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Fabrication and Photovoltaic Properties of Cu_2O/ZnO p-n Heterojunction Solar Cells

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Abstract: Single-crystal n-type zinc oxide (ZnO) nanorod arrays, p-type cuprous oxide (Cu_2O) film, and Cu_2O/ZnO heterostructures were fabricated by electrochemical deposition. The diameter of ZnO nanorods can be controlled by changing the $ZnCl_2$ concentration as it increases with the concentration of $ZnCl_2$. Electrical measurements demonstrate a p-n junction forms between Cu_2O film and ZnO nanorod arrays. External quantum efficiency of the p-n junction is higher than that of ZnO nanorod arrays and Cu_2O film, which indicates that the formation of a p-n junction between Cu_2O film and ZnO nanorod arrays can efficiently facilitate the separation and transport of charge carriers for applications in solar cells.

Key words: ZnO; Cu_2O; heterojunction; photovoltaic; external quantum efficiency
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Cu_2O-ZnO 异质结太阳能电池的制备及光电性能研究

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摘要: 电化学沉积是一种绿色高效的材料制备方法。本实验使用电化学沉积法分别制备了单晶的氧化锌(ZnO)纳米棒阵列和 p 型的氧化亚铜(Cu_2O)薄膜,并对样品进行了扫描电镜、X 光衍射、外量子效率和光电性能测试等一系列的表征和测试。试验结果表明,通过改变反应溶液中的 $ZnCl_2$ 浓度可以来调控 ZnO 纳米棒的直径。光电性能测量显示在 Cu_2O/ZnO 间形成了 p-n 异质结。量子效率的测试证明该异质结可有效地促进载流子的分离和传送,从而提高太阳能电池的转化效率。

关 键 词: ZnO; Cu_2O; 异质结; 光电性能; 外量子效率

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1 Introduction

Oxide semiconductor nanostructures have attracted increasing interest during the past decades in many fields such as field emission, gas sensors, and solar cells[1-2]. Although these nanostructures can be obtained through various methods, electrochemical deposition has advantages in low-temperature, low-cost and precise morphology control in comparison to other methods. ZnO is a well-known n-type semiconductor material with a wide band gap of 3.37 eV. Arrays of ZnO nanorods have attracted many researchers for their applications in solar cells due to their high specific surface area, exceptional electrical, optical and chemical properties. For example, ZnO has been investigated as a very promising window material in solar cells[3-4]. On the other hand, Cu_2O is an important p-type semiconductor material with a direct band gap of 2.17 eV, and thereby, it can be used as the absorber layer in solar cells due to its high absorption coefficient in the visible region and suitable minority carrier diffusion length[5]. Recently, researches on Cu_2O/ZnO heterostructure solar cells have been reported, and different configurations of Cu_2O and ZnO layers have been investigated, such as, ZnO thin film deposited on Cu_2O sheet *via* pulsed laser deposition[6], Cu_2O deposited on ZnO nanorods through chemical vapor deposition[7], and aluminium-doped ZnO film sputtered onto Cu_2O films by chemical deposition[8]. However, the conversion efficiencies of Cu_2O/ZnO heterostructure solar cells were low. For instance, Cu_2O/ZnO heterojunction obtained by an electrodeposition method had an efficiency of 0.1%, which is much lower than theoretical limitation of 18%[9-10].

In this study, n-type ZnO nanorod arrays, p-type Cu_2O film and Cu_2O/ZnO heterostructures were synthesized *via* electrochemical deposition, and their morphology, crystal structures, electrical and optoelectronic characteristics, and external quantum efficiency (EQE) are reported.

2 Experiments

The electrodeposition of ZnO nanorods was performed using a CHI 660D electrochemical workstation with the fluoride-doped tin oxide (FTO) glass as the working electrode, a Zn sheet as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. ZnO nanorod arrays were obtained in two steps. The first step was galvanostatic electrolysis at 1×10^{-5} A for 30 min in an oxygen-saturated solution of 0.01 mol/L $ZnCl_2$ and 0.1 mol/L KCl. The second step was carried out at 80 ℃ and −1 V for 3 h in an oxygen-saturated solution of 9×10^{-4} mol/L $ZnCl_2$ and 0.1 mol/L KCl.

The electrodeposition of Cu_2O film was performed on FTO glass substrate, a Pt wire, and Ag/AgCl as the working, counter, and reference electrode, respectively. The deposition was conducted at 60 ℃ and −0.4 V for 60 min in a solution of 0.4 mol/L $CuSO_4$ and 3 mol/L lactic acid. The pH value was adjusted to 10 ~ 11 by adding NaOH solution. For the fabrication of a Cu_2O/ZnO heterojunction, Cu_2O film was directly deposited on ZnO nanorods instead of a FTO substrate, and other conditions were the same as above.

