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Wet-process Fabrication of Low-cost All-solid Wire-shaped Solar Cells on Manganese-plated Electrodes

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ABSTRACT

All-solid wire-shaped flexible solar cells are assembled for the first time on low-cost Mn-plated wires through wet-process fabrication under low temperature and mild pH conditions. With a price cheap as the steel, metal Mn can be easily plated on almost any substrates, and evidently promote the photovoltaic efficiency of wire-shaped solar cells on various traditional metal wire substrates, such as Fe and Ti, by 27% and 65%, respectively. Flexible solar cell with much lower cost and weight is assembled on Mn-plated polymer substrate, and is still capable of giving better performance than that on Fe or Ti substrate. Both its mechanical and chemical stability are good for future weaving applications. Owing to the wire-type structure, such low-cost metals as Mn, which are traditionally regarded as unsuitable for solar cells, may provide new opportunities for highly efficient solar cells.

1. Introduction

The rapid development of wearable electronic equipment has given rise to the global need to identify a flexible power source. Considerable effort has been devoted to nano-oxide-based solar cells, such as dye-sensitized solar cells (DSSCs) and perovskite-type solar cells [1–4], because of their advantages in achieving low cost and high flexibility. For flexible nano-oxide-based solar cells, such nano oxides as ZnO and TiO_2 are assembled on a flexible conducting substrate as the photoanode in which photoelectric conversion reaction occurs [5–9]. A serious hindrance preventing the widespread application of flexible solar cell is the shortage of cost-effective electrode. Traditional electrodes based on expensive transparent conductive oxide (TCO) substrates have serious troubles with the high cost, the low conductivity, the poor flexibility, and the energy-level mismatch [10]. A novel TCO-less wire-shaped solar cell has recently been reported [11–13]. Owing to the new device structure, the range of electrode materials is significantly enlarged to include even opaque metal materials, such as Ti or Fe [14–16]. However, neither Ti nor Fe are suitable for wide applications in flexible solar cells because of their disadvantages, such as high mass density, high melting point, and difficulties in plating on other substrates via wet process.

In this work, stable all-solid flexible wire-shaped dye-sensitized solar cells (W-DSSC) were for the first time assembled on various Mn-plated wires through a simple all-wet process under low temperature and mild pH conditions. All-solid dye-sensitized solar cells is best known for its stability. After a layer of Mn is inserted between the nano oxide layer and the conducting substrates, energy-conversion efficiency could be evidently improved because of the good conductivity and low surface working function (4.1 ev) of Mn [17]. A flexible solar cell is also assembled on lightweight and low-cost polymer wire. Theoretically, Mn-based electrode is suitable for other solar cells, such as perovskite-type solar cells. Owing to the wire-type device structure, such low-cost metals as Mn, which are traditionally regarded as unsuitable for solar cells, will provide new chances for various types of solar cells.

2. Experimental

2.1. Methods and Materials

Mn was deposited via electroplating on different wire substrates, including Cu (200 μm), Ti (200 μm), Fe (250 μm), and polymer wire (260 μm). For an insulated polymer wire, a layer of Cu was deposited via the chemical plating method [18,19] before the electro-plating. During the chemical-plating process, the substrate was bathed at 50 °C for 40 min in a solution of $CuSO_4$ (0.032 M), ethylenediaminetetraacetic acid disodium salt (EDTA) (0.054 M), HCHO (0.096 M), and NaOH (0.188 M). During the electroplating process, the wire substrate was employed as the cathode, whereas $PbSb_{0.0003}Sn_{0.0003}Ag_{0.0003}$ alloy rod (diameter = 5.0 mm) was employed as the anode. The distance between the

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two electrodes was 1 cm. The electrolyte is an aqueous solution of $MnSO_4$ (0.059 M) and H_2SeO_3 ($2.7\cdot10^{-4}$ M). After electro-plating for 1 min, the substrate was cleaned using de-ionized water and then dried. ZnO-nanowire arrays were grown on the substrate in a solution of zinc acetate and hexamethylene tetramine at 95 °C for 10 h [20–23]. After cleaning with de-ionized water and drying in vacuum, the as-prepared photoanode was sensitized in an ethanol solution of N719 (Solaronix, Switzerland) for 24 h. Before testing, a layer of CuI was coated on the sensitized photoanode at 130 °C under N_2 atmosphere using CuI/CH_3CN solution [11]. Then, the Au wire (99.9%) was evenly twisted around the photoanode (pitch = 0.75 mm) for use as the counter electrode (CE).

2.2. Characterization

The photo-electrochemical tests were conducted on the electrochemical working station (CHI660D, Shanghai Chenhua). The light source was an AM1.5 standard solar simulator (San-Ei Electric, XES40, Japan). The light intensity was at 100 mW/cm^2. The effective area employed in the photocurrent density calculation was the projecting area of the wire device. The morphology of the electrode was characterized using scanning electron microscopy (SEM) (S570, Hitachi). The electrochemical impedance spectroscopy (EIS) was also recorded on the electrochemical working station (CHI660D, Shanghai Chenhua). EIS was conducted at a bias voltage of 0 V in the dark.

