Solid-state Synthesis of Phase Pure CuBi$_2$O$_4$ by Sequential Ball Milling

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Abstract— Bismuth-based metal oxides are an intriguing class of photoelectrode materials that can potentially enable large-scale solar hydrogen production via photoelectrochemical (PEC) water-splitting. For realizing such PEC devices, Kusachiite (copper bismuth oxide) is one of the most promising photocathode materials for high solar-to-hydrogen efficiency. Here we attempt to synthesize phase pure copper bismuth oxide (CuBi$_2$O$_4$) nanopowders using a facile solid-state reaction technique subsequently sintered at ~750 °C for 4 h in air. These CuBi$_2$O$_4$ (CBO) powders have been further sequentially ball milled (SBM) up to 25 h to elucidate the milling duration effect on the optical bandgap of the ball-milled CuBi$_2$O$_4$ (SBM-CBO). The structural, optical, and Raman studies suggest that phase pure tetragonal CBO could be grown from raw CuO and Bi$_2$O$_3$ powders. The variations in morphology and chemical composition of CBO with increasing milling hours were examined using field emission scanning electron microscopy (FE-SEM) and Energy Dispersive X-ray (EDX) microanalysis, respectively. The optical bandgap was measured in the range of ~1.70 – 1.85 eV from the UV-VIS-NIR Diffuse reflection data of SBM-CBO powders. The CBO photocathode materials with variable structural and optical properties could be a promising candidate for self-sustained PEC generation of hydrogen fuel.

Keywords— Photoelectrochemical device, sunlight-driven H$_2$ production, Photocathode materials, Kusachiite, CuBi$_2$O$_4$

I. INTRODUCTION

Since the first industrial revolution, the development of civilization has been immensely dependent on fossil fuels (coal, oil, natural gas, etc.) as energy sources. These nonrenewable energy sources are not only limited and exhausting but also cause damage to our environment by producing many harmful byproducts like CO$_2$. Therefore, finding renewable, eco-friendly, affordable, and long-term storable energy sources as an alternative to fossil fuels to satisfy ever-growing energy demand has become a pressing need in the era of the 4th industrial revolution (4IR). To this end, one of the most promising approaches could be utilizing the immense and ubiquitous energy reservoir - the sun and earth-abundant water to establish a sustainable solar energy conversion and storage system. Photoelectrochemical (PEC) water-splitting is a such system to overcome the worldwide energy crisis by producing hydrogen fuel using sunlight and water as the only inputs [1]. Hydrogen (H$_2$), a versatile energy carrier, is believed to be one of the most promising clean energy sources that stores energy as a molecular bond. There are different kinds of devices for solar water-splitting ([2] and refs. therein). We aim to build a self-sustained PEC [3] device for sunlight-driven hydrogen production using bismuth-based metal oxides as active photoelectrode materials.

Green and renewable energy researchers have devoted tremendous efforts to developing multinary metal oxides due to inherent drawbacks in light absorption, carrier transport, and stability of binary metal oxide-based photoelectrodes. Bismuth-based metal oxides are promising candidates for photoelectrodes (for example, n-type photocathode BiVO$_4$ and p-type photocathode CuBi$_2$O$_4$) in solar water splitting devices since they have demonstrated excellent visible light harvesting capability and a right band edge for water splitting ([2] and refs. therein). Kusachiite (copper bismuth oxide), a p-type semiconductor with an ideal direct bandgap of 1.6–1.8 eV, shows great potential to be used as an active photocathode in PEC devices [1,3]. Copper bismuth oxide (CuBi$_2$O$_4$) is not only just eco-friendly but also its high solar-to-H$_2$ (STH) conversion efficiency, durability, and abundance on the earth, making it one of the most suitable photocathode materials. Moreover, the conduction band of CuBi$_2$O$_4$ (CBO) is located at a more negative potential than the reduction potential of H$^+$/H$_2$, allowing adequate driving force for solar H$_2$ production. Furthermore, a positive photocurrent at 1.0 V$_{SHE}$ makes CBO a potential photocathode material for self-sustainable water-splitting systems [3,4].

There are many wet-chemical, solid-state reaction, and physical vapor methods to synthesize pure phase CuBi$_2$O$_4$ ([4] and refs. therein) with tunable optoelectronic properties. However, we used sequential ball milling (SBM) for synthesizing phase pure CuBi$_2$O$_4$ (CBO), which is rarely reported in the literature. The SBM method is facile, cost-effective, and industrially scalable compared to other existing methods in the literature [3].

