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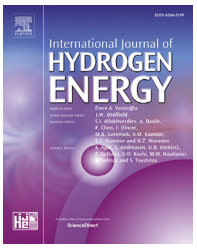

Effect of alkaline-doping on photoelectrochemical activity of electrodeposited cuprous oxide films

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ABSTRACT

P-type Cu_2O films with alkaline ions (Li^+, Na^+ and K^+) of unintentional dopants on indium tin oxide coated glass substrate are successfully fabricated via a simple electrodeposition method for photoelectrochemical (PEC) hydrogen generation. The SEM and XRD analysis show the as-grown films with the pyramid-like morphology and cubic structure, and the composition of alkaline-doped Cu_2O films are examined using XPS spectroscopy to demonstrate the substitution of alkaline ions in the Cu_2O lattice. The optical analyses, including the absorbance and low-temperature photoluminescence spectra, confirm a bandgap of 2.3 eV and the presence of structural defects in alkaline-doped Cu_2O films. The Mott-Schottky plot shows the flat band potentials of the alkaline-doped Cu_2O films to be approximately −0.1 V and the hole concentrations in the order of 10^{17} cm^{-3}. Significantly, the Cu_2O:Li film photocathode exhibits a higher photocurrent of −2.2 mA cm^{-2} at a potential of −0.6 V vs Ag/AgCl which are greater than those of Cu_2O:K and Cu_2O:Na films due to greater preferred orientation degrees along (111) and less structural defects, because the ionic radii of Cu and Li is similar. These results demonstrate the great potential of alkaline doped Cu_2O films in solar-related applications.

Introduction

Since carbon emission through burning fossil fuels causes the serious problem of greenhouse gases in the atmosphere and has been getting worse the last several decades, development of an alternative and sustainable energy to replace the traditional fossil fuels is urgency needed. Within various clean energy production technologies, the solar-driven splitting of water into hydrogen is a favorable route to convert solar energy into a chemical fuel owing to the abundance of water and sunlight [1–5]. The technology of photoelectrochemical (PEC) water decomposition under solar illumination to produce hydrogen has attracted more attention in recent years. Cuprous oxide (Cu_2O) thin film with a *p*-type nature and direct band gap of 2.1–2.3 eV is considered one of most potential photocathodes to achieve great solar-to-hydrogen conversion efficiency [6,7]. For example, M. Grazel et al. demonstrated that the highly active photocathode of Cu_2O thin film with a decoration of ZnO, TiO_2 and Pt, which can reach the high photocurrents of −7.6 mA cm^{-2} at a potential of 0 V and remain active for 1 h of testing was a possibility [8]. In general, the technology of electrochemical deposition is an efficient and facile way to synthesize p-type Cu_2O film, but the control of the basic electrolyte by the alkaline hydroxide is necessary. The main reason for this is that the hydroxide ions in an electrolyte

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play an important role as an oxygen precursor for the growth of Cu_2O film. Meanwhile, it is worth noting that the unintentional dopant of an alkaline ion in Cu_2O film is inevitable [9,10]. Although the isovalent substitutions on Cu by an alkaline ion would not significantly alter the electrical properties, the effects on the morphologic, structural and optical characteristics of Cu_2O film are still unclear. In the past year, only the electronic structure of p-type Cu_2O films by alkaline doping and the effects of lithium on lithium-cuprous-oxide composite films have been investigated [11,12]. Hence, according to our investigations, studies targeted at different alkaline ion doped Cu_2O films for PEC water decomposition have been rare. In this work, a basic electrolyte is utilized to electrochemically grow Cu_2O films by the control of LiOH, NaOH and KOH, respectively, to realize the effects of an unintentional alkaline-dopant on PEC water splitting. The PEC activities of Cu_2O films grown in three different electrolytes are systematically analyzed. Moreover, these alkaline-doped Cu_2O films not only function as photocathodes for PEC hydrogen generation, but also offer a new opportunity to develop solar and photoelectronic devices based on our results.

