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Regular Article

Effective performance for undoped and boron-doped double-layered nanoparticles-copper telluride and manganese telluride on tungsten oxide photoelectrodes for solar cell devices

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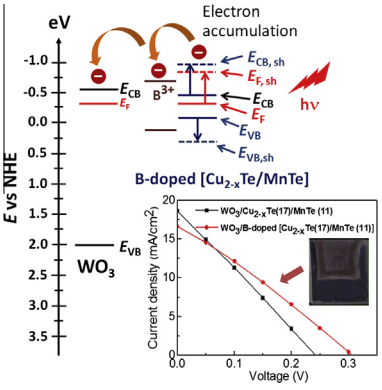
HIGHLIGHTS

- Boron-doped [$Cu_{2-x}Te$(17)/MnTe (11)]/WO_3 was first synthesized for solar cells.
- The band alignment was organized for boron/MnTe onto boron/$Cu_{2-x}Te$ NPs.
- A narrower E_g = 0.58 eV was yielded by a boron-doped double layer structure.
- Electron accumulation attributes the gap widening and electron transferring.
- The highest η of 1.41% was yielded for the boron-doped double-layered structure.

GRAPHICAL ABSTRACT



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ABSTRACT

This work demonstrates the synthesis of a novel double-layered $Cu_{2-x}Te$/MnTe structure on a WO_3 photoelectrode as a solar absorber for photovoltaic devices. Each material absorber is synthesized using a successive ionic layer adsorption and reaction (SILAR) method. The synthesized individual particle sizes are $Cu_{2-x}Te$(17) ~5–10 nm and MnTe(3) ~2 nm, whereas, the aggregated particle sizes of undoped and boron-doped $Cu_{2-x}Te$(17)/MnTe(11) are ~50 and 150 nm, respectively. The larger size after doping is due to the interconnecting of nanoparticles as a network-like structure. A new alignment of the energy band is constructed after boron/MnTe(11) is coated on boron/$Cu_{2-x}Te$ nanoparticles (NPs), leading to a narrower E_g equal to 0.58 eV. Then, the valence band maximum (VBM) and conduction band minimum (CBM) with a trap state are also up-shifted to near the CBM of WO_3, leading to the shift of a Fermi level for ease of electron injection. The best efficiency of 1.41% was yielded for the WO_3/boron-doped [$Cu_{2-x}Te$ (17)/MnTe(11)] structure with a photocurrent density (J_{sc}) = 16.43 mA/cm^2, an open-circuit voltage (V_{oc}) = 0.305 V and a fill factor (FF) = 28.1%. This work demonstrates the feasibility of this double-layered structure with doping material as a solar absorber material.

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1. Introduction

Semiconductor-sensitized solar cells (SSCs) have attracted particular attention and have shown a promising start toward the development of next generation solar cells [1–3], which can replace dye-sensitized solar cells. Fabrication of SSCs for photovoltaic applications has been based on two types, namely, liquid junction and solid-state solar cells. The key component of an SSC is a metal oxide photoelectrode covered with thin semiconductor nanoparticles or quantum dots as a sensitizer. Nanostructured semiconductor sensitizers have several advantages such as high extinction coefficients [4], tunable absorption ranges based on the quantum dot size effect [5] and multiple excitons generated by a single photon [6]. Although semiconductor sensitizers have several advantages in the promotion of high power conversion efficiency, one of the factors that should be considered is doping with a nonmetal element in a semiconductor solar absorber.

The doping of a nonmetal element into semiconductor materials for a broad-band solar absorber is one of the treatments that yield up-converted-efficient photovoltaic properties due to the suppression of the impaired thermal instability of the cells, which leads to a reduction in charge carrier recombination. It has also been introduced to improve the crystalline morphology and the photovoltaic performance [7]. Nonmetal doping in materials has been reported by many researchers such as multilayered-phosphorus-doped silicon on a SiO_2 matrix [8], nitrogen-doped CdSe as the sensitizer on a TiO_2 photoelectrode [9] and carbon-doped CdS which played a crucial role in enhancing the photoelectrochemical activity [10]. In our previous work, boron-doped MnTe semiconductor nanoparticles were reported and a slight decrease in the energy band gap was performed after boron doping due to the larger scale in the size of the material. The optimal SILAR cycles yielded the best power conversion efficiency of 0.04% and the efficiency decreased by 85% for the undoped condition [11]. In recent developments, co-sensitized photoelectrodes, each with a different energy gap, have been studied for their photovoltaic properties, their effective range of absorption and their cascade structure for efficient charge transport, such as co-sensitization-CdS/CdSe [12–16], CdSe/CdTe [17], PbS/Bi_2S_3 [18], PbS/CdS [19] and CdS/Bi_2S_3 [20].

