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Electrochemical synthesis of cuprous oxide on highly conducting metal micro-pillar arrays for water splitting

Sanghwa Yoon [a], Jae-Hong Lim [b, *], Bongyoung Yoo [a, **]

[a] Department of Materials Engineering, Hanyang University, Ansan-si, Gyeonggi-do 426-791, Republic of Korea
[b] Electrochemistry Research Group, Materials Processing Division, Korea Institute of Materials Science, Changwon-si, Gyeongnam 641-831, Republic of Korea

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ABSTRACT

Three-dimensional (3D) metal/cuprous oxide (Cu_2O) micro-pillar arrays were fabricated by electroless deposition of Ni on Si micro-pillars followed by the electrochemical deposition of Cu_2O on the metal micro-pillars. The metal micro-pillars with heights of 16 μm and diameters of 1–1.5 μm showed low reflectance and conductance values similar to Cu_2O plates, indicating that the 3D metal/Cu_2O micro-pillars are good current collectors. The photocurrent of the 3D metal/Cu_2O micro-pillar arrays was more than twice that of the Cu_2O plates. This high photocurrent for the 3D metal/Cu_2O micro-pillar results from its large surface area, long optical absorption depth (micro-pillar length) and short carrier diffusion length (thin Cu_2O absorber).

1. Introduction

In recent years, harvesting sunlight to produce hydrogen as a clean energy source has attracted significant interest to address the issues of the rapid decrease in fossil fuel resources and the CO_2 greenhouse effect. The photoelectrochemical (PEC) splitting of water is an environmentally friendly method for producing hydrogen and oxygen without the formation of any undesired reactants/pollutants. Following the early report by Fujishima and Honda who presented for the first time, the use of a TiO_2 semiconducting electrode for a PEC cell [1], many research groups have made extensive efforts to improve the PEC cell performance by adopting different approaches. Yang et al. reported N-doped ZnO nanowire arrays with a photo-to-hydrogen conversion efficiency of 0.15% [2]. Paracchino et al. fabricated a highly active metal oxide photocathode that was passivated with Al-doped ZnO and TiO_2 by atomic layer deposition [3]. Cheng et al. investigated quantum dot-sensitized TiO_2 inverse opals for PEC hydrogen production [4]. Oh et al. reported a silicon (Si) nanowire array photocathode with a high photocurrent formed by the successful chemical etching of bulk silicon [5]. MoS_x films have been deposited on TiO_2-protected Cu_2O photocathodes by Morales-Guio et al. [6] Hsu et al. fabricated a novel Cu_2O micro/nanostructured photocathode on a copper foil by chemical oxidation followed by thermal reduction [7]. Han et al. investigated heterogeneous Cu_2O/CuO photocathode with improved stability [8]. Recently, Lin et al. fabricated the p-InP photocathodes with TiO_2 by ALD [9]. Also, Wang et al. reported electrodeposited Cu_2O films with controllable conductivity [10]. Further, Luo et al. synthesized Cu_2O nanowires with 10 mA/cm^2 by anodization and annealing and reported stable solar water splitting [11].

The major parameters that determine the efficiency of a PEC cell are surface area, charge transport, minority carrier diffusion length, and the optical absorption depth of the photocathode material. To increase the optical absorption and the surface area as well as to ensure sufficient number of charge carriers, an excellent choice is a core-shell structure made of a conducting material/thin light absorber combination [3,11–16]. The conducting material core plays the role of the current collector due to its fast charge transport and the thin light absorber shell has a long optical absorption depth and a short minority carrier diffusion length. Cuprous oxide (Cu_2O), in view of its direct band gap (2.1 eV), is an attractive candidate as a

* Corresponding author.
** Corresponding author.
E-mail addresses: lim@kims.re.kr (J.-H. Lim), byyoo@hanyang.ac.kr (B. Yoo).

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photoelectrode in PEC cells. In addition, its conduction band lies above the hydrogen generation potential and it is abundant in nature [3,17–21]. However, until now, the solar to hydrogen efficiency is relatively low in comparison with the theoretical efficiency for this material. One factor that negatively influences the efficiency is the opposing effects of the minority carrier diffusion length (20–100 nm) and the light adsorption depth (~10 μm) [13].

Here, the metal core/absorber shell structure was fabricated on a micro-scale using a solution-based method. The metal micro-pillar arrays were synthesized by Ni electroless deposition following which the Cu_2O absorber layer was electrodeposited onto the Ni micro-pillar arrays. The micro-pillar structure with a metal core/absorber shell provides a strong absorption, which minimizes the effect of the short minority carrier diffusion pathway of Cu_2O. Unlike other synthesis methods, these processes are highly scalable and compatible with conventional Si based processes. In addition, preliminary results from photoelectrochemical cells (PECs) suggest that the fabricated micro-pillar array structures are highly efficient active materials in view of their ability to decouple the effects of light absorption and charge-carrier collection leading to a photocurrent of −1.2 mA/cm^2, which is larger than that for plates without micro-pillars (−0.6 mA/cm^2).

