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Effect of KOH treatment on structural and photovoltaic properties of ZnO nanorod arrays

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Abstract: ZnO nanorod arrays (NRs) were synthesized on the fluorine-doped SnO_2 transparent conductive glass (FTO) by a simple chemical bath deposition (CBD) method combined with alkali-etched method in potassium hydroxide (KOH) solution. X-ray diffraction (XRD), scanning electron microscopy (SEM) and current—voltage (I—V) curve were used to characterize the structure, morphologies and optoelectronic properties. The results demonstrated that ZnO NRs had wurtzite structures, the morphologies and photovoltaic properties of ZnO NRs were closely related to the concentration of KOH and etching time, well-aligned and uniformly distributed ZnO NRs were obtained after etching with 0.1 mol/L KOH for 1 h. ZnO NRs treated by KOH had been proved to have superior photovoltaic properties compared with high density ZnO NRs. When using ZnO NRs etched with 0.1 mol/L KOH for 1 h as the anode of solar cell, the conversion efficiency, short circuit current and open circuit voltage, compared with the unetched ZnO NRs, increased by 0.71%, 2.79 mA and 0.03 V, respectively.

Key words: ZnO nanorod arrays; SnO_2 transparent conductive glass; alkali etching; structural properties photovoltaic properties; solar cells

1 Introduction

As an important II−VI semiconductor, ZnO has attracted great interests owing to its unique properties, such as a wide band gap (3.37 eV), a large exciton binding energy (60 meV), high electrochemical and thermal stability, transparency, biocompatibility, acoustic characteristics and excellently electronic properties. It has been widely used in solar cell [1,2], chemical sensors [3], varistors [4], surface acoustic wave device [5], photonic crystals [6], photodiodes [7] and so on. In particular, one-dimensional (1D) ZnO NRs have been applied to dye sensitized solar cells (DSSC) because of their specific optoelectronic properties [8]. As we know, the photoanode plays an important role in determining the electron diffusion coefficient [9], the dye absorption surface area and photon-to-charge carrier efficiency [10]. At present, mesoporous nanoparticles are used as photoanodes because of their larger inner surface, but the electron transport is slower due to the multi-trapping events. One way of addressing this problem is to introduce nanorod arrays to the photoanode. The ZnO NRs provide direct path from the point of photogeneration electron to the conducing substrate and greatly enhance their surface area, leading to improved light harvesting and overall efficiency [11]. In addition, ZnO NRs have advantage in that nanorods can be easily synthesized using a hydrothermal method [12].

Until now, different methods to synthesize ZnO NRs have been used, such as metal organic chemical vapor deposition (MOCVD) [13], template-based method [14], laser ablation [15], spray pyrolysis technique [16], and solution methods [17]. Compared with those methods, the chemical solution deposition method (CBD) can be controlled easily under low temperature, and no sophisticated equipment is required [18]. Now just a little work has focused on tuning the array size of ZnO NRs [19], and the effects of KOH treatment on the morphologies and photovoltaic

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properties of ZnO NRs have been reported rarely.

Therefore, in this article the authors reported the two-step synthesis of ZnO NRs by a chemical bath deposition method followed by alkali-etching in KOH solution. The size and the surface area of ZnO NRs can be well tuned by varying the concentration and etching time. Eventually, the influence of this KOH treatment on the photoelectric properties of ZnO NRs is investigated by studying photocurrent—voltage (*I*—*V*) characteristics of the DSSC.

2 Experimental

2.1 Preparation process

High density ZnO NRs used in this work were grown on FTO coated glass substrates by CBD method. The FTO-coated glass substrates were first cleaned in the ultrasonic bath with acetone, ethanol and deionized water to remove adsorbed dust and surface contamination. Then, ZnO seed layer was fabricated on the substrates by a dip-coating method. The precursor aqueous solution for the preparation of ZnO NRs was composed of 0.1mol/L $Zn(NO_3)_2$ and $(CH_2)_6N_4$ in a 1:1 molar ratio. The pH value of the solution was adjusted to 9.0 by the addition of ammonia. The precursor solution (60 mL) was then transferred to a Teflon-sealed autoclave comprising substrates precoated with a ZnO seed layer. The reaction was run at 95 °C for 6 h to synthesize ZnO nanorod film. After deposition, the samples were cleaned with deionized water several times and allowed to dry in air. Finally, the resulting films were immersed into 0.05, 0.1, 0.2 mol/L KOH for 0.5, 1 and 2 h, respectively.