Experiment

In a typical electrodeposition process, a piece of platinum foil (area ~2.25 cm^2), indium tin oxide (ITO) coated glass substrate and a standard silver/silver chloride electrode (Ag/AgCl electrode) were used as the counter electrode, working electrode and reference electrode, respectively. ITO-coated glass was cleaned with acetone and rinsed with deionized water before use. All reagents were of an analytical grade and used without further purification. First, p-Cu_2O thin films were fabricated using a basic electrolyte, including aqueous solutions of 20 mM $CuSO_4$ and 0.34 M lactic acid. Three kinds of alkali hydroxide, KOH, NaOH and LiOH, were also added in the aqueous electrolyte. The different concentrations of alkali hydroxide were tested, and a concentration of 0.375 M for KOH, NaOH and LiOH was chosen by PEC current response, as shown in Fig. S1. Deposition was carried out at 60 °C with a constant potential of −0.4 V for 15 min (charge passed for deposition = 0.67 C cm^{-2}). Electrodeposition was carried out using an electrochemical analytical instrument (CHI 6273D). Finally, all of the samples were cleaned in DI water and dried in air.

The morphology of three alkaline-doped Cu_2O films was examined by Scanning electron microscopy (SEM, JEM-4000EX), and the structure of the films was determined using an X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu K_α radiation ($\lambda = 0.1506$ nm). The chemical states of the elements were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer model PHI 1600). The Raman spectra were measured using a LabRAM HR 550 system equipped with a HeNe laser (light power of 5 mW). The Photoluminescence (PL) spectra were measured using a LabRAM HR 320 system equipped with a diode laser (405 nm, 50 mW) and optical cryostat (ST-100). The resistivity characteristics were measured by four point probe technique. The PEC properties of the films were measured in 0.5 M Na_2SO_4 solution by CHI 6273D potentiostat/galvanostat. A conventional three-electrode setup, consisting of alkaline-doped Cu_2O film as the working electrode, a square platinum sheet as the auxiliary electrode and a Ag/AgCl reference electrode in 3 M KCl solution was implemented. All potentials reported in this article were regarding Ag/AgCl. A 150 W Xe lamp light source with an AM 1.5 filter was used, and the light intensity of the illumination per area at the sample position was determined to be 100 mW cm^{-2}. In addition, a 150 W Xe lamp equipped with a monochromator was used as the excitation light source to obtain monochromatic light for incident photon-to-electron conversion efficiency (IPCE) measurement. The incident light was irradiated onto alkaline-doped Cu_2O film electrodes from the front face through the quartz window and the electrolyte, unless otherwise noted.

Results and discussion

Structural and compositional characterizations

The crystal phase of as-grown Cu_2O thin films that were deposited in three different alkaline electrolytes respectively,

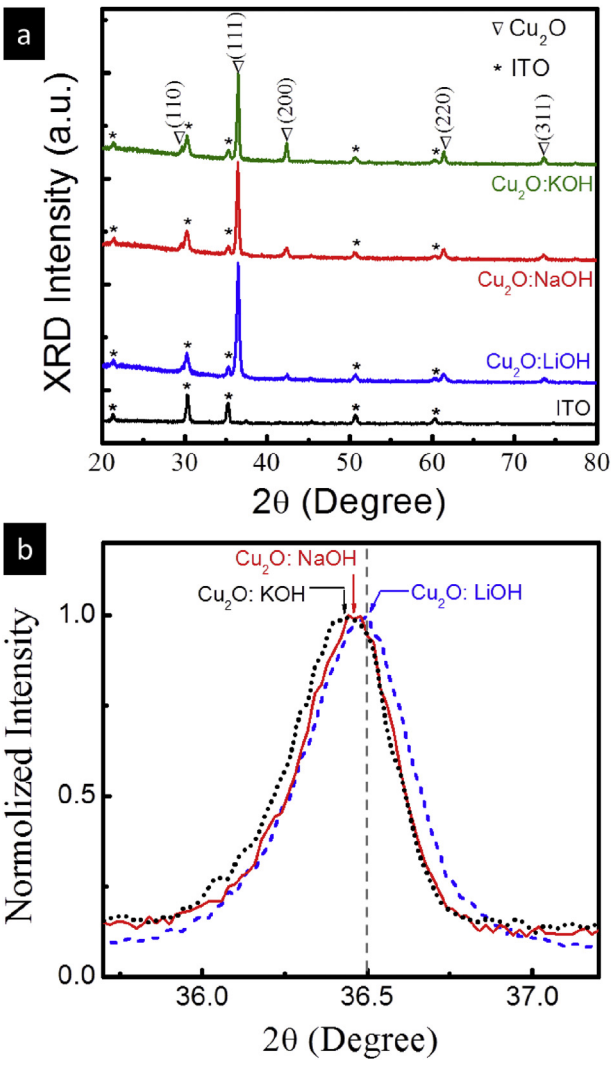

Fig. 1 – (a) XRD patterns of three alkaline-doped Cu_2O film; (b) Relative change in (111) peaks taken from (a).

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