3. Results and Discussion

3.1. The structure and performance of the devices

As demonstrated in Figs. 1a and b, wire-shaped DSSCs with spiral-wound structure were assembled. A layer of Mn (1 μm) was coated on various wires (Fig. 1c). A layer of ZnO nano arrays with a thickness of 7∼8 μm was then grown on the Mn layer. The CuI penetrated into tiny gaps between ZnO nano wires to collect holes from the dye and then transferred to the counter electrode (Fig. 1e). The photovoltaic performances of all-solid devices based on different wire substrates are compared in Fig. 1f. For devices on Fe wire and Ti wire, their photovoltaic performance could be promoted by 27% and 65%, respectively, after a layer of Mn was plated. It worked not only on commonly used metal wires, such as Fe and Ti, but also on Cu wire, which was originally unsuitable for DSSC applications. A device based on the lightweight and low-cost polymer wire was also assembled. Its photovoltaic performance was even better than that of the traditional substrate, such as Ti and Fe. For traditional liquid or quasi-solid type DSSC, Mn is inapplicable due to certain drawbacks, including opaque and chemical instability in liquid or quasi-solid electrolyte ($\psi_{Mn(II)/Mn(0)}<0$). These disadvantages overshadow advantages, such as low work function of 4.1 V. These problems were well avoided in all-solid wire-shaped DSSCs based on semiconductive hole-transport materials, such as CuI, which is known for its stability.

It is noteworthy that, all-solid DSSCs based on Cu\\Mn wire were better than those on Ti\\Mn or Fe\\Mn. The efficiency of these DSScs reached above 0.818%, which is the best ZnO-type wire-shaped DSSC based on all-solid CuI electrolyte [15,24]. Such metals as Cu, which are traditionally regarded as unsuitable photoanode materials, may provide new chances for solar cells.

3.2. Optimization of the Mn plating condition

The electroplating voltage and time for preparing Cu/Mn electrodes were optimized (Fig. 2). As indicated in Fig. 2a, Mn tends to grow slowly and to form island-shape crystals at low voltage, which is difficult to cover the entire Cu surface. At about 3.1 V, a

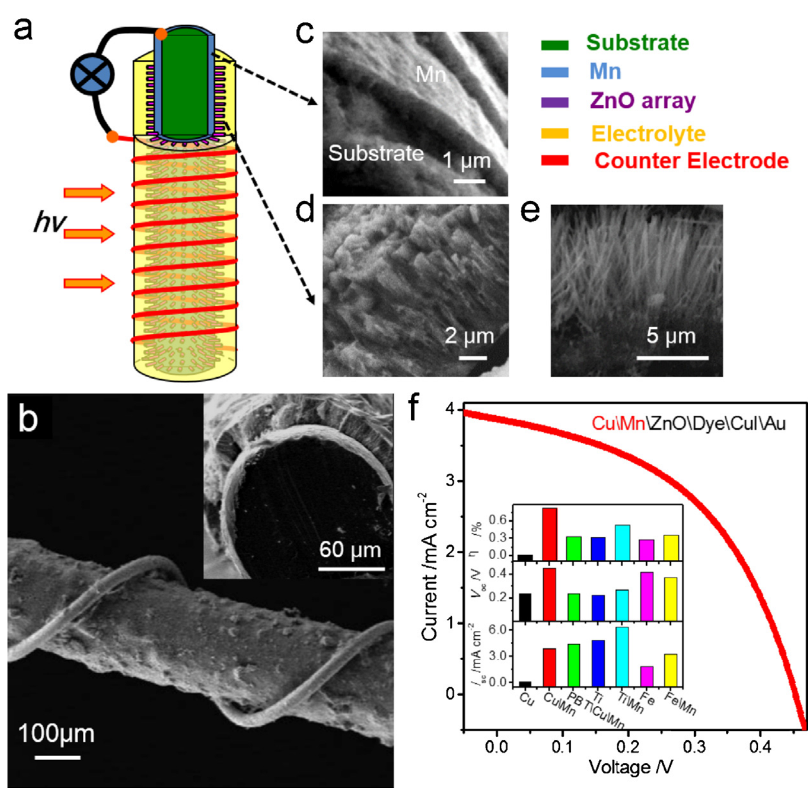

Fig. 1. (a) Schema of the device; (b–e) SEM images of the DSSC: a complete device, Cu\\Mn wire, CuI\\ZnO interface, and the ZnO nano arrays, respectively; (f) I–V curve under illumination. Insert is a comparison among different metal substrates: Cu, Cu\\Mn, PBT\\Cu\\Mn, Ti, Ti\\Mn, Fe, and Fe\\Mn.