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Highly efficient tandem photoelectrochemical solar cells using coumarin6 dye-sensitized $CuCrO_2$ delafossite oxide as photocathode

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ABSTRACT

In this study, we introduce a new concept for the highly efficient tandem p-n photoelectrochemical cell consisting of coumarin6 organic dye-anchored p-type $CuCrO_2$ delafossite semiconductor as photocathodes coupling with traditional n-type TiO_2 based photoanodes. Also, we have systematically studied the photovoltaic performance of tandem cells as a function of post-annealing of $CuCrO_2$ films before sensitization. Hydrothermally synthesized $CuCrO_2$ nanocrystals exhibited a high surface area with small crystallite size of 12 nm, phase-pure and well-crystalline after the optimized post-annealing conditions. The experimental results indicated that the optimal post-annealing temperature was 450 °C for 1 h due to the larger active surface area, lower R_{ct}, and higher J_{sc} and V_{oc} values. This tandem cell, fabricated by employing the $CuCrO_2$ photocathodes, iodide-based redox mediator and a coumarin6 organic dye, afforded an impressive efficiency of 2.33% with V_{oc} of 813 mV, J_{sc} of 4.83 mA cm^{-2}, and fill factor of 0.59. The obtained parameters are acceptably high in comparison to NiO photocathode-based tandem cells previously reported in literature under similar experimental conditions. Therefore, this work opened the way for developing highly-efficient tandem photoelectrochemical solar cells.

1. Introduction

Dye-sensitized solar cell (DSSC) working on the sensitization of n-type semiconductor (usually titanium dioxide; TiO_2) consists of a photoactive anode and a photoelectrochemically inactive cathode (Akin et al., 2016a, 2017, 2016b; Oregan and Gratzel, 1991; Ozel et al., 2016; Sonmezoglu et al., 2016, 2012, 2014a, 2014b; Tas et al., 2017, 2016). This architecture is relatively cheaper to produce than crystalline silicon photovoltaic devices but is less efficient and also less stable. Forming a dye-sensitized tandem solar cell (T-DSSC) based on a p-type semiconductor combined with a photoactive anode may be a promising approach to reach the theoretical upper limit of solar energy conversion efficiency. For example, the theoretical conversion efficiency for the DSSCs having only one active electrode is approximately 30%, while the efficiency limit for a system containing two photoactive electrodes is 43% (Green, 2003; Morandeira et al., 2005). Therefore, the synthesis of p-type semiconductor materials and understanding of the charge recombination processes between the injected hole in the semiconductor and the dyes are of great importance, if target efficiencies were to be achieved. In this regard, a better understanding of the energy conversion mechanism in p-type DSSCs will help to increase the efficiency of tandem cells.

Currently, nickel oxide (NiO) has been used as the hole conducting layer in many p-type DSSCs. However, the performance of NiO has been limited by high light absorption property in the visible range, (30–40% for a 2.3 µm thick film) (Nattestad et al., 2009), due to *d-d* electron transition (Boschloo and Hagfeldt, 2001) or trace amount of Ni^0 metal in the NiO films (Renaud et al., 2013). In addition, the relatively low mobility and diffusion coefficient of holes in NiO (*i.e.* 10^{-8}–10^{-7} $cm^2 s^{-1}$, depends on preparation method which is 2–3 orders lower than that of TiO_2), results in low photocurrent due to fast charge recombination (Kavan, 2017; Xiong et al., 2012; Yu et al., 2014). Further, for a thick NiO film, *i.e.* > 1 µm, the light harvesting efficiency decreases significantly due to the limited sensitization of dye via illumination through the transparent conductive oxides (TCOs) side of the photocathode. On the other hand, with a very thin NiO film, it is difficult to reach a significant absorbance if the dye molecules do not exhibited a very high extinction coefficient, which must lie much above $4 \times 10^4 M^{-1} cm^{-1}$ (Renaud et al., 2012).

Among the alternative p-type materials, cuprous delafossite oxides ($CuXO_2$) have gained significant attention, because Cu 3*d* orbitals strongly hybridize with the O 2*p* orbitals, making the holes to be