II. SYNTHESIS OF CuBi$_2$O$_4$ (CBO)

In this study, the standard solid-phase reaction technique for ceramic materials [2,5] was slightly modified to synthesize CBO samples. For the starting raw materials, we took cupric oxide (CuO) and bismuth oxide (Bi$_2$O$_3$) powder and pre-activated them by individually hand-milled (HM) for 1 h. The CuO and Bi$_2$O$_3$, taken in the molar ratio 1:1, were mixed and HM for another 1 h. Afterward, the mixture was ball-milled (BM) for 5 h at 150 rpm and had a ball-to-powder ratio of 1:1 (Ball diameter: 10 mm, ball material: alumina). The mixture was stirred with a spoon every ~2 h to get a homogenous combination. After 6 h of hand milling and ball milling (HBM), the powder was sintered at 750 °C in
a furnace (model: Nabertherm P-310, Germany) over 4 h with a heating rate of 5 °C/min and then cooled down to room temperature naturally. The resultant sample was preserved in a container after grinding (GS), and a small amount was deduced as a part of the sample collection. Then, the rest of the GS sample was further sequentially ball milled (SBM) for different durations up to 25 h for more CBO formation and grain size degradation, and samples at different ball milling hours (5, 10, 15, 20, and 25 h) were collected. We also changed the ball-to-powder ratio (2:1, 2.35:1, 2.60:1, 2.98:1, and ≈ 3:1) during SBM. Finally, the collected samples were preserved in airtight glass vials. The flow diagram of the complete synthesis process of CBO with sample notation is shown in Fig.1.

![Fig. 1. The flow diagram of the CuBi2O4 (CBO) sample synthesis process by sequential Ball Milling (SBM).](image)

III. RESULTS AND DISCUSSION

A. X-Ray diffraction analysis

The crystal structure, phase, and purity of the materials were analyzed by their powder X-ray diffraction (XRD) patterns (see Fig. 2) recorded by a Thermo Scientific ARL EQUINOX 1000 X-Ray Diffractometer (X-ray anode source of Cu-Kα radiation, λ = 1.5406 Å). The XRD peaks in the Cu-Bi-O-HBM 6 h sample match neither CuO [6,7] nor Bi2O3 [8]. In contrast, the XRD pattern of CBO (750°C-4 h) shows that the ternary copper bismuth oxide formation started after sintering at 750 °C for 4 h. Notice that the dominant diffraction peak near 2θ = 28° significantly shifted to the higher Bragg angles for CBO (750°C-4 h) compared to those of Cu-Bi-O-HBM 6 h (see dashed vertical lines in Fig.2). The XRD patterns of SBM-5 h and SBM-25 h suggest that the crystallinity of CBO materials increases with increasing milling duration. Notably, most of the diffraction planes (marked by dashed lines) of the CBO (750°C-4 h), SBM-5 h, and SBM-25 h samples match the XRD patterns of CuBi2O4 reported in the literature [9] and confirm the tetragonal phase with space group P4/nnc (130) [10]. The most intense diffraction peak at about 2θ = 27.99° can be assigned to the (211) lattice plane of CuBi2O4. The Full Width at Half Maximum (FWHM) of 211 Bragg peak was considered to estimate the average crystallite domain size of CBO samples by viewing a pseudo-distribution for the peak broadening and using Scherrer’s formula [11]:

$$D = \frac{k\lambda}{FWHM_{\text{sample}} \cos\theta}$$

where D is the crystallite domain size, FWHM_{\text{sample}} is the full width at half maximum, k (≈ 0.9) is Scherrer constant, λ is the wavelength of Cu-Kα radiations (1.54056 Å), and θ is the Bragg diffraction angle. The crystal size of Cu-Bi-O-HBM 6 h, CBO (750°C-4 h), SBM-5 h, and SBM-5 h were estimated to be 66.0 nm, 51.5 nm, 55.2 nm, and 50.0 nm, respectively.

In Fig.2, two diffraction peaks appeared at 2θ = 35.48° and 37.41° may respectively match the (111) and (202) Bragg planes of monoclinic CuO [6,7], suggesting a possible presence of a tiny amount of CuO in the CBO matrix. This was presumably because of the unreacted CuO raw powder during low-temperature sintering or produced from the decomposition of CBO during SBM processing. Similar results can also be found in refs. [11,12]. The benefits of CuO phase segregation in CBO have also been reported [11].

