1. Introduction

Recently, there has been significant interest in finding carbon-free energy resources because fossil fuels are limited and the world energy demand is continuously increasing. Solar energy is one of the best choices to replace with fossil fuel. The sun provides about 120,000 terawatts to the earth’s surface which is equivalent to six thousand times the present rate of the world’s energy consumption [1].

Quantum dot sensitized solar cells (QDSSC) have been greatly under focus because of their potentially high efficiency [2–4]. In these cells, a semiconductor with a direct and relatively large band gap (ZnO (3.3 eV) or TiO₂ (3.4 eV)) is used as the charge transport channel. A nanostructure of these two materials e.g. a nanowires (NW) could be easily synthesized by many different methods [5–7]. In this study, ZnO NWs were preferred as an alternative TiO₂ NWs due to their relatively easy synthesis. A thin layer of ZnS usually plays the role of a shell for QDs to prevent recombination of electrons in the QDs and also the cell performance [13,14]. Photocurrent generation is directly related to the size of the QDs. By varying the size of the QDs (from smaller to larger dots), excitonic peak of the curve shifts from blue to red. On the other hand, in smaller dots, the electron relaxation time is also smaller, so smaller dots have led to much more IPCE (%). As a result of changing the size of these nanoparticles, different wavelengths of light can be absorbed and the theoretical cell efficiency will thus increase up to 44% [15]. CdS [16–19], CdSe [20–24], Si [25,26], PbS [27–29], CdTe [16] and InAs [30–32] are the most common QDs that are used in solar cells due to their relatively easy synthesis. A thin layer of ZnS usually plays the role of a shell for QDs to prevent recombination of electrons in the cell [33,34]. Peng et al. reported an efficiency of 4.15% for a CdS QDSSC using TiO₂ Nanotube-Array Photoelectrode [35].

There are two main methods to link QDs electrically to ZnO NWs:

a) Chemical covalent bonding of the QDs with or without bifunctional linkers [30,36,37].

b) QD growth directly from the precursor solution, i.e. direct growth of the semiconductor QDs on the electrode surface by successive ionic layer adsorption and reaction (SILAR). This
process leads to a dense distribution of the grown dots. Application of these QDs must theoretically lead to relatively efficient solar cells [38–40]. In this study, the effects of the counter electrode choice, size of the CdS QDs, thickness of ZnS blocking layer and the concentration of components of polysulfide electrolyte on the cell efficiency were investigated.

2. Methodologies

2.1. Growth of ZnO NWs

Chemical bath deposition (CBD) method was used to grow ZnO NWs with relatively high aspect ratio. Fluorine-doped Tin Oxide (FTO) glasses were used as the substrate for the solar cell fabrication. Substrates were first chemically cleaned by placing them into an ultrasonic bath of acetone for 6 min. This step was followed by an ultrasonic bath with ethanol for another 6 min. RF sputtering with AZO (2% aluminium-doped zinc oxide) target was then utilized to deposit 200 nm of AZO as the seed layer on the FTO glass substrate. The ZnO NWs were grown by hydrothermal method [7,10,41]. The substrates containing the seed layer were placed in a solution of 25 mM zinc nitrate hexahydrate ((Zn(NO3)2·6H2O, Merck) and 25 mM hexamethylenetetramine ((CH2)6N4, Merck) for 7 h at 90°C. In such a condition, NWs with 2.4 μm length and the diameter of 120 nm were grown. Shape and size of the NWs were studied using a field emission scanning electron microscope (FESEM, HITACHI S-4160) and transmission electron microscopy (TEM, JEM-2010-JEOL, Japan). X-ray diffraction (XRD) by Philips Xpert, with Cu-Kα radiation (λ = 0.15418 nm) was performed to explore the crystallinity of ZnO NWs.

