Preparation of ZnO-AZO Core-Shell Nanoarrays and Its Application in Dye Sensitized Solar Cells

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Abstract. High quality one-dimensional ZnO nanometer array (ZnO NAs) was synthesized by low-temperature hydrothermal method. The length and diameter of ZnO NAs was regulated by controlling hydrolysis time (Th) and the concentration of hydrolysate, and the surface was modified by aluminum-doped ZnO (AZO) to obtain ZnO/AZO core-shell nanometer array, which was used as the photoanode of dye-sensitized solar cells. The ZnO NAs provide a direct and stable channel for charge transfer. The electron recombination caused by the reaction of the acid dye and ZnO photoanode have reduced as adding AZO shell, and increased the array surface roughness to improve the load of dye molecules. As a result, the DSSC of composite film has a high power conversion efficiency of 1.75%.

1. Introduction
Dye-sensitized solar cells (DSSC) have attracted extensive attention due to their high theoretical photoelectric conversion efficiency, simple preparation process, abundant raw materials, stable photoelectric performance, low price, environmental friendliness and other advantages[1]. In recent decades, in order to improve the power conversion efficiency (PCE) of DSSC, researchers have carried out a lot of work, especially for the photoanode which plays the role of absorbing dye molecules and transferring electrons. In general, the photoanode is TiO2 of traditional DSSC, and ZnO can be also used as photoanode, as their similar conduction band energy levels and suitable energy gap. Compared to TiO2, ZnO has far-reaching developing space in the DSSC, because of its higher electron mobility, which can effectively reduce energy losses, richer crystal morphology, and simpler preparation method[2]. For the DSSC, it will get higher PCE as absorbing more dye molecules. Therefore, it is an important research direction to optimize the preparation and synthesis of ZnO with different morphologies and structures. In order to increase the amount of dye adsorption, and improve the PCE, many researchers have developed one-dimensional ZnO nano array (ZnO NAs) used as the photoanode[3,4]. Yang et al. obtained conversion efficiency of 1.2%-1.5% by vertically growing ZnO NAs on FTO as the photoanode of DSSC[5]. Wu et al. added ZnO nanowires to the ZnO nanocrystalline photoanode, and the PCE of DSSC increased from 0.84% to 5.0%[6]. Qiu et al. prepared ZnO nanorod-nanosheets as photoanode, and the PCE of DSSC reached 3.12%[7]. These studies show that ZnO NAs photoanode can provide an axial direct and stable electron transport channel for electron transmission, and it accelerates the high-speed electron migration and improves the PCE of DSSC. However, as ZnO is a amphoteric oxide, it is easy to react with Ru dye molecules
containing -COOH group, which affects the electron injection efficiency from dye molecules to ZnO, thus limiting the further improvement of PCE of ZnO based DSSC. Therefore, some researchers applied semiconductor material coating on ZnO NAs surface, which needed matching the level of dye molecules. It would reduce the contact probability between dye molecules and ZnO, and decrease the recombination rate of interfacial charge, so as to improve the PCE of DSSC. Gao and others make TiO2 coating on the ZnO NAs, forming ZnO/TiO2 core-shell multilayer nanoarrays photoanode, and achieve the PCE of 5.65%[8]. Other semiconductor such as Al2O3 and SiO2 have also be used to coat on the surface of ZnO NAs to suppress electronic composite, so as to improve the performance of the solar cells[9,10,11].

Herein, in order to improve the PCE of ZnO based DSSC, ZnO NAs were synthesized via low temperature hydrothermal method, and the length and diameter of the ZnO NAs were controlled by regulating hydrolysis time (Th) and the concentration of hydrolysate, to obtain the suitable material for the DSSC. The one dimensional ZnO provides a direct and stable transmission channel for photo-electron transmission. In order to further improve the performance of DSSC, aluminum-doped zinc oxide (AZO) was used to cover on the ZnO NAs surface to form ZnO/AZO NAs core-shell structure, which would reduce the contact interface between acid dye molecules and ZnO, and decrease the electron injection rate. At the same time, due to the introduction of shell layer, the surface roughness of the photoanode is increased, and the adsorption amount of dye molecules is improved, thus improving performance of the DSSC.

2. Experimental Section

2.1 Preparation of ZnO NAs, ZnO/AZO NAs substrates
ZnO NPs layer fabricated via an easy and convenient in situ method were covered on fluorine-doped tin oxide glass (FTO, Shenzhen Laibao Hi-Tech Co., Ltd., China) for nucleation. ZnO NAs were hydrothermally grown by suspending ZnO NPs in a hydrothermal solution of zinc acetate dihydrate (Zn(CH3COO)2·2H2O) and hexamethylenetetramine with different concentration (0.025 M, 0.05 M, 0.075 M, 0.1 M) at 90 ºC for 2, 4 and 6 h. After annealing at 200 ºC for 60 min in air, and cooling to room temperature, ZnO NAs with different length and diameter was obtained. Then the AZO precursor[12] was spin-coated on the ZnO NAs, and annealed at 140 oC for 20 min to achieve ZnO-AZO NAs core-shell.

2.2 Device fabrication
The DSSC was configured by assembling a N719 sensitized ZnO/AZO NAs photoanode and a Pt counter electrode, between which was separated by using a 50 m m thick spacer. The surface area of both ZnO-AZO NAs film and Pt film was ca. 0.7 cm * 0.7 cm. Then the photoanode was into a N719 ethanol solution (0.5 mM) at room temperature for 24 h. The electrolyte was 0.5 M LiI, 0.05 M I2, 0.5 M 4-tert-butylpyridine (TBP) in a solvent of 3-methoxypropionitrile (MPN).