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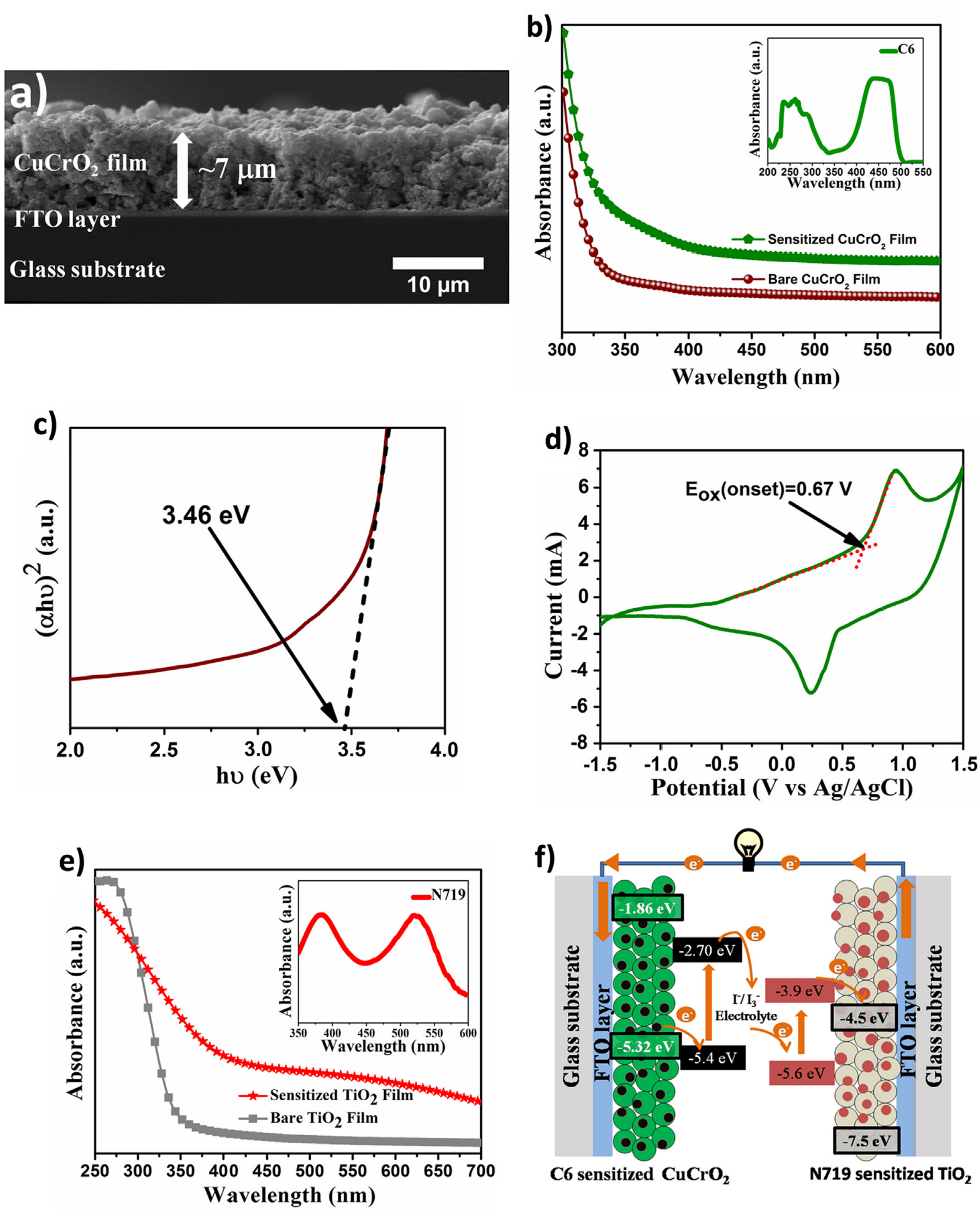

Fig. 1. (a) SEM image of a typical $CuCrO_2$ photocathode on FTO coated glass substrate as viewed along the through thickness direction (fracture surface) after post annealing at 350 °C in air, (b) The absorption spectra of the bare and C6 sensitized $CuCrO_2$ films, (c) The estimated direct band gap and (d) Cyclic voltammetry curve of $CuCrO_2$ (e) The absorption spectra of the bare and N-719 sensitized TiO_2 films, (f) Schematic illustration of the T-DSSCs consisting of C6 sensitized $CuCrO_2$ photocathode and N-719 sensitized TiO_2 photoanode; insets in (b) and (e) show the absorption spectra of C6 and N-719 dyes, respectively.

delocalized both on oxygen and copper atoms. This facilitates the hole mobility and subsequently, should minimize electron–hole recombination at the dye/p-type semiconductor interface due to a regular charge flow from the surface to the interior of the nanoparticles. When this is combined with an *X* species that has a d^0 or d^{10} valence electron configuration (Al, Ga, Cr, B, In, Sc, Y, La, Fe, etc.), the resulting compound can be transparent in the visible range, with a large optical band gap (> 3.2 eV) (Draskovic et al., 2015; Jiang et al., 2016a; Kawazoe et al., 1997; Nattestad, 2011; Renaud et al., 2012; Xu et al., 2014; Yu et al., 2012; Zhu et al., 2016). Among them, $CuCrO_2$ has become more prominent due to its easy synthesis with small particle size, high hole mobility (0.2–1 $cm^2 V^{-1} s^{-1}$), and suitable energy–level match (~ 5.3 eV below vacuum level) with the sensitizer and electrolyte which provides a promising photoelectric conversion efficiency (Barnabe et al., 2015; Powar et al., 2014; Sanchez-Alarcon et al., 2016; Xiong et al., 2012). Although, several works on $CuCrO_2$ based p-DSSCs were reported to date, surprisingly, there is no report on the performance of T-DSSCs constructed with $CuCrO_2$ photocathode layer in the literature.

The other possible strategy for enhancing the efficiency of T-DSSCs is to use an efficient sensitizer, which absorbs the light and transfers the