2.2. Deposition of multilayered QDs on ZnO NWs using SILAR method

SILAR method was employed to assemble QDs on the ZnO NWs’ surface. In this process, the dots grew and consequently, epitaxial bonds were formed on the surface of the active part. For CdS SILAR, ZnO NWs were immersed in two different solutions sequentially; first in cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O, Merck) 0.5 M in ethanol for 5 min. After the immersion, the sample was rinsed with ethanol for 5 min to remove excess precursors and then dried. Second, sample was immersed in sodium sulfide (Na2S, Sigma-Aldrich) 0.2 M in methanol/water (7:3/v:v) for 5 min, rinsed in methanol for 5 min and dried again. This sequence was repeated until dots with required size were obtained. This process is one cycle (C) of SILAR and was done for 2, 4, 6 and 8 cycles. To have a shell with a proper electrical and optical characteristics, ZnS shell was applied to have the optimum hole transfer to the electrolyte. For ZnS deposition on the CdS using SILAR, samples were immersed in a 0.1 M solution of zinc nitrate hexahydrate ((Zn(NO3)2·6H2O, Merck) in ethanol for 1 min, rinsed in methanol and dried in the air. This step was followed by immersion of samples in 0.1 M Na2S in methanol/water (7/3/v:v), rinsing with methanol (each step for 1 min) and drying. This sequence was repeated for different number of cycles to see the effect of the ZnS thickness on the cell performance. Transmission electron microscopy (TEM, JEM-2010-JEOL, Japan, 400 kV) was used to see the size and morphology of CdS QDs on ZnO NWs.

2.3. Preparation of counter electrode

The counter electrode of the solar cell was also investigated in this study. After cleaning the FTO glass, CuS and Au were deposited and examined to find out the optimum choice to play the role of the...
counter electrode. For Au deposition, RF sputtering was used to deposit 10 nm of Au. But for CuS deposition, SILAR method was used. FTO was immersed in a solution containing 0.5 M copper (II) nitrate trihydrate (Cu(NO3)2·3H2O, Merck) in ethanol, rinsed with ethanol and dried. Then, FTO was immersed in 0.5 M Na2S in methanol/water (7:3), rinsed with methanol again and dried. This SILAR cycle was repeated 4 times to deposit CuS counter electrode.

2.4. Electrolyte solution

Polysulfide electrolyte containing Na2S, Sulfur (S, Sigma Aldrich) and Potassium Chloride (KCl, Merck) in methanol/water was used as an electrolyte. In order to study the effect of KCl concentration and solvents of the electrolyte on the cell parameters, different electrolyte solutions were prepared and examined.

2.5. Fabrication of QDSC

The schematic of fabricated solar cell is shown in Fig. 1. On the counter electrode, there has been an aperture to inject electrolyte after bonding two electrodes, like a sandwich from top and bottom. The cell was fabricated by placing anode electrode (with the grown ZnO NWs and QDs on them) on the cathode electrode (with CuS as the catalysis), with a sheet of (Surlyn) polymer between them for spacing. Then, they were annealed at 120 °C for 2 min, so the polymer was provided a good adhesion. After that, polysulfide electrolyte was injected into the cell via the aperture of counter electrode. This aperture was sealed immediately by an adhesive coated layer with a piece of glass.

3. Results and discussion

The shape and morphology of ZnO NWs were observed by FESEM and are shown in Fig. 2. The θ-2θ diffractogram of the grown array is illustrated in Fig. 3. The sharp peak in this figure in (002) orientation displays a high quality growth of ZnO NWs along the c-axis [42].

The TEM picture of the material to see the morphology of CdS QDs on ZnO NWs is presented in Fig. 4. CdS QDs in this figure were synthesized by 8 cycles of SILAR on ZnO NWs. It can be seen that with SILAR method, QDs were well-distributed all over the surface of NWs and created a shell with at least 10 nm thickness.