As a sensitizer, binary p-type semiconductor-copper telluride ($Cu_{2-x}Te$) has a high thermal conductivity at a room temperature of 4 W/m K [21] and the highest field effect hole mobility was found to be ~18 $cm^2/V\,s$ [22], in which the crystal structure depended upon the value of x ($1 \leqslant x \leqslant 2$) [23,24]. The energy gap of the copper telluride is about 0.9–1.1 eV, leading to the absorption of an incident light in the near-infrared (NIR) region [25] and also is equal to the optimal band gap of 1.13 eV for a photovoltaic device [26], resulting in a good solar absorber. $Cu_{2-x}Te$ has a high absorption coefficient of $\alpha = 4 \times 10^4$–$2 \times 10^5\ cm^{-1}$ as well as a high carrier concentration of 10^{19}–$10^{22}\ cm^{-3}$ [27]. Manganese telluride (MnTe) is a p-type semiconductor with a narrow optical direct band gap of 1.25–1.35 eV [28–30]. Its absorption coefficient is almost $\alpha = 8 \times 10^4\ m^{-1}$ [30], with a high density of impurity charge carriers (donor density) of 4×10^{17} photons/cm^3 and charge carrier mobility (μ) of 5.41 $cm^2/V\,s$, favoring it as a charge transport in a device and this value increases almost linearly with increasing temperature [31–33].

Furthermore, an appropriate metal oxide photoelectrode provides good power conversion efficiency in SSCs due to the electrical structure of the conduction band alignment compared with that of a semiconductor sensitizer. Note that the lower conduction band alignment will support a higher mobility of injected photoelectrons to the external circuit and also up-shifts the Fermi level of metal oxides compared with a redox level of electrolyte. These factors provide a higher open-circuit voltage (V_{oc}). However, higher power conversion efficiency continues to require investigation.

Indeed, tungsten oxide (WO_3), as a metal oxide photoelectrode, has carrier mobility of 10 $cm^2/V\,s$ for photoelectrochemical (PEC) water splitting [34] and a diffusion coefficient of 0.25 cm^2/s in a single crystal [35], which can replace ZnO and TiO_2 due to its lower conduction band edge. The conduction band edge (E_{CB}) of WO_3 is equal to −4.60 eV compared to that of ZnO (E_{CB} = −4.19 eV) and TiO_2 (E_{CB} = −4.21 eV) [36], which allows the injection of more photogenerated electrons from the semiconductor sensitizer to the photoelectrode.

In this work, $Cu_{2-x}Te$ and MnTe were synthesized as a broad band co-sensitizer on a WO_3 electrode for solar cell devices and a non metal-boron (B^{3+}) element was used as a dopant in double-layered nanoparticle sensitizers. The characteristics, optical, electrical and photovoltaic properties on a number of SILAR cycles and the effect of boron doping were investigated. Furthermore, the determination of valence bands was performed using X-ray photoelectron spectroscopy (XPS) to explain the mechanism of electron injection supporting the photovoltaic performance. In addition, surface analysis was studied by obtaining the chemical composition of each sample surface.

2. Experimental section

2.1. Preparation of WO_3 photoelectrodes

A 1.42 g tungsten oxide nanopowder (particle size ≈ 35–40 nm) was mixed with 0.7 g ethyl cellulose and 7 mL terpineol, and then the mixed substance was dissolved in 10 mL ethanol and stirred for 60 min. The WO_3 film was prepared by spin coating of WO_3 droplets on a clean fluorine-doped tin oxide glass (FTO, 13 Ω/cm^2, Aldrich) and then the coated film was fired at 450 °C for 30 min.

2.2. Synthesis of MnTe and $Cu_{2-x}Te$ nanoparticles (NPs)

To synthesize MnTe NPs, the WO_3 photoelectrode was immersed in a 0.05 M $Mn(NO_3)_2{\cdot}4H_2O$ ethanol solution at room temperature for 1 min as a precursor for Mn^{2+} depositing on the WO_3 surface, and then rinsed thoroughly with ethanol and heated in air at 60 °C until dry. Then, the photoelectrode was immersed in a 0.05 M Na_2O_3Te methanol/water (7:3 v/v) solution at room temperature for another 1 min as a precursor for Te^{2-}, then rinsed again with methanol and heated in air at the same temperature. The reaction of the Mn^{2+} and Te^{2-} ions on the WO_3 surface transformed into MnTe NPs coated on the WO_3 surface. The step of the dipping and heating procedures was referred to as one SILAR cycle. The SILAR cycle of MnTe was determined as n, MnTe(n). In addition, the WO_3 photoelectrode was applied using the same procedure as above. Instead of the $Mn(NO_3)_2{\cdot}4H_2O$ precursor, a 0.05 M $Cu(NO_3){\cdot}3H_2O$ ethanol solution was prepared to obtain Cu^{2+}. The SILAR cycle of $Cu_{2-x}Te$ was determined as m, $Cu_{2-x}Te(m)$. Single-layered and double-layered structures were prepared to investigate the efficient photovoltaic properties in terms of various SILAR cycles of MnTe and $Cu_{2-x}Te$, the inner and outer layer structures of each material and the effect of a cascade alignment structure, i.e., $Cu_{2-x}Te(n)$/MnTe(m) or MnTe(m)/$Cu_{2-x}Te(n)$. A 0.3 M boron powder was used as a dopant for both $Cu_{2-x}Te$ and MnTe sensitizers deposited on the WO_3 photoelectrodes to compare the respective photovoltaic performances.

2.3. Preparation of Cu_2S counterelectrodes (CEs)

A brass plate was polished using sand paper and immersed in 37% by volume HCl at 70 °C for 10 min, then washed thoroughly