Comparative Study of p-type CuBi$_2$O$_4$ Films and CuBi$_2$O$_4$ Nanopillars Photocathode for High Performance Photoelectrochemical Water Splitting

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Abstract. Traditional thin films and nanostructure are the most reasonable candidates to build the next generation of photoelectrochemical water splitting system with outstanding optical and electrical properties. Especially the use of nanostructure arrays as photoelectrodes might complement the traditional semiconductor photoelectrodes in providing close transfer distance of photoinduced carriers and the increase in the surface reaction sites than thin films. Both of the reasons reduce the probability of carriers recombination and thus enhancing the photoelectrochemical performances. In this work, we demonstrated highly efficient water splitting performance of CuBi$_2$O$_4$ nanopillars compared to thin film CuBi$_2$O$_4$ photocathode. The CuBi2O4 nanopillars were fabricated by electrodeposition on anodized aluminum oxide (AAO) template. The CuBi$_2$O$_4$ nanopillars photocathode gave a notable improvement in photocurrent, from $-0.50$ to $-1.50$ mA cm$^{-2}$ at $-0.45$ V vs. Ag/AgCl by the external quantum yield more than 3 times at wavelength 420 nm. Finally, the result of the study appeared that the photoelectrode based on CuBi$_2$O$_4$ nanostructure arrays is an encouraging system for showing efficient water splitting system under visible light.

1. Introduction
The conversion of solar energy to fuels cell through water splitting into hydrogen and oxygen evolution in photoelectrochemical (PEC) cell was initiated in 1972 by Fujishima and Honda using TiO$_2$ electrode [1]. Since then, the technique becoming popular due to its abundance and environmental-friendly nature of hydrogen fuel toward the worldwide sustainable energy questions. Most research on hydrogen energy production has been performed repeatedly up to now, however, the reported efficiencies are still too low to be practical [2-6]. An alternative method to solve this challenge is encouraging novel morphologies of the photoelectrode. This approach has been shown to enormously enhancing the performance of solar water splitting, likely due to their unique size-geometry and shape-dependent features. Nanopillar as a representative nano-structure has been successfully fabricated in various semiconductors for enhancing the PEC performances, such as TiO$_2$, Cu$_2$O [7].

Through a direct band gap around 1.6 up to 2.1 eV, CuBi$_2$O$_4$ (CBO) has long been considered as an assurance nominee for solar energy conversion. Theoretically, the maximum photocurrent of 15 mA cm$^{-2}$ and 18% solar-to-hydrogen conversion efficiency under AM 1.5 illumination is expected to be achieved.[6-10] Furthermore, the p-type materials such as copper are abundant and can be produced at an industrial scale in a cost-effective method [10]. In our previous work, in which the highly active photocathode of CBO thin films was proposed, the photocurrent can reach as high as 1 mA/cm$^2$ and maintained active for 1h of testing [10]. There have we reported successful treatment for CBO...
photocathodes using very thin Au and Pt to realize an impressive PEC performance [10]. These remarkable performances determine the unique potential for CBO in PEC water splitting. Furthermore, in this purpose, we synthesize CBO nanopillars arrays efficaciously by the convenient and cost-effective AAO template method. From comparison by the photocathode based on CBO films, the CBO nanopillars photocathode presents a remarkable improvement in photocurrent, from $-0.50$ to $-1.5$ mA cm$^{-2}$ at $-0.45$ V vs. Ag/AgCl.

2. Experimental section

2.1 Materials and Chemicals

Bi(NO$_3$)$_3$·5H$_2$O (≥98.00%), Cu(NO$_3$)$_2$·3H$_2$O (≥99.1%), sodium sulfate (≥99.0%), latic acid (≥70%), acetone (≥99.8%), ethanol (≥95%), FTO-coated glass (Product Number: 735213; L×W×D: 100mm×100mm×3mm; Surface resistivity:~10 Ω/sq; Transmittance: ≥83.0% (visible)) were used as received from Sigma-Aldrich. Insulating epoxy (EA 3450) was purchased from Loctite. Copper tape (AT528) was purchased from Advance Tapes.

