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OPINION

Flexible fiber-shaped $CuInSe_2$ solar cells with single-wire-structure: Design, construction and performance

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Abstract
Fiber-shaped solar cells (FSCs) have attracted increasing interest in recent years due to their numerous advantages. Herein we report the first prototype of highly flexible all-solid-state single-wire FSCs by using $CuInSe_2$ (CIS) as the model photoactive semiconductor. CIS layer is electrodeposited on a flexible Mo wire as the substrate. Subsequently, CdS, ZnO and ITO layers are orderly deposited on the Mo/CIS wire, and each upper layer ensures full contact with the underlying layer, resulting in an excellent structural uniformity along circumference of the FSC. This Mo/CIS/CdS/ZnO/ITO single-wire FSC exhibits a power conversion efficiency of 2.31%, which is one of the highest values in all reported FSCs. More importantly, the present all-solid-state single-wire FSC exhibits stable conversion efficiency (2.16-2.32%) during rotation (0~360°), bending (0~360°) and long-time aging (stored at 60 °C for 600 h) processes, which makes it possible to fabricate very long single-wire FSC with stable efficiency for weaving large-area devices and/or the stereoscopic cell textiles. Our method provides a new and general approach for fabricating flexible single-wire FSC with various kinds of photovoltaic semiconductor materials, and it also would be applicable to develop other flexible electronic circuits.

Introduction

The quest and demand for clean and economical energy sources have drawn much attention in the development of solar applications for many decades [1]. Direct conversion of

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solar energy to electrical energy by using fiber-shaped solar cells (FSCs) has attracted increasing interest in recent years. Compared with traditional planar solar cells, FSCs have many advantages, such as lightweight, device flexibility and the expanded substrate sources (conductive metal wire, optical fiber, carbon etc.) [2–4]. In particular, the length of FSCs could stretch greatly, which provides more space for large-area devices and makes the stereoscopic cell textiles in various forms be possible.

Up to now, three kinds of FSCs with different structures have been chiefly developed. The first kind is solar cells with optical fiber as the wire-shaped substrate [5–7]. Such organic solar cells [5] and dye-sensitized solar cells (DSSCs) [6,7] were constructed by depositing typical organic materials (P3HT: PCBM) and (dye-sensitized-) ZnO nanowire on optical fibers as the working electrode (WE), respectively. The light illuminated the optical fiber from one end along the axial direction, and its internal reflection within the fiber created multiple opportunities for energy conversion at the interfaces [6]. But the optical fiber has relatively high cost and poor flexibility for potential weaving process of FSCs. The second kind of FSCs has a double-wire structure, in which a metal wire as the counter electrode (CE) is twisted along another primary core wire coated by active layers as the WE. For example, Gaudiana et al. [8] used the stainless wire coated with PCBM as the WE, and then wrapped another metal wire as the CE, resulting in an organic FSC with a power efficiency of up to 3.27%. In addition, Zou et al. [9] firstly reported a FSC based on DSSC by using stainless steel fiber coated with dye-sensitized porous TiO_2 as the WE and Pt wire coated with a polymer protective layer as the CE. Subsequently, FSCs based on DSSCs with the double-wire structure have been well investigated and developed by several famous research groups [10–14], for example, Zou et al. [13] and Wang et al. [14] developed novel FSCs by replacing stainless steel fiber with carbon fiber, respectively. However, for the second kind of FSCs, electrical contact between the two wire electrodes is not good and reliable, particularly when FSCs are bent [15]. Moreover, the shadow effect from the metal-wire CE limits the photoabsorption of active layer on the wire-shaped WE. In addition, a major portion of the active layer may not be directly covered by the wire-shaped CE, and the holes (or I^-/I_3^- ions) have to travel a certain distance along the circumference before reaching the CE [15]. To solve these problems, the third kind of FSC with a single-wire structure has been proposed, in which one primary core wire with active layers is fully covered by a film-shaped CE, and the film-shaped CE ensures full coverage, minimal distance of holes (or the I^-/I_3^- ions) diffusion and uniform illumination along circumference through the entire FSC. Very recently, two stable single-wire FSCs based on DSSCs with a photoelectric conversion efficiency of 1.6% and 0.02% have been fabricated by using transparent carbon-nanotube (CNT) films and graphene film as the CE to wrap one primary core wire coated with dye-sensitized TiO_2 nanotube and ZnO nanowire, respectively [15,16]. For all three kinds of FSCs based on DSSCs, unfortunately, the presence of organic liquid electrolytes would cause some problems, such as leakage and evaporation of solvent, and therefore results in practical limitations to sealing and long-term operation, particularly when FSCs are deformed during the weaving process. Therefore, it is necessary to further develop single wire FSC without the liquid component.

It is well known that there are many kinds of thin film solar cell based on different inorganic semiconductor including CdTe [17,18], PbSe [19,20], PbS [21,22], GaAs [23], $Cu(In,Ga)(S,Se)_2$ [24–26]. All these semiconductor film solar cells have been constructed on the flat (solid or flexible) substrates and exhibit high power conversion efficiencies. To the best of our knowledge, there is no report on the preparation of FSCs based on these inorganic semiconductors. Herein, we report the first prototype of fabricating all-solid-state flexible single-wire FSCs by using $CuInSe_2$ (CIS) as the model photoactive semiconductor. Such CIS-based FSC exhibits a power conversion efficiency of 2.31%, and it can be easily bended and deformed with excellent performance stability.

Materials and methods

Materials

All of the chemicals were AR grade and used as received from Sinopharm Chemical Reagent Co. (China). Flexible Mo wire with diameter of 50 ± 5 μm was obtained from Nanjing Sysure Material Company (China). The saturated calomel electrode (SCE) was purchased from Shanghai Chenhua Instrument Company (China).

Fabrication of Mo/CIS/CdS/ZnO/ITO single-wire FSC

A flexible Mo wire with the length of 15–20 cm and diameter of 50 ± 5 μm was fixed at both ends on a plastic support that was designed by our group (Figure S1a in the Supporting information), and then it was cleaned with piranha solution (concentrated sulfuric acid/30% hydrogen peroxide, 3:1 v/v) for 10 min and rinsed with distilled water. One end of Mo wire on plastic support was untied, then threaded through a clean titanium tube (tube diameter: 2 cm, length: 10 cm, thickness: 1 mm), and fixed on the plastic support again (Figure S1b and c). Then the plastic support with Mo wire and titanium tube was immersed in an aqueous electrolyte solution containing $CuSO_4$ (1 mM), $InCl_3$ (20 mM), SeO_2 (4 mM) and citrate sodium (25 mM) with pH of 2.0 adjusted by H_2SO_4 (0.1 M). The Mo wire was used as the wire-shaped WE with titanium tube as the CE and a saturated calomel electrode (SCE) as the reference electrode (Figure S1d). Electrochemical experiments were performed on a CHI 660D workstation (Shanghai Chenhua Instrument Company). CIS layer on the Mo wire was electrodeposited at room temperature (25 °C) under potentiostatic condition of $-0.7\sim-0.8$ V (versus SCE) for $5\sim20$ min. After rinsed with distilled water, Mo/CIS wire was untied from the plastic support and then annealed in an Ar/Se atmosphere at 500 °C for 10 min. Subsequently, CdS layer (ca. 50 nm thick) was deposited on the annealed Mo/CIS wire by using a chemical bath approach similar to that described previously (Figure S1e) [27]. At last, the fabrication of single-wire FSC was completed by depositing 60-nm-thick ZnO layer and 300-nm-thick ITO layer on the continuously rotating Mo/CIS/CdS wire (Figure S1f) with JPG-450 (SKY Technology