To explore how QD’s band gap changes with the size, UV-Vis analysis was performed. Fig. 5 shows that the QDs, which were synthesized with 2 cycles of SILAR, absorb photons with wavelengths less than 390 nm which is actually similar to absorption of ZnO NWs. This means that 2 cycles of growth have no advantage in increasing the absorption. However, QDs synthesized with 4 cycles of SILAR absorb photons with wavelengths less than 520 nm. This value increases for samples grown with 6 cycles to 540 nm and strangely decreases to 530 nm in larger dots (8 cycles). These wavelengths are respectively corresponds to 2.38, 2.29 and 2.33 eV bandgaps. The unusual decrease in QDs grown for 8 cycles refers to...
a large lattice mismatch between the CdS and ZnO which is a sign of relaxation in this layer.

Smaller QDs leads to quantum confinement with smaller dimensions and this finally results in energy levels located further apart from each other in the reciprocal space. Thus, smaller dots will absorb lower wavelengths (or higher energies).

Finally, J-V measurements were performed by Solar Simulator (model, SIM 1000) at 1 sun illumination (AM 1.5, 100 mW/cm²) to extract the cell efficiency, Jsc, Voc and the fill factor. This measurement was performed on the fabricated of QDSSC to see the effect of the size of the CdS QDs on the cell performance (see Fig. 6). CdS was synthesized by 4, 6 and 8 cycles of SILAR. Au was used as the counter electrode and polysulfide electrolyte of the cells was contained Na₂S 0.6 M, S 0.2 M and KCl 0.2 M in methanol/water (7:3/v:v). However, it can be observed that from cells with CdS(6C) to cell with CdS(8C), JSC and efficiency are decreased. The reason is the lattice mismatch between ZnO and CdS (aZnO = 3.25 Å [43] and aCdS = 4.135 Å) which led to a large amounts of defects in the grown layer. As a result, the cell performance was degraded remarkably. Table 1 shows the cell parameters of different sizes of CdS QDs.

It is expected that as diameter of QDs increases, their band gap becomes smaller, and as a result, larger amounts of photons are absorbed and consequently Jsc and efficiency will be increased.

To optimize the elements of electrolyte solution, the ratio of methanol/water and the concentration of KCl were studied (Fig. 7). Fig. 7a shows a huge difference in the cell performance by changing the ratio of methanol/water. However, keeping water as the solvent will ease solving other elements in the electrolyte. Fig. 7b exhibits that the best concentration of KCl is 0.4 M. The role of KCl in the electrolyte is decreasing the resistivity of electrolyte by increasing the ions in the solution which results in higher current density. But for concentration more than 0.4 M, Voc was decreased.

So the best polysulfide electrolyte was obtained with: KCl 0.4 M, Na₂S 0.6 M and S 0.2 M in methanol/water (7:3/v:v). The cell fabricated using these parameters with Au as the counter electrode acquired Voc, Jsc, FF and the efficiency about 0.444 V, 0.672 mA/cm², 0.22 and 0.066%, respectively.

Au and CuS were also evaluated as the candidates for the counter electrode. As it is demonstrated in Fig. 8, the sample with Au as a catalyst had much lower Jsc. Because sulfur ions in the electrolyte have a good adhesion to Au and form covalent bonds with Au, so this thin layer of thiols on the Au blocks the electron current from Au to the electrolyte and Jsc decreases.

There is a concavity in the J-V measurement for Au curve in Fig. 8. This phenomenon is believed to occur due to tunneling of electrons via thiol layer on the catalyst. For high voltages, electrons on the cathode electrode can tunnel form Au to the electrolyte and thiol layer can’t block the current anymore, so Voc happens at higher voltages.

