



Novel Semiconductor-Liquid Heterojunction Solar Cells Based on Cuprous Oxide and Iodine Electrolyte



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ABSTRACT

In this study, we report a novel cuprous oxide-electrolyte heterojunction solar cell fabricated on a copper foil substrate. A chemical oxidation method was used to fabricate a cuprous oxide electrode that was then combined with an electrolyte and platinum electrode to form a cuprous oxide-electrolyte heterojunction solar cell. Various analytic technologies were employed to characterize the cuprous oxide electrodes. Scanning electron microscopy (SEM) was employed to observe the surface morphology; energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were used to characterize the material properties; and ultraviolet-visible (UV-vis) spectroscopy was used to analyze the optical properties of the cuprous oxide. The results show that the particle size of the cuprous oxide ranged from approximately 1–2 μm , which agglomerated and formed coral-shaped structures with lengths and widths of 10–20 and 5–6 μm , respectively, and with absorption wavelengths of 300 to 640 nm. The cuprous oxide-electrolyte heterojunction solar cell was also characterized, and the influence of various iodine (I_2) concentrations on device efficiency was studied. The results show that when the I_2 concentration of the electrolyte was 10 mM, the short-circuit current density, open-circuit voltage, fill factor, and device conversion efficiency of the cuprous oxide-electrolyte heterojunction solar cell were 3.52 mA/cm², 0.64 V, 0.32, and 0.72%, respectively.

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1. Introduction

Energy shortage and global environmental pollution have led to an increased interest in solar cells [1–3]. In 1991, Grätzel et al. developed dye-sensitized solar cells (DSSCs) based on high-surface-area TiO_2 nanoparticles [4]. DSSCs immediately attracted substantial attention because of their high efficiency, simple device structures, cost-effective manufacturing, and variety and flexibility in applications [5–8]. DSSCs are composed of transparent conductive oxides (TCO), TiO_2 nanoparticle thin-film electrodes, dye, electrolyte, and platinum counter electrodes [9]. Numerous scientists have focused on enhancing the efficiency of DSSCs [10–15]. These efforts include developing porous TiO_2 nanoparticle-electrode fabrication technologies, designing highly effective and organic dye formulas, developing solid-state electrolytes, studying flexible plastic substrates, identifying favorable counter electrodes, and improving

device encapsulation technologies. Many of these studies have generated breakthroughs. In DSSCs, the main function of the TiO_2 electrode is to provide a transport path for photo-generated electrons. The electrode must also provide a large dye-absorption surface area and pores for electrolyte penetration. Thus, TiO_2 electrodes are critical structures in DSSCs. In addition to TiO_2 , other wide-bandgap oxides, such as ZnO [16], SnO_2 [17], and Nb_2O_5 [18], can also be used in the working electrode of the DSSC.

Cuprous oxide is a direct-bandgap semiconductor with an energy bandgap of 2.0 eV. Its favorable material properties have gained considerable attention in applications involving photoelectric devices [19–21]. Cuprous oxides are economical, nontoxic, naturally abundant, highly absorptive in the visible spectrum, and they can be deposited as thin-film structures by using various simple low-cost deposition methods. Therefore, studying of the material properties of cuprous oxide contributes to improvements in its effectiveness and applicability in cuprous oxide solar cells. Georgieva et al. used an electroplating method to directly deposit cuprous oxide on an indium tin oxide (ITO) TCO to form an ITO- Cu_2O -graphite structure, yielding 4–6 μm films with an optical energy bandgap of 2.38 eV [22]. Jeong et al. proposed using an

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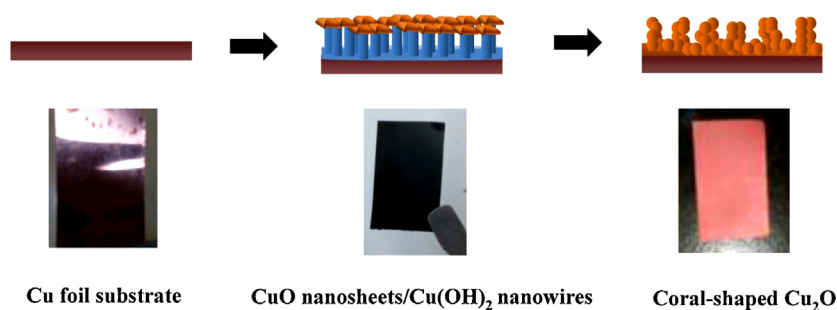


Fig. 1. The fabrication process of the cuprous oxide electrode.

electrodeposition method to fabricate ZnO-Cu₂O heterojunction solar cells, but yielded a maximal conversion efficiency of only 0.41%. Numerous improvements are yet to be implemented, such as the rigorous control of electrodeposition conditions that could improve defects in Cu₂O [23]. Mittiga et al. injected a mixture of N₂ and O₂ gas into a high-temperature tube furnace to oxidize copper that was used to fabricate high-quality cuprous oxide products. Subsequently, TCO and anti-reflective MgF₂ film were deposited onto the cuprous oxide by using an ion-beam sputtering and a vapor deposition method, respectively, to form a Cu₂O-ZnO-ITO-MgF₂ structure, yielding a conversion efficiency of 2.01% [24]. In addition, Cu₂O was sputtered onto n-ZnO nanowire solar cells on a ZnO-Ga/glass template. The ZnO used is an n-type semiconductor with a bandgap of 3.37 eV; the Cu₂O is a p-type semiconductor. Thus, a p-n junction was formed by depositing the p-Cu₂O onto the n-ZnO [25,26].