2.2 Construction of dye-sensitized solar cell

The obtained ZnO nanorod electrodes were dipped in a N3 solution (0.5 mmol/L in dry ethanol solution) for 12 h. The counter Pt-electrode was obtained by coating with a drop of H_2PtCl_6 solution (5 mmol/L in isopropanol solution) on FTO and heated at 300 °C for 15 min. The dye-covered ZnO electrode and Pt-counter electrode were assembled into a sandwich type cell. The electrolyte solution composed of 0.5 mol/L KI, 0.05 mol/L I_2 in acetonitrile was introduced to the gap between the counter and working electrodes by the capillary force. Then, the DSSC cell was obtained.

2.3 Characterization

The X-ray diffraction (XRD) patterns were recorded on an X-ray diffraction system (XRD, SEMENS D5000). The morphology was observed by a scanning electron microscope (SEM, JEOL JSM°C 6700F).

The current—voltage (*I*—*V*) characteristics were measured with a computer-controlled digital source meter (Keithley, model 2400) under illumination with a Newport solar simulator (AM1.5, 100 mW/cm^2).

3 Results and discussion

3.1 Morphology and microstructure

Figure 1 shows the SEM images of unetched and ZnO NRs etched by KOH with different concentrations for 1 h. The growth temperature and time of high density ZnO NRs were 95 °C and 6 h, respectively. It can be seen that the morphology of as-grown ZnO NRs is closely related to the KOH concentration. The SEM image of unetched ZnO NRs is shown in Fig. 1(a). It can be seen that the arrays consist of dense ZnO NRs with different diameters, and the average diameter is about 200 nm. The size of the ZnO NRs is varied by changing the concentration of the KOH. As shown in Fig. 1(b), the average diameter of ZnO NRs is about 50 nm. Though the diameter decreased, the ZnO NRs were still arranged densely after etching at a low concentration of the KOH (0.05 mol/L). Figure 1(c) shows that ZnO NRs were vertically well-aligned and uniformly distributed on the FTO substrate after etching by 0.1 mol/L KOH, and the average diameter was about 30 nm. However, for samples under higher KOH concentration, sparse ZnO NRs with local defects were obtained, which could be seen from Fig. 1(d).

To investigate the effect of the etching time on the morphology and aspect area of ZnO NRs, a series of experiments were performed by varying the etching time of 0.1 mol/L KOH but keeping other parameters constant. Figure 2 shows the SEM images of unetched and KOH-etched ZnO NRs with different time. It can be seen that the morphology of as-grown ZnO NRs is closely related to the etching time. The diameters of ZnO NRs decreased after etching by KOH, and within certain etching time range (0.5h to 2h), the density of the ZnO NRs decreases with increasing the etching time. Because ZnO could react with KOH, the diameters decreased after etching by KOH. Furthermore, increasing the etching time is beneficial for sufficient reaction, which would lead to a decrease in the arranged density of ZnO NRs. And these can be represented by the following reaction [20]:

$$ZnO+2OH^- \rightarrow ZnO_2^{2-}+H_2O \quad (1)$$

The SEM image of untreated ZnO NRs is shown in Fig. 2(a). It can be seen that the arrays consist of dense ZnO NRs with different diameters, and the average diameter is about 200 nm. With the increase in the etching time while the concentration of KOH was kept at 0.1 mol/L, the density and diameters of zinc oxide nanorods also decreased (Figs. 2(b)−(d)). From Fig. 2(b), we can see that the ZnO NRs treated in 0.1 mol/L KOH