorods grown for 20 min and covered with ZnS QDs. Solar cells illuminated at 100 mW/cm²; the active area is 6 mm².
NR20 covered with ZnS(4). For this device, the short circuit current (Jsc), open circuit voltage (Voc), fill factor (FF) and efficiency were all improved. The detailed values of these parameters are given in Table 1.

**TABLE 1.** Photovoltaic performance of solar cells based on ZnO nanorods grown for 20 min and covered with ZnS QDs (100 mW/cm² and AM 1.5 simulated solar light).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference cell</td>
<td>0.58</td>
<td>10.05</td>
<td>54.35</td>
<td>3.33</td>
</tr>
<tr>
<td>ZnS(2)</td>
<td>0.60</td>
<td>10.62</td>
<td>53.60</td>
<td>3.40</td>
</tr>
<tr>
<td>ZnS(4)</td>
<td>0.59</td>
<td>10.64</td>
<td>57.57</td>
<td>3.59</td>
</tr>
<tr>
<td>ZnS(6)</td>
<td>0.59</td>
<td>10.43</td>
<td>58.33</td>
<td>3.56</td>
</tr>
<tr>
<td>ZnS(8)</td>
<td>0.58</td>
<td>10.42</td>
<td>56.70</td>
<td>3.44</td>
</tr>
<tr>
<td>ZnS(10)</td>
<td>0.57</td>
<td>10.01</td>
<td>49.80</td>
<td>2.91</td>
</tr>
<tr>
<td>ZnS(12)</td>
<td>0.27</td>
<td>8.26</td>
<td>49.54</td>
<td>1.12</td>
</tr>
</tbody>
</table>

In this study, the reference cell with ITO/ZnO film/ZnO NR20/P3HT/PCBM/Ag structure as shown in Figure 1(a). has an open-circuit voltage, a short-circuit current density and power conversion efficiency of 0.58 V, 10.05 mA/cm² and 3.33%, respectively. To improve the cell performance, ZnS QDs with different number of SILAR cycles (n) were deposited on the nanorod arrays. At the beginning of the deposition of ZnS QDs, SILAR process is supposed to increase the coverage ratio of ZnS on the surface of ZnO nanorods by replenishing the uncovered area and the thickness of ZnS QD layer increases with the increase the number of SILAR cycles (ZnS(n)). Such increment of ZnS loading leads to more excited electrons under the illumination of light, which is advantageous to the photocurrent. Compared to the reference cell, photovoltaic parameters increase when nanorods are covered by ZnS (2). This improvement can be described as below. The light absorption is enhanced by using ZnS QD layer. In such device, both P3HT and ZnS layers absorb the incident light. As a result, Jsc, Voc and efficiency are improved. On the other hand, ZnS QDs act as a blocking layer which decreases electron-hole recombination in the ZnO & P3HT/PCBM interface, as shown in Figure 4(b).

As it was mentioned, an optimized thickness of ZnS QD layer was obtained for n=4, which results in a highest Jsc, FF and efficiency by providing a good interfacial structure between ZnO and P3HT/PCBM layers and reducing the recombination of the injected electrons from ZnO to P3HT/PCBM due to a well-covered ZnS on the ZnO nanorods. Maximum efficiency (3.59%) was obtained for 4 SILAR cycles (ZnS (4)). The higher efficiency of this device is attributed to its broader light absorption range which leads to a higher Jsc (10.64 mA/cm²) compared with that of other ones.

However, as the thickness of ZnS QD layer further increases, it becomes darker, so the incident light cannot reach to P3HT layer, meanwhile, it will be more difficult to transport an electron from the ZnS QD layer into the ZnO film, leading to unfavorable electron transportation at ZnO/ZnS/P3HT/PCBM interface. A slight reduction in Jsc was observed in solar cells with further increasing number of SILAR cycles (n>4) due to the aggregation of the quantum dots on top of nanorods as explained earlier. Meanwhile, the FF of device containing ZnS (4) is smaller than that of ZnS (6), probably due to the low driving force for the electron injection.

### 4. CONCLUDING REMARKS

In present study, ZnS QDs were prepared using SILAR technique with different SILAR cycles (n) on ZnO nanorod arrays. The photovoltaic properties of these cells with ITO/ZnO film/ZnO NR/ZnS(n)/P3HT/PCBM/Ag structure were compared to that of the reference cell with ITO/ZnO film/ZnO NR/P3HT/PCBM/Ag structure. Without using ZnS QDs, the maximum efficiency of 3.33% was obtained for the reference cell. While for devices containing ZnS QDs, the highest power conversion efficiency of 3.59% was achieved for ZnS (4). This improvement of photovoltaic properties has 2 main reasons. First, the light absorption is enhanced by using ZnS QD layer, and second, superior ability of ZnS QD layer in inhibiting the charge recombination at the ZnO and P3HT/PCBM interface. The results further indicated that using ZnS QD layer beside ZnO nanorod arrays has a significant effect on solar efficiency.

### REFERENCES


