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p-Type $CuBi_2O_4$ thin films prepared by flux-mediated one-pot solution process with improved structural and photoelectrochemical characteristics

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ABSTRACT

The flux-mediated one-pot solution process based on the metal-organic decomposition (MOD) has been developed for the preparation of p-type complex oxide semiconductor $CuBi_2O_4$ thin films. The precursor solutions with the various concentrations (0.5, 2, 5, and 10 mol% vs. $CuBi_2O_4$) of aliovalent Li(I) flux produced the continuous and dense $CuBi_2O_4$ thin films with stoichiometric composition by facilitating the crystallization from the liquid precursor solution. These films showed the high hole density and charge transfer characteristics, which lead to the high photoelectrochemical activity for water reduction.

1. Introduction

The metal-organic decomposition (MOD) method has been extensively used as an effective solution process for the preparation of complex oxides because of its easy composition tuning and simple rapid processing route with a minimal reactivity between precursor compounds [1]. The MOD route generally uses the metal carboxylates where a long-chain length of the organic moieties increases their dissolution tendency and concomitantly limits their hydrolysis tendency [1]. Therefore, the nature of the precursor species in solution is little changed compared to sol-gel and chelate processes, leading to simple mixtures of the starting reagents and thus less complex and stable chemical route. However, a dense and continuous thin film of the material with a high cohesive strength is hard to be prepared via the conventional solution routes. For example, $CuBi_2O_4$ is deposited in the form of non-continuous, loosely packed particles on the substrate [2].

Recently, as a means of the solar energy conversion, the production of hydrogen from sunlight and water through photoelectrochemical (PEC) water splitting is promising [3]. To utilize the hydrogen production via such a PEC method, the p-type semiconductor photocathodes with more negative conduction band minimum (E_{CB}) than the reduction potentials of water and with narrow band gap conforming to visible light are required. Among various p-type semiconductors, $CuBi_2O_4$ has been regarded as a potential photocathode material for PEC water reduction because it has a highly negative conduction band edge enough to cover water reduction potentials [2,4–6].

Herein, we show the direct growth of p-type $CuBi_2O_4$ thin films with a high cohesive strength on the substrate with controlled morphology, compositional stoichiometry, charge density, and PEC properties through a novel flux-mediated one-pot MOD solution process. The novelty was originated from the introduction of Li(I) ionic flux with low melting point and high solubility in the MOD precursor solution and the aliovalent ionic flux can increase the hole density in the $CuBi_2O_4$ and thus enhance its catalytic activity. The flux-mediated synthesis of inorganic materials has been conventionally used in the preparation of complex oxide nanoparticles where it reduces a melting point of the mixed starting reagents and thus controls the shape and composition of final products [7–9].

2. Experimental

The solutions of 0.045 M $Cu(C_5H_7O_2)_2$ and 0.15 M $Bi(NO_3)_3{\cdot}5H_2O$ in acetic acid were separately prepared. Thereafter, two solutions were mixed with a 1:2 mol ratio and 20 mL of acetylacetone was further added. $Li(CH_3COO){\cdot}2H_2O$ was chosen as a Li(I) flux and the precursor solutions with 0, 0.5, 2, 5, and 10 mol% Li(I) vs. $CuBi_2O_4$ were prepared. A spin-coating method produced more secondary phase compared to a drop-casting method (see Supplementary Material, Fig. S1). The calcination temperature was determined to be at 550 °C by considering the phase diagram of Cu-Bi [10]. In addition, the extension of the calcination time from 1 to 4 h and the increase of coating number from one to three cycles produced a single phase with high crystallinity. Thus, the $CuBi_2O_4$ photocathodes were finally prepared on FTO substrate by three-cycle dropping of the solution,