2.3 Characterization
The morphologies and microstructures of the ZnO-AZO NAs were characterized by a field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Japan) and a high-resolution transmission electronic microscopy (TEM; JEM-2100, JEOL, Japan). The crystal microstructures of the samples were identified by an X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany). The DSSC performance was measured by an electrochemical workstation (CS310, Corr-test, China) at 10 mV of amplitude. The light intensity was 100 mW/cm2.

3. Results and Discussions
The scanning electron microscopy (SEM) was carried out to investigate the morphology of ZnO NAs. The different length and densities of ZnO NAs are adjusted by controlling the hydrolysis time (Th). a, b, c and d symbolize Th are 0 (ZnO NPs), 2, 4 and 6 h, respectively. As shown in Figure 1, by
comparing to ZnO NPs with Th = 0 min, and there is obvious variation for b image when Th is 2 h, the ZnO NAs appears. It is clearly exhibited that all ZnO NAs are almost vertically arrayed on the substrate, and it would be favor for charge transmission. And with increasing Th, the diameter and length of ZnO NAs become larger. The NAs collapses into the surroundings as increasing the Th to 6 h., and it would go against the dye absorbing and charge transferring.

Figure 1. The SEM images of ZnO NAs synthesized with different hydrolysis time (Th) of 0 (a), 2 (b), 4 (c) and 6 h (d).

In order to investigate the change of concentration of hydrolysate on the morphology of ZnO NAs, the experiment were carried out by controlling the concentration of hydrolysate of 0.025 M (Fig. 2a), 0.05 M (Fig. 2b), 0.075 M (Fig. 2c), 0.1 M (Fig. 2d). As can be seen from the figure, when the concentration is too small, the array distribution is uneven (Fig. 2a), if used as photoanode, the leakage is easy to occur. And the nanometer array no longer grows vertically on the glass substrate, causing accumulation and collapse when increasing the concentration of hydrolysate, it is also bad for DSSC.
Figure 2. The SEM images of ZnO NAs synthesized with different Zn(COO)\(^2\)-2H\(_2\)O concentration.

In order to further prove that the ZnO NAs have been successfully prepared, the X-ray diffraction (XRD) tests were carried out. From the Fig. 3a, the ZnO NAs are grown along the (002) direction in agreement with literature, further demonstrates that ZnO NAs is successfully synthesized. To modify ZnO surface and increase the amount of the dye, the AZO has been deposited on ZnO NAs surface by spin-coating precursor technique, the transmission electron microscopy (TEM) have been employed to get a insight into the morphologies of ZnO/AZO NAs with core/shell hybrid structure. From the image (Fig. 3b), the AZO covered on the ZnO NAs surface.

Figure 3. The XRD of ZnO NPs, NAs (a) and TEM of ZnO/AZO NAs (b).

The current density-voltage (J-V) curves under illumination of the DSSCs based on ZnO NAs with different concentration of hydrolysate and AZO sensitized ZnO as photoanode, as well as the dye of N719 are shown in Figure 4 and the photovoltaic parameters of the devices are listed in Table 1. As the concentration of hydrolysate increases, the corresponding PCEs of the device with ZnO NAs (0.025 M), ZnO NAs (0.5 M), ZnO NAs (0.075 M) and ZnO NAs (0.1 M) ETL were 0.63%, 1.1%,
0.61% and 0.21%, respectively. With adding the sensitizer of AZO shell layer, the PCE from 0.63% and 1.1% increased to 0.91% and 1.75%. The enhanced performance mainly originates from the improvement of Jsc and FF, which may be attributed to ZnO NAs’ direct and stable electron transport path and improving the amount of dye after modification of AZO.

![Figure 4. The J-V curve of the DSSC with different photoanode.](image)

Table 1. Photovoltaic parameters of the DSSC devices based on different photoanodes of ZnO NAs with different concentration of hydrolysate and ZnO/AZO NAs.

| sample      | Voc (V) | Jsc (mA/cm²) | FF   | PCE (%) |
|-------------|---------|--------------|------|---------|
| 0.025 M     | 0.58    | 2.21         | 0.49 | 0.63    |
| 0.05 M      | 0.52    | 3.42         | 0.62 | 1.10    |
| 0.075 M     | 0.53    | 2.26         | 0.51 | 0.61    |
| 0.1 M       | 0.47    | 1.18         | 0.37 | 0.21    |
| 0.025 M/AZO | 0.56    | 3.01         | 0.54 | 0.91    |
| 0.05 M/AZO  | 0.57    | 4.71         | 0.65 | 1.75    |

4. Conclusions
ZnO/CdS core/shell NAs with different density and length adjusted by controlling hydrolysate concentration and Th via hydrothermal process have been successfully applied as photoanode in dye-sensitized solar cells. The DSSC based on 0.05 M/AZO as photoanode owning the highest PCE of 1.75% (Jsc = 4.71 mA·cm⁻², Voc = 0.57 V, FF = 65.0%), mainly originates from the enhancement of Jsc and FF, which may be attributed to ZnO/AZO NAs’ direct electron transport path and the amount increasement of dye after modification of AZO.

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