2.2 Fabrication of Ni nanopore arrays

The production process of pores from Al nickel pore arrays has the same steps as has been written before [12-16]. After the imprinting phase, on a sheet of aluminium by using oil pressure system around 10 kP for 3 minutes, the process of anodization is conducted at 4 °C temperature for one hour with applied voltage 160 V which later be called as AAO template. To open and broaden AAO pores after the anodized, AAO template is soaked in a 5 wt% H$_3$PO$_4$ solution. The duration of the soaking process will control the width of the pore we use. In this work, we made same the condition for deposition time and solvent. After the AAO template was cleansed and dried, the deposition process of Au thin film 25 nm was conducted by using electron beam deposition (Kurt J. Lasker PVD225) procedure with the rate of 0.2 Å s$^{-1}$.

2.3 Preparation of the CBO films

Firstly, FTO glass was cleaned with acetone, ethanol and DI water, respectively. Secondly, a thin layer of Au was deposited on the cleaned and dried FTO glass as the substrate via a physical vapor deposition (Kurt J. Lasker PVD225) procedure with the rate of 0.2 Å s$^{-1}$. Then, CBO thin films were cathodically electrodeposited from a bath solution of 8 mM Bi(NO$_3$)$_3$·5H$_2$O and 4 mM Cu(NO$_3$)$_2$·3H$_2$O in 10% nitric acid. Nitric acid was purposely used to dissolve bismuth nitrate precursor. The pH value of the bath was carefully adjusted to 12.0 by the addition of 3 M sodium hydroxide. The films were grown at a constant potential of $-0.40$ V vs. Ag/AgCl in a normal three-electrode configuration for a nominal duration of 30 min. The bath temperature was controlled at 45 °C using a heating plate with an in situ temperature probe. Following deposition, the samples were rinsed with DI water and dried in an air stream. A final annealing procedure at 550 °C for 120 min in the air was performed to achieve better crystallinity. For comparison, we also prepared CBO nanopillars directly using the same procedure.

2.4 Fabrication of CBO photocathodes

A strip of conductive copper tape was stuck on the exposed FTO part of the FTO/Au/CBO to extend the conductor circuit and threaded through a glass tube and then sealed with an insulating epoxy. Electrode areas were optically measured at 0.25 cm$^2$.

2.5 Photoelectrochemical measurements

External quantum yield was measured with an Oriel 150 W Xe arc lamp (Newport) and a quarter-turn single-grating monochromator (Newport). Sample measurements were recorded with chopped illumination. The output current signal was connected to a Merlin digital lock-in radiometry system, and the output signal from the lock-in amplifier was fed into a computer controlled by TRACQ BASIC software. Current–potential plots and impedance characterization were measured by using the digital BioLogic potentiostat (SP-200) and 0.1 M sodium sulfate...
aqueous solution served as the electrolyte. A Pt counter electrode and Ag/AgCl reference electrode were used during the measurements. A standard 300 W Xe lamp (Newport) served as the light source, and the light intensity was characterized to 100 mW cm$^{-2}$ by a Si photodiode (Newport). The evolution of hydrogen gas during the water-splitting reaction was measured by the gas chromatograph-mass spectrometer (GC-2010 plus).

2.6 Characterizations
The powder X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance equipped with graphite monochromatized high-intensity Cu Kα radiation ($\lambda = 1.54178$ Å). The energy-dispersive X-ray mapping (EDX) mapping was obtained on S4800 HITACHI (Japan). Room-temperature UV-Vis absorption spectroscopy was measured by Varian Cary 5000 UV-Vis-NIR spectrophotometer.

3. Results and discussion
The approach aimed at the outgrowth of the CBO nanopillars was separated into five exhaustive processes that are showed schematically in Figure 1, which here the color of the Al, AAO, Au, Ni, and CBO are described as blue, gray, yellow, orange and black, respectively. The procedure contains anodization (I), gold layer deposition (II), Ni electrodeposition (III), aluminum and barrier layer removal (IV), CBO nanopillars fabrication (V), and template removal (VI). The AAO template was implemented as the dominant templates in our preparation course, the cause of its gorgeous benefits, containing uniform and homogenous oriented nanoporous structures, tunable structural parameters, large area, chive cost, and outstanding thermal and mechanical stability. [11-13]

Figure 1. Illustration of the fabrication process of CBO with AAO template: anodization (I), gold layer deposition (II), Ni electrodeposition (III), aluminum and barrier layer removal (IV), CBO nanopillars fabrication (V), and template removal (VI).