In this study, a novel Cu₂O-electrolyte heterojunction solar cell was fabricated. A copper foil substrate was first immersed in an aqueous solution containing a mixture of (NH₄)₂S₂O₈ and NaOH. After 30 min of reaction at room temperature (25 °C), the copper substrate formed a Cu(OH)₂/CuO structure. After sintering at 500 °C in a nitrogen atmosphere, the Cu(OH)₂ dehydrated to CuO, which then deoxidized to Cu₂O. Cuprous oxide was used as a working electrode in combination with an electrolyte and platinum counter electrode to form a cuprous oxide-electrolyte heterojunction solar cell. Furthermore, the influence of various iodine concentrations on the solar cell device efficiency was investigated.

2. Experiments

2.1. Fabrication of the Cuprous Oxide Electrode

The copper foil substrate was first cleansed using acetone in an ultrasonic bath for 5 min, and then further cleansed using deionized (DI) water, 1 M hydrochloric acid, and DI water solutions, after which the copper substrate surface was blow dried using nitrogen gas. Subsequently, 10 g of NaOH and 2.85 g of (NH₄)₂S₂O₈ were added to 10 mL of DI water and ultrasonically vibrated for 30 min. The copper substrate was placed into this solution for 30 min. Subsequently, the sample was removed from the solution and left to dry at room temperature and then placed into a tube furnace. Initially, the gas pressure of the tube furnace was vacuum pumped to 7 mTorr, and then the tube furnace was purged with nitrogen at a rate of 300 cc/min. The outlet pressure of the nitrogen bottle was maintained at a fixed value, and the vacuum-pumping and nitrogen-purging processes were maintained for 3 min to ensure that the tube furnace contained a pure nitrogen atmosphere. Finally, the vacuum pump was deactivated and the nitrogen injection was switched off after the N₂ pressure inside the furnace reached 300 torr. The sample in the tube furnace was heated to 500 °C and sintered for 4 h in a pure nitrogen

atmosphere. In this study, a chemical oxidation method was used to immerse the copper substrate in a solution of 0.125 M (NH₄)₂S₂O₈ and 2.5 M NaOH for 30 min at room temperature. The copper substrate was converted into Cu(OH)₂/CuO structures. Subsequent heat treatment at 500 °C in nitrogen atmosphere dehydrated the Cu(OH)₂ into CuO, which then deoxidized to form Cu₂O. Fig. 1 depicts the fabrication process of the cuprous oxide electrode.

2.2. Characterization of the Cuprous Oxide Electrode

This study employed various analytic technologies to characterize the cuprous oxide electrode. Scanning electron microscopy (SEM) was employed to analyze the surface morphology of the cuprous oxide electrode. Energy-dispersive X-ray spectroscopy (EDS) was used to obtain the elemental ratio of Cu and O atoms. Raman spectroscopy was used to confirm the material composition of the cuprous oxide electrode. X-ray diffraction (XRD) was used to identify the crystal structure of the cuprous oxide electrode. X-ray photoelectron spectroscopy (XPS) was used to determine the surface composition of the cuprous oxide electrode. Ultraviolet-visible (UV-vis) spectroscopy was used to analyze the optical characteristics of the cuprous oxide electrodes.

2.3. Fabrication of the Solar Cell Device

Fig. 2 shows the schematic structure of the cuprous oxide-electrolyte heterojunction solar cell. The heterojunction solar cell was composed of a cuprous oxide working electrode, electrolyte, and a Pt counter electrode. The fabrication method of the cuprous oxide is detailed in Section 2.1. Fabrication of the counter electrode proceeded as follows. A fluorine-doped tin oxide (FTO) glass substrate was obtained, and two holes had been drilled into the substrate in advance to enable injection of the electrolyte. The substrate was then ultrasonically cleaned using DI water and ethanol (each for 3 min). The cleaned substrate surface was then

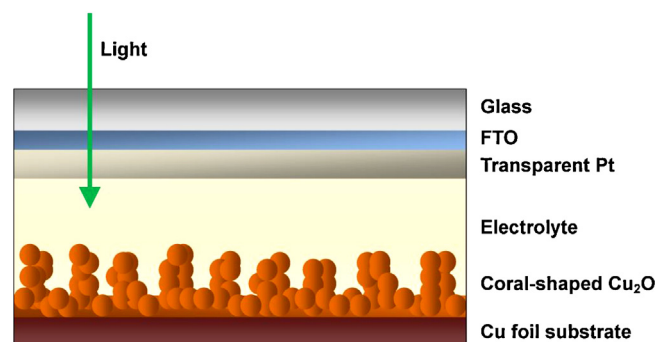


Fig. 2. The schematic structure of the novel cuprous oxide-electrolyte heterojunction solar cell.

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