

Enhanced Efficiency of ZnO Nanowires Based Dye-Sensitized Solar Cells with Heterosensitizer

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been examined eagerly as a new generation of solar cell because of their low cost and high performance [1]. In general, DSSCs based on TiO₂ nanoparticle network consist of a metal oxide layer to serve as the photoanode, a dye to serve as the light absorber and an organic solvent containing redox system. Photo-excitation takes place in the dye molecules and the photogenerated charges are separated at the dye/oxide interface; electrons are injected into the conduction band of semiconductor oxide and then transported through the semiconductor oxide to the collecting electrode. Based on the TiO₂ nanoparticle network, the DSSC has achieved AM 1.5 solar efficiencies more than 10% [2-3]. However, the further improvement in power conversion efficiency (PCE) is difficult, partly resulting from charge recombination and reduced electron transport rate through the nanocrystalline photo-electrodes. Single crystal nanorods or nanowires, such as ZnO, could offer direct electrical pathways for photogenerated electrons and increase the electron transport rate, which in turn may improve the performance of DSSCs.

To achieve a wide use of ZnO nanowires (ZnO-NWs) based DSSC, it is important to enhance its PCE to a much greater degree. The further improvement in PCE of the DSSC can be expected by enhancing charge transport and increasing light absorption over a broad region of the solar spectrum. For hydrothermal grown (HTG) nanowires using different conditions, the efficiency of 1.0% for 11 μm , 1.5% for 17 μm , 1.8% for 22 μm , and 2.1% for 33 μm in NW-length was demonstrated [4]. However, compared with all solid-state inorganic-based tandem solar cells, it is hard to fabricate a DSSC with different dyes due to the high processing temperature. In this work, to increase PCE, we report a tandem structure with two different sensitizer dyes (heterosensitizer) as well as ZnO-NWs by a simple hydrothermal growth method for DSSCs.

2. Experiments

The key fabrication processes for ZnO-NWs based DSSCs with heterosensitizer were shown in Fig. 1. First, ITO-glass was used as the substrate which was cleaned ultrasonically using acetone, methanol, rinsed in DI water, blown dry with N₂, and then dipped into chemical

solution (HCl:H₂O = 3:1) for 10 min to remove the surface particle. And, a 100 nm-thick aluminum-doped zinc-oxide (AZO) film was sputtered onto ITO-glass substrates to serve as a seed layer for the growth of ZnO-NWs by HTG method (Fig. 1(a)). For the first synthesis of ZnO-NWs, the samples were placed in a mixed solution of 0.07 M Zn(NO₃)₂·6H₂O and 0.09 M C₆H₁₂N₄ at 90°C for 3 h (Fig. 1(b)). Subsequently, the electrodes were immersed in a 5 mM ethanolic solution of the dye cis-bis-(isothiocyanato) bis (2, 2'-bipyridyl-4, 4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (N719) at room temperature for 3 h. For the second synthesis of ZnO-NWs, the sample were again placed in a mixed solution of 0.07 M Zn(NO₃)₂·6H₂O and 0.09 M C₆H₁₂N₄ at 90°C for 3 h. Note that vertically aligned ZnO-NW arrays were synthesized at lower temperature (85°C) to avoid the decomposition of adsorbed dye at previous process stage. To adsorb another sensitizing dye, the electrodes were immersed in a 0.2 mM ethanolic solution of the dye triisothiocyanato-(2,2':6', 6''-terpyridyl-4,4',4''-tricarboxylato) ruthenium(II) tris(tetra-butylammonium) (Black dye) at room temperature for 3 h (Fig. 1(c)). The solar cells were assembled using an electrolyte consisting of 0.5 M LiI, 0.05 M I₂ redox system, and 0.5 M 4-tertbutylpyridine (an ionic electrolyte which can improve charge transport and increase V_{oc}) in 3-methoxypropionitrile solvent, and a platinum coated conductive oxide glass as a counter electrode (Fig. 1(d)). Note that the samples having one-step and two-step growth ZnO-NWs soaked with single N719 dye, referred to as sample A and sample B, respectively, were also prepared for comparison.

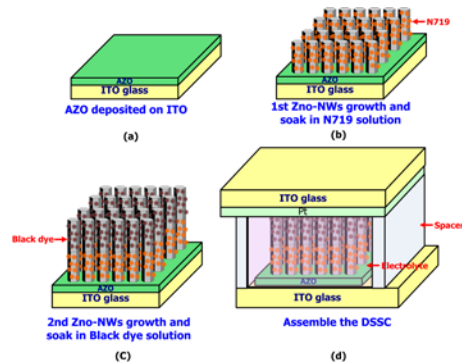


Fig. 1 The flowchart of the synthesis of ZnO-NWs based DSSC with heterosensitizer.