The morphology and crystal structures of the obtained nanostructures were characterized using a scanning electron microscope (SEM, JEOL JSM-6700F) and an X-ray diffractometer (XRD, D-MAX 2500/PC), respectively. The EQE of different nanostructures was measured on a Newport QE-PV-SI QE/IPCE system. Optoelectronic measurements were conducted on a Cascade M-150 probe station equipped with a sun simulator (Newport 96000) and a semiconductor analyser (Agilent B1500A).

3 Results and Discussion

SEM image of the obtained ZnO nanorod arrays is shown in Fig. 1(a). The product composed of uniform nanorods with an average diameter of ~150 nm and a length of ~1.5 μm. The diameter of ZnO nanorods became smaller with the decrease of $ZnCl_2$ concentration. On the other hand, it has been reported that Cl^- can convert ZnO nanorods into ZnO nanotubes[11-12]. As given in Fig. 1(b), Cu_2O film with a dimension of ~5.0 μm can be directly formed on the FTO substrate or the top surface of

ZnO nanorods. It is also found that some ZnO nanorods had been transformed into nanotubes during the deposition of Cu_2O film, which led to a weak contact/interface between ZnO nanorods and Cu_2O film, as revealed in Fig. 1(c). As an amphoteric oxide, ZnO can react with both acidic and alkaline ions to form salts. Thus, the electrodeposited ZnO nanorods can be transformed into nanotubes by a chemical etching process with H^+ or OH^- [9, 11]. In this study, the ZnO nanorods are transformed into nanotubes in the alkaline solution during the electrodeposition process of Cu_2O film.

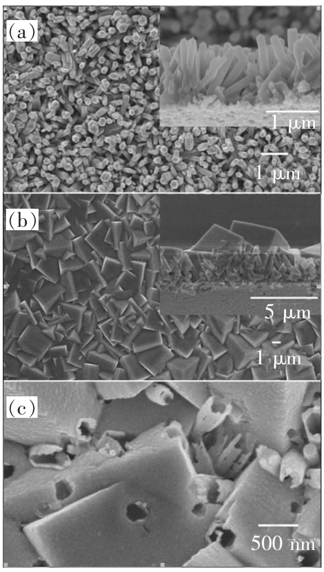

Fig. 1 SEM images of (a) ZnO nanorods, (b) Cu_2O/ZnO heterostructures, and (c) ZnO nanotubes formed from ZnO nanorods. Inset: SEM images of the cross sections of the samples.

The XRD patterns of ZnO nanorods, Cu_2O film, and Cu_2O/ZnO heterostructures are presented in Fig. 2. Besides the diffraction peaks of the FTO glass substrate (Fig. 2(a)), other typical peaks can be identified as hexagonal ZnO (JCPDF: 65-3411) or cubic Cu_2O (JCPDF: 05-0667). In Fig. 2(b), the strongest signal of ZnO nanorods is from (002), suggesting that ZnO nanorods grew along the *c*-axis; and other weak peaks including (101), (102) and (111) may result from the ZnO buffer layer formed by the galvanostatic electrolysis process. In Fig. 2(c), all peaks can be indexed to cubic Cu_2O, and the strongest peak at (111) indicates the fastest growth direction along (111) direction. In comparison to Fig. 2(b) and Fig. 2(c), no new peaks appeared for Cu_2O/ZnO heterostructures, and all peaks can be assigned to Cu_2O or ZnO (Fig. 2(d)). The signal of Cu_2O (111) is much stronger than that of ZnO (002), indicating that most of ZnO nanorods were covered by the Cu_2O film.

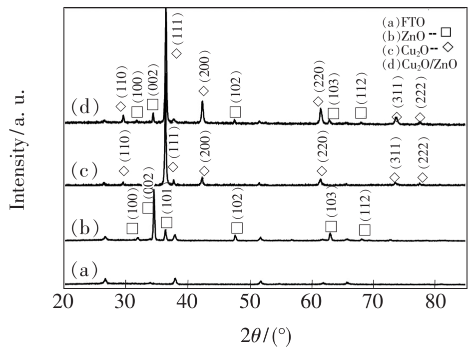

Fig. 2 XRD patterns of (a) FTO glass, (b) ZnO nanorods, (c) Cu_2O film and (d) Cu_2O/ZnO heterostructures.