But with CuS as the catalyst, electrons could easily inject from external circuit to the electrolyte and current density was increased. Covering the surface of CdS QDs with a thin layer of ZnS (with SILAR) has improved the cell performance, because the

<table>
<thead>
<tr>
<th>QDSSC parameters for different sizes of CdS.</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/CdS(4C)</td>
<td>0.27</td>
<td>0.416</td>
<td>0.199</td>
<td>0.022</td>
</tr>
<tr>
<td>ZnO/CdS(6C)</td>
<td>0.606</td>
<td>0.63</td>
<td>0.212</td>
<td>0.081</td>
</tr>
<tr>
<td>ZnO/CdS(8C)</td>
<td>0.527</td>
<td>0.465</td>
<td>0.202</td>
<td>0.0496</td>
</tr>
</tbody>
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conduction band of ZnS is placed at higher energies compared to the conduction band of CdS. So it creates quantum electrical confinement for the generated charge carriers (see Fig. 9). Charge transfer in the electrolyte is happened via oxidation and reduction of the sulfur ions. The redox couple in the polysulfide electrolyte are S^{2-} and S^{2-}/S^{2-} [44]. S^{2-}/S^{2-} ions absorb the electrons from the external circuit and turn to S^{2-}. To regenerate the QDs, which have loosed their electron because of light absorption, S^{2-} ions give their electrons to the valence band of QDs and QDs regenerate. With light absorption, electrons in the valance band of QDs are excited and transfer into the conduction band. Because of the location of the conduction band of ZnO NWs (which is placed below the CdS), electrons in the valance band of QDs are excited and transfer into the conduction band. It means that there is 7.83% lattice mismatch between ZnO and CdS (2.72%) which leads to a large amounts of defects in the grown layer. The optimized size of the CdS QDs was obtained. The effect of the components of the polysulfide electrolyte on the charge transfer was studied. The performance of the cell with Au and CuS as the counter electrode was analyzed. The cell with ZnO NW/CdS(4C)/ZnS(3C) as the photosensitizer, CuS as the counter electrode and Na2S 0.6 M, S 0.2 M and KCl 0.4 M in methanol/water (7:3) had the best performance with the efficiency of 0.419%. It was found that there is a meaningful window for each parameter in the cell fabrication which exceeding beyond will degrade the cell performance.

4. Conclusion

ZnO NWs were grown by hydrothermal method to increase the active area for solar application. ZnS shell-like CdS QDs were synthesized on the surface of ZnO NWs by SILAR method. As diameter of QDs increases, their band gap become smaller, and larger amounts of photons are absorbed. However, for the cell with larger CdS QDs, efficiency is decreased. The reason is the lattice mismatch between ZnO and CdS. The optimal condition for the generated charge carriers (see Fig. 9). Charge transfer in the electrolyte is happened via oxidation and reduction processes, Chem. Mater. 22 (2010) 5636–5643, http://dx.doi.org/10.1021/cm102042s.

Presence of ZnS was tested in a cell using 4 cycles of SILAR to grow both CdS dots and the counter electrode (CuS) (see Fig. 10). ZnS shell was synthesized with 1, 3 and 5 cycles of SILAR. Results showed that for the first sample with just 1 cycle SILAR, there wasn’t any improvement on the short circuit current. This happened because electrons, which were destined to go through the ZnO NWs, can also tunnel through one ZnS layer and leak into the electrolyte. With increasing the thickness of the shell to three ZnS layers, J_{sc} increases. In such a condition, ZnS blocked the direction of excited electrons in CdS QDs to the electrolyte and limited the leakage into the electrolyte, so fill factors (from 0.29 to 0.34 for going from 1 to 3 layers of ZnS shell) of the cells were increased. For the last sample with 5 cycles of SILAR, the performance was drop-off. This can be explained by the fact that the grains layer on the ZnO became such thick that the layer got relaxed, so lots of defects were generated and efficiency of the cell was decreased dramatically. It is worth mentioning here that the lattice constant of CdS is 4.135 Å, while for ZnS, this parameter is 3.811 Å, which means that there is 7.83% lattice mismatch between them.

References


Please cite this article in press as: M. Ganjian, et al., ZnS shell-like CdS quantum dot-sensitized solar cell grown by SILAR approach; effect of electrolyte, counter electrode, and shell thickness, Vacuum (2017), http://dx.doi.org/10.1016/j.vacuum.2017.02.007
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