3. Results and Discussion

Figure 2(a) shows the TEM image and corresponding SAED pattern of an individual ZnO-NW obtained from the sample with an HTG time of 2 hr. Clear stripes of lattice plane were observed extending through whole of the wire. The inter plane distance of d-space was determined to be 0.26 Å, indicating the main crystalline phase of the wire should be ZnO [0001] phase. The ZnO-NW arrays grown on the AZO layer were preferentially oriented along the c-axis direction normal to the substrate. This is similar to that prepared by CVD or synthesized on metallic Zn and ZnO films [5-6]. Based on the corresponding SAED pattern shown in the inset, it reveals that the ZnO-NW is a well single-crystalline n-type semiconductor with the wurtzite structure. The X-ray diffraction pattern shown in Figure 2(b) confirms that the ZnO-NWs are quasicaligned predominantly with (002) orientation. The inset of Fig. 2(b) shows the EDS analyses of the ZnO-NWs. It reveals that the chemical components of the grown ZnO-NWs were confirmed, mainly comprising pure metallic Zinc and oxygen.

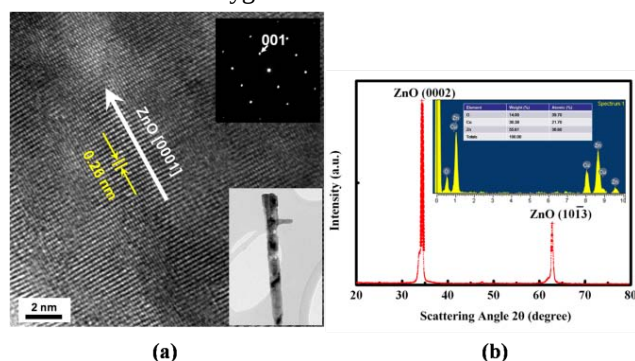


Fig. 2 (a) HRTEM image and SAED pattern of single ZnO-NW, (b) XRD spectra and EDS analyses of ZnO-NWs grown on AZO.

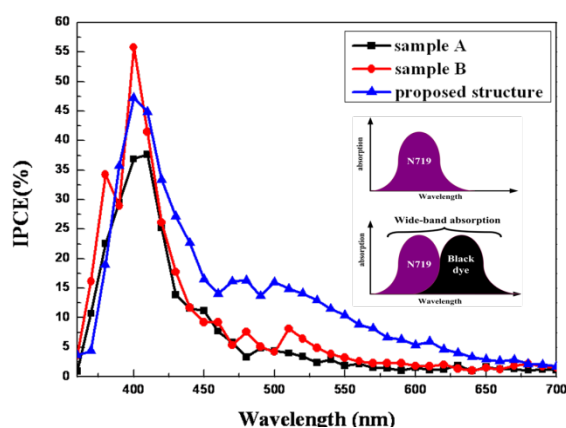


Fig. 3 The incident monochromatic photo-to-current conversion efficiency spectra of the prepared DSSCs.

Figure 3 and 4 shows IPCE and photocurrent density-voltage (J - V) characteristics of the prepared solar cells, respectively. Sample A and B were prepared having the ZnO-NW length of 5 μm and 9 μm , respectively, for the single dye (N719) structure. The power conversion efficiency (PCE) of sample A and B were 0.27% and 0.98%, respectively. Compared with sample A, the sample B shows an enhancement in efficiency and IPCE, resulting from the increase in surface area for dye absorption. The reason why there is

no linear dependence is due to the increase in ZnO-NW length and density by the growth time. The PCE of proposed DSSC with hetsensitizer having the ZnO-NWs length of 9 μm was improved up to 1.92%, with V_{oc} of 0.44 V, J_{sc} of 16.81 mA/cm^2 and a FF of 25.96%. The result could be attributed to the use of multi-dye for expansion of the light absorption region.

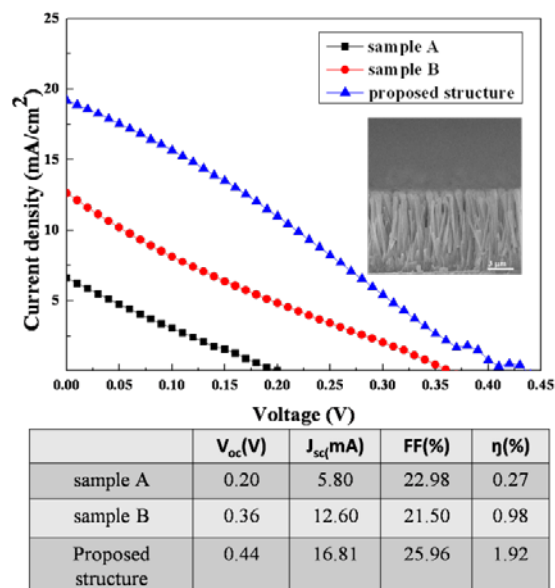


Fig. 4 The photocurrent density-voltage curves and performance of the prepared DSSCs under AM 1.5G illumination.

4. Conclusion

In summary, a ZnO-NW based DSSC structure with broad absorption region of the solar spectrum was fabricated and characterized. The developed approach allows two different dyes to be adsorbed on ZnO-NWs in identical cell without thermal decomposition of dye molecules. Compared with N719-sensitized samples, the proposed DSSC having N719 and black dye sensitizers on ZnO-NW shows an enhancement in PCE by 96%, all without chemical modification and antireflection coating. The increase in PCE could be attributed mainly to the realization of more-efficient light energy utilization in the DSSCs.

Acknowledgments

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