Electrical characterizations on ZnO nanorods and Cu_2O film are given in Fig. 3(a). Current density-voltage (*J-V*) curves of both ZnO nanorods and Cu_2O film are nearly linear and symmetric, which indicates that there are Ohmic contacts between ZnO nanorods/Cu_2O film and the electrode materials of FTO substrate and silver paste. On the other hand, the *J-V* curve of Cu_2O/ZnO heterostructures is nonlinear and shows characteristics of p-n junctions (Fig. 3(b)). For example, at an external potential of −1.0 V, the current density was 0.015 and 0.045 $mA\cdot cm^{-2}$ in the dark and under the illumination of 46 $mW\cdot cm^{-2}$, respectively; while at +1.0 V, the current density was 0.117 and 0.31 $mA\cdot cm^{-2}$, respectively. The results are similar to another report on Cu_2O/ZnO nanostructures[9]. Under the illumination, electrons diffuse to the n-type ZnO region, whereas holes diffuse to the p-type Cu_2O region in the applied electric field. As a result, the electrons and holes are transferred to two opposite electrodes to generate a photocurrent as shown in Fig. 3(b). However, no obvious open-circuit voltage (V_{oc}) or short-circuit (J_{sc}) current could be observed from the Cu_2O/ZnO nanostructures. This could be due to the weak contact between ZnO nanorods and Cu_2O films. As demonstrated in Fig. 1(c), ZnO nanorods had been converted to ZnO nanotubes while Cu_2O was formed surrounding the ZnO nanorods. On the other hand, ZnO buffer layer could also have been damaged during the formation of Cu_2O films.

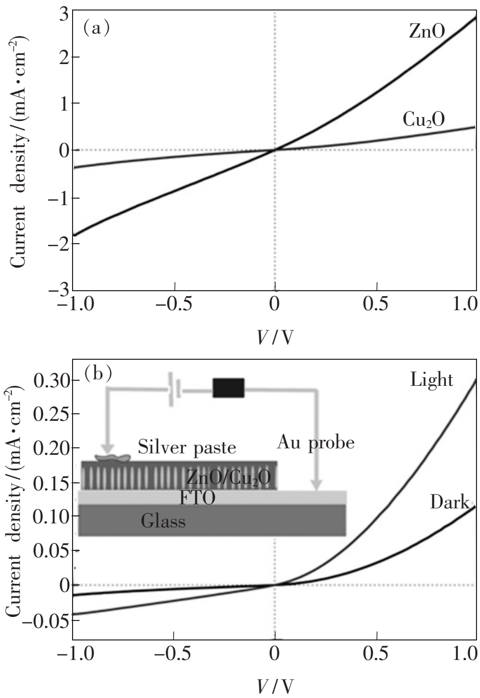

Fig. 3 *J-V* characteristics of (a) ZnO nanorods, Cu_2O films, and (b) Cu_2O/ZnO heterostructures (Inset: an illustration of the testing configuration).

EQE measurements (Fig. 4) show that there is a singular strong EQE peak at 340 nm for ZnO nanorods, but there are three EQE peaks at 340, 450, and 560 nm for Cu_2O film. It is interesting to observe that there are only two EQE peaks at 340 nm and 450 nm for the Cu_2O/ZnO heterostructure and the peak at 560 nm disappears, which could be related

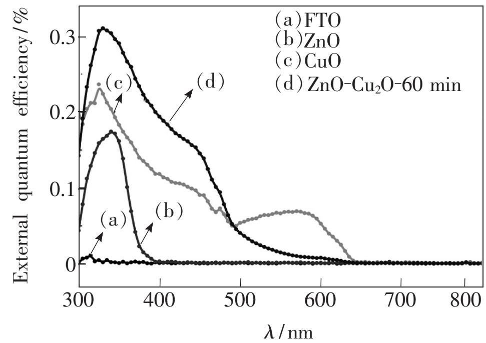

Fig. 4 External quantum efficiency of (a) FTO glass, (b) ZnO nanorods, (c) Cu_2O film, and (d) Cu_2O/ZnO heterostructures measured in 0.1 mol/L Na_2SO_4 solution.

to the formation of an interface between Cu_2O and ZnO. Detailed mechanism on the optoelectronic conversion at the Cu_2O/ZnO interface is under study for future applications of Cu_2O/ZnO heterojunction solar cells[13].

4 Conclusion

ZnO nanorod array, Cu_2O film and Cu_2O/ZnO heterojunctions can be fabricated by a low-cost and environment-benign electrochemical deposition method. Both ZnO nanorods and Cu_2O film have Ohmic contacts with FTO substrate and silver paste while a p-n junction forms between Cu_2O film and ZnO nanorods. The external quantum efficiency of the Cu_2O/ZnO heterojunction is higher than that of ZnO nanorods and Cu_2O film, which clearly indicates that the p-n junction between Cu_2O film and ZnO nanorods can facilitate the separation and transport of charge carriers.

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