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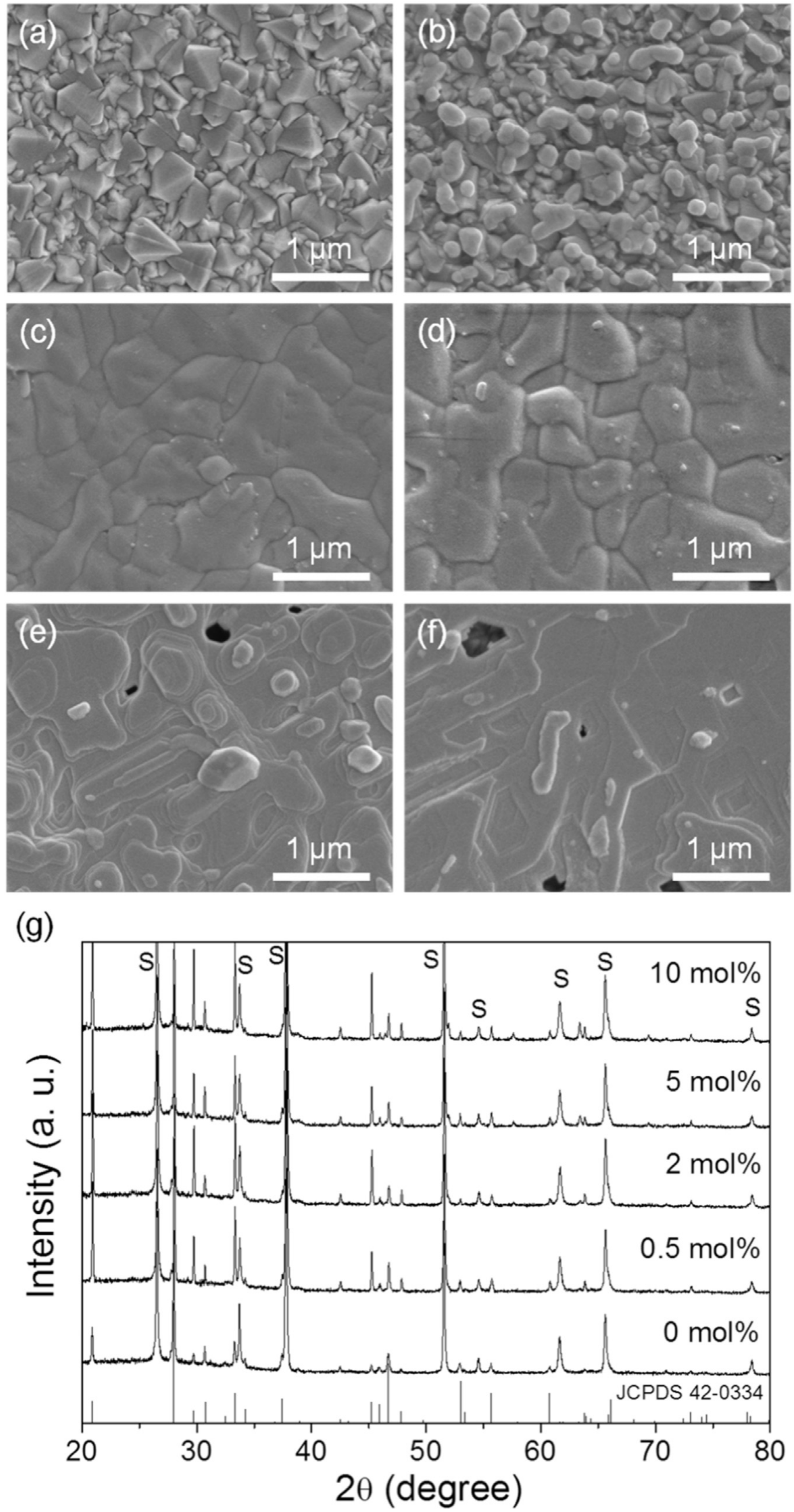

Fig. 1. FE-SEM micrographs of (a) bare FTO substrate and $CuBi_2O_4$ prepared with the Li(I) flux of (b) 0, (c) 0.5, (d) 2, (e) 5, and (f) 10 mol% vs. $CuBi_2O_4$ and (g) their XRD patterns (S: FTO substrate peaks).

followed by the calcination for 4 h at 550 °C in air. The films were homogeneously deposited on the photoactive area of 1 cm^2 on the substrate surface.

The film morphology and phase were observed by field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) and X-ray diffraction (XRD, D8-Advance), respectively. The chemical composi-