2. Experimental methods

2.1. Preparation of 3D metal pillar and Cu_2O micro-pillars

The schematic of the fabrication of the three-dimensional metal/Cu_2O micro-pillar is shown in Fig. 1. First, silicon micro-pillar arrays were fabricated by commercial photolithography and the deep reactive-ion etching (DRIE) process, using the facilities at Korea Advanced Nano Fab Center. Secondly, nickel plates and micro-pillars were synthesized by electroless deposition. The electroless bath contained 0.5 M $NiSO_4$, 0.5 M $(NH_4)_2SO_4$, and 3 M NH_4F at a temperature of 80 °C. To adjust the pH to 8, ammonia was added to the solution. After preparing the electroless solution, Si wafers with and without micro-pillars were immersed in the solution for 10 min and Ni was electrodeposited in a Watt's bath (1 M $NiSO_4$, 0.4 M $NiCl_2$, 0.5 M boric acid, pH of the bath = 4.2) for 600 to 5400 s at −0.7 V vs. Ag/AgCl to control the diameter of the metal micro-pillars. Au was deposited on the Ni plates and micro-pillars by electrodeposition to provide ohmic contact between the metal and Cu_2O. Finally, Cu_2O photoelectrode with {100} planes were potentiostatically electrodeposited from 0.1 M copper sulfate, 1 M sodium citrate, and 4 M KOH at a pH of 12 at −0.3 V vs. a Ag/AgCl reference electrode in a three-electrode system, using a platinum plate as the counter electrode. The temperature of the bath was maintained at 60 °C using a circulating chiller (Labkorea Inc, HLTC08).

2.2. Characterization of 3D Cu_2O micro-pillars

The structure of the Ni/Cu_2O micro-pillars was elucidated using field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3). The crystalline structure was evaluated from X-ray diffractometer (XRD, Rigaku, D/MAX-2500/PC). The optical characteristics of the Cu_2O/Ni plates and micro-pillars were obtained by UV–VIS spectrophotometry (Lambda 750, PerkinElmer). The conductance of the Ni micro-pillar was determined from current-voltage sweep curves obtained using a two probe system (HP 4145B).

2.3. Photoelectrochemical characterization

The PEC characteristics of the Ni/Cu_2O micro-pillar photoelectrodes were measured using 0.5 M sodium sulfate (pH 6.8) as the electrolyte under light illumination (125 mW cm^{-2} halogen lamp). A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively, in the three-electrode system. Linear sweep voltammetry was performed both under light and in the dark for voltages ranging from 0 V to −0.6 V (vs. Ag/AgCl) at a scan rate of 2 mV s^{-1}. Prior to the PEC cell measurements, the electrolyte was bubbled with N_2 gas for 1 h to remove dissolved oxygen in the solution.

3. Results and discussion

3.1. Structure and electrical analysis of metal micro-pillars

Fig. 2 shows the FE-SEM image and the I-V characteristics of the Si/Ni/Au micro-pillars. The pillars had heights of 16 μm and diameters of 1–1.5 μm. The Au and Ni layers were deposited by electrodeposition and electroless deposition techniques, successively, in order to obtain a high conductance and a fast electron

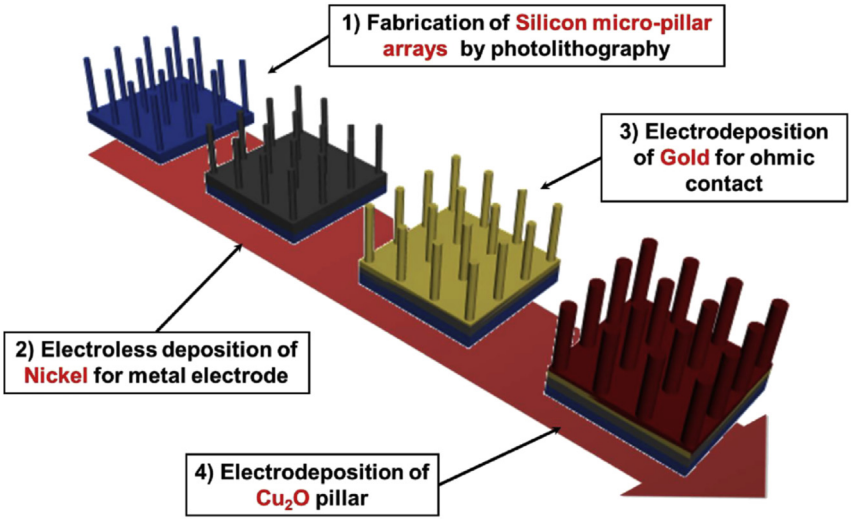

Fig. 1. Schematic of the fabrication of 3D metal/Cu_2O micro-pillar arrays.