Figure 2a shows that the bare AAO template, which was fabricated with one-time oxidization after applied Ni stamp under pressure 10 Pa until 3 minutes, [11,12] gives pretty well-distributed nanopores. It had a diameter of around 150 nm and a length of around 1.5 µm. By succeeding the previously report procedures, the electrodeposition for CBO nanopillars and films were both achieved in a copper sulfate bath holding 3 M lactic acid [14]. Figure 2b demonstrations the representative scanning electron microscopic image of the completed nanopillars on Cu bulk substrates. The nanopillars are vertically joined on the substrate. The size of these nanopillars is assessed as $\sim$ 85 nm in diameter and $\sim$ 1.2 µm in length, respectively. As additional, the CBO films grown on Au/FTO glass are fabricated by unceasingly dispersed polyhedral particles, with the shape chances out to be
cuboid, as shown in Figure 2c [14]. It is still in agreement with the reported values,[14,15,16] the band gap of the grown CBO nanopillars and CBO films on Au/FTO glass is characterized as 1.85 and 1.79 eV by the absorption analyses, respectively.

Figure 2. Top view SEM images of the prepared AAO template (a), CBO nanopillars (b) CBO films (c). (d) XRD patterns of CBO nanopillars and substrates.

The XRD patterns of the CBO nanopillars and films are given in Figure 2d, presents the XRD patterns of these two films, where a series of diffraction peaks attributed to Kusachiite CBO phase could be observed (PDF#48-1886), though the peaks of Au and FTO are unavoidable. The highest diffraction peak belongs to the (211) facet [17]. The phases of CBO and Cu are not discernible, indicating a pure CBO structure in the nanopillars and films.

Figure 3a demonstrates the representative steady-state EQY spectra of PEC electrodes of CBO nanopillars and films. The nanopillars photoelectrode on the bulk Cu shows an enhanced EQY below the absorption edge of CBO nanopillars (580 nm) than to CBO thin film photoelectrode. An enhancement of 2-fold is obtained; demonstrating that CBO nanopillars based electrode have a higher photo-to-current efficiency than that with CBO thin films. This result still reliable with those reported in current studies that have focused on the excellent optical and electrical properties of nanopillars and advance in the photocatalytic performance of semiconductor [18,19-25].
Figure 3. (a) plot of $(\alpha h v)^{1/2}$ vs $h v$ for estimating the band gap value of the film, (b) potential photocurrent profiles, (c) time-dependent photocurrent density spectra and (d) EQY spectra of CBO nanopillars and films photodeode.

The tested Photocurrent–potential shapes by immersing the photoelectrodes into 0.1 M Na$_2$SO$_4$ aqueous solutions, with the Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. Each plot represents a typical photo-response obtained under illumination (AM1.5G, 100 mW cm$^{-2}$), as shown in Figure 3b. Were J−V curves exhibit a cathodic photocurrent and show a separate p-type feature of two booths CBO nanopillars and films, consistent with our previous report [10]. In work, photo-induced electrons transfer from films and nanopillars to the electrolyte to drive PEC reactions, and in parallel time consistent holes carriage from films and CBO nanopillars to FTO electrode throughout the PEC measurement. To be exciting, likened to the CBO films electrode, the photocathode of CBO nanopillars has a notable improvement in PEC performance, in good bonds with EQY measurement.

As showed in Figure 3c, to examine the photocathode PEC performance and stability under sunlight, the time-dependent photocurrent density was approved out on the CBO nanopillars and films through repetitive chopped on–off sunlight illumination cycles at −0.4 V vs. Ag/AgCl. The result indicates that both samples demonstration fast and reproducible photocurrent reactions upon each illumination. The plateau photocurrent density of the CBO films electrode was 0.45 mA cm$^{-2}$, and that of the CBO nanopillars was 1.2 mA cm$^{-2}$, which denotes a more than 2 times increase from the CBO films. Again, the result demonstrates that nanostructure of materials its attain the enhancement of the photoelectric conversion, due to the capability of contribution large surface area and more reaction sites, disassociate light absorption and charge carrier collection, easy carrier diffusion distance compared to the bulk structures [20,21-25].
4. Conclusion
Finally, this study has presented that a novel photocathode based on CBO nanopillars was successfully fabricated via the AAO template method, in comparison with the photocathode of CBO films. The CBO nanopillars photocathode offers notable improvement in photocurrent, from ~0.5 mA cm\(^{-2}\) to ~1.5 mA cm\(^{-2}\), assigning to advantages of the nanostructure with high specific surface area, light-trapping, and small carriers transfer. The results from this study provide an effective-cost, naturally abundant nanopillars material for use in photoelectrochemical cells.

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6. References
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