![Fig. 2. X-ray diffraction (XRD) patterns of the samples.](image)
Bi-O-HBM 6 h sample match neither with CuO [6,7] nor with Bi2O3 [8] corroborating the XRD results given in section A. In contrast, the three Raman bands centering at about 259.6 cm\(^{-1}\), 399.6 cm\(^{-1}\), and 583.3 cm\(^{-1}\) are observed for CBO (750C-4 h), SBM-5 h, and SBM-25 h samples without any detectable vibrational peaks of CuO and Bi2O3. These Raman bands agree with the vibrational structure of tetragonal CuBi2O4 reported previously [14,15]. This observation confirms that phase pure CBO could be grown from raw CuO and Bi2O3 powders using the SBM technique. Furthermore, the gradual peak broadening (for example, the 259.6 cm\(^{-1}\) peak) of the samples indicates grain size reduction is due to SBM with increasing milling durations. Both stoichiometric changes and grain size reduction due to SBM may affect the optical bandgap of the synthesized CBO, which will be discussed in the following sections.

![Raman Shift (cm\(^{-1}\))] {250 500 750 2000 2500 3000 3500}

**Fig. 3.** The room temperature Raman spectra of Cu-Bi-O-HBM 6 h, after sintered at 750\(^{\circ}\)C for 4 h (CBO(750C-4 h)), SBM-5 h, and SBM-5 h samples.

**C. SEM and EDX analyses**

The morphological features and elemental percentage of the CBO samples were explored using a field emission scanning electron microscope (FE-SEM, JOEL 7610F) coupled with a dispersive X-ray (EDX) microanalyzer (JED 2300). SEM micrographs of SBM-5 h and SBM-25 h samples are shown in Fig. 4a and 4b, revealing average grain sizes of ~145 nm and ~102 nm, respectively. The grain size reduction with the SBM duration is clearly evident from the SEM micrographs. In fig. 4, EDX spectra of the SBM-5 h and SBM-25 h samples exhibit the signatures of the constituent elements (Cu, Bi, and O) of CuBi2O4. The detected chemical species and their percentages (atomic and weight) are enlisted along with the corresponding EDX spectra (see the inset of the bottom panel of Fig. 4a and 4b). The stoichiometric changes with SBM milling durations are evident in both samples.

![SEM micrographs and EDX spectra](image)

**Fig. 4.** SEM micrographs and EDX spectra of the SBM-5 h (a) and SBM-25 h (b) samples.

**D. UV-VIS-NIR absorption spectra**

To get insight into the light-harvesting capability of the CBO, the diffuse reflection data of SBM powder samples were recorded at room temperature using a UV-VIS-NIR spectrometer coupled with an integrating sphere (Shimadzu ISR-2600 plus). The measured diffuse refection data of all samples were converted to absorption spectra by Kubelka-Munk (KKM) function [2] and displayed in Fig. 5. The absorption edge wavelength (energy) of raw CuO and Bi2O3 powders is around 900 nm (~1.38 eV) and 437 nm (~2.84 eV), respectively.

![UV-Vis diffuse absorption spectra](image)

**Fig. 5.** UV-Vis diffuse absorption spectra of raw CuO, raw Bi2O3, and synthesized CBO powders with different milling conditions. Notably, the primary absorption edges of synthesized CBO samples are located within the 650-850 nm wavelength range. The absorption edge variation (different from CuO and Bi2O3) is presumably due to the combined effect of grain size and elemental concentration variation in CBO. Many parameters, such as grain shape and size, presence of different vacancies and interstitials, and defects, controls...
optical absorption [2]. For instance, the red shift in the absorption edge usually comes from grain size increment [16]. This redshift is evident in the case of hand-milled samples. The optical properties of nanostructured materials strongly depend on the prepared samples' microstructure. However, further experimental investigations such as more sensitive X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectroscopy (ICPMS) are needed to confirm the presence of CuO phase (if any) as well as Cu:Bi ratio of CBO samples for tunable optical bandgap, which is along with the Density Functional Theory (DFT) based theoretical calculations are currently in progress and will be communicated elsewhere.

IV. CONCLUSION

This paper presents XRD, Raman, SEM, EDX, and optical absorption of sequential ball milled (SBM) derived phase pure CuBi₂O₄. The phase purity and size reduction of the CuBi₂O₄ were confirmed from XRD and Raman data. The SEM micrographs confirmed the grain size reduction with SBM milling durations. The formation of CBO has also been verified from the elemental composition conducted by SEM coupled EDX analysis. The optical absorption studies revealed that a facile SBM technique could successfully achieve CBO with a tunable optical bandgap.

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