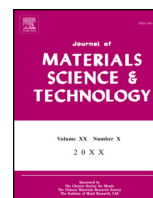




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Effects of electrochemical synthetic conditions on surface property and photocatalytic performance of copper and iron-mixed p-type oxide electrodes

Sun Hee Yoon^a, Dong Suk Han^{a,*}, Unseock Kang^b, Seung Yo Choi^b,
Wubuliksimu Yiming^c, Ahmed Abdel-Wahab^a, Hyunwoong Park^{b,*}

^a Chemical Engineering Program, Texas A&M University at Qatar, Education City, Doha 23874, Qatar

^b School of Energy Engineering, Kyungpook National University, Daegu 41566, Republic of Korea

^c Department of Mechanical Engineering, Texas A&M University at Qatar, Education City, Doha 23874, Qatar

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ABSTRACT

Earth-abundant copper and iron-mixed oxide (CuO/CuFeO₂; CFO) film electrodes are synthesized using an electrochemical deposition (ED) technique at two different ED potentials (−0.36 and −0.66 V vs saturated calomel electrode (SCE); denoted as ED-1 and ED-2, respectively). Then, their surface morphologies are compared, and the photo(electro)catalytic activities for the reduction of Cr(VI) are examined in aqueous solutions at pH 7 under simulated sunlight (AM 1.5G; 100 mW cm^{−2}). The degree of the electrical potential applied to the ED process significantly affects the thickness of the synthesized electrode film and the intensity ratio of the diffraction peaks of CuO (111) and CuFeO₂ (012). A 200 μm thick ED-2 sample with a distinct stacking of CuO on CuFeO₂ exhibits a larger broadband absorption spectrum than the 50-μm thick ED-1 with less separate stacking. Furthermore, the ED-2 sample has a higher intensity ratio of the diffraction peaks of CuO (111) and CuFeO₂ (012) than ED-1. As-synthesized ED-2 samples produce larger photocurrents, leading to faster Cr(VI) reduction on the surface under given potential bias (−0.5 V vs SCE) or bias-free conditions. The energy levels (i.e., flatband potential) for the two samples are almost the same (only 10 mV difference), presumably supposing that the enhanced photoactivity of the ED-2 sample for Cr(VI) reduction is due to the facilitated charge transfer. The time-resolved photoluminescence emission spectra analysis reveal that the lifetime (τ) of the charge carriers in the ED-1 sample is 0.103 ns, which decreases to 0.0876 ns in the ED-2. The ED-2 sample synthesized at a high negative potential is expected to contribute greatly to the application of other solar-to-fuel energy conversion fields as a highly efficient electrode material.

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1. Introduction

Over the past decades, significant efforts have been made to develop photoelectrodes made of earth-abundant elements that are highly efficient in producing various solar fuels [1–4] and treating environmental contaminants [5–7]. Of these photoelectrodes, Cu-based oxides (CuO [8], CuFeO₂ [9–11], Cu₂FeO₄ [12], CuAlO₂ [13,14], CuAl₂O₄ [15], etc.) have been considered to be

the most suitable for such applications because of their narrow bandgap energies, low cost, easy fabrication, and non-toxicity [16]. While many studies have been done in the field of producing solar fuels, there have been few reports on the use of Cu-based oxides for environmental applications. For example, p-type CuAlO₂ was directly used to produce molecular hydrogen [14], and it was further coupled with n-type CdS to reduce Cr(VI) to Cr(III) species at a circum-neutral pH under visible light [17]. Similarly, p-type CuFeO₂ has been tested for hexavalent uranium reduction [18], and it exhibited low photoelectrocatalytic activity due to an intrinsic, rapid charge recombination inside the bulk [19].

Recently, the coupling of p-type CuO and p-type CuFeO₂ via a sol-gel process was reported to form a staggered band align-

* Corresponding authors.

E-mail addresses: dong.suk.han@qatar.tamu.edu (D.S. Han), hwp@knu.ac.kr (H. Park).

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ment (type II) that increases p-type conductivity [18–20]. Our previous study on a p–p heterojunction of CuO and CuFeO₂ made by the electrochemical deposition (ED) process on transparent conducting oxide (TCO) substrates showed not only a very stable photocurrent response under simulated sunlight (AM 1.5G; 100 mW cm⁻²), but also a highly selective formate production (>90% selectivity) over 24 h from CO₂ and water [10,19]. Furthermore, the high selectivity was maintained over 35 days after weekly healing the deformed CuFeO₂/CuO film electrode with oxidative annealing [19]. It was found that the photoelectrocatalytic (PEC) activity of CuO/CuFeO₂ was higher than those of individual CuO and CuFeO₂. This composite material was further demonstrated to be able to effectively convert seawater uranyl (U(VI)) to reduced states (e.g., U⁴⁺ and U^{14/3+}) under simulated sunlight [18]. Although a straddling band alignment (type I) was proposed, a close valence band level (~100 mV) between the two could virtually lead to an enhanced charge separation upon a potential bias [10,19]. Furthermore, the analytical difficulty in determining the exact valence band level of porous, three-dimensional semiconductors using conventional techniques [21] opens a possibility that this vicinity could result in straddling and/or staggered band alignments.

This study focused on synthesizing mixed CuO and CuFeO₂ (CFO) film electrodes with different surface heterogeneity by applying two different ED potentials. The typical ED potential for synthesizing CFO films was close to the Cu(I or II) reduction peak in cyclic voltammograms (e.g., -0.36 V vs saturated calomel electrode (SCE)) in aqueous perchlorate solutions [9,10,18,19]. However, this study adopted a 300 mV-more negative ED potential (i.e., -0.66 V vs SCE) to accelerate the deposition kinetics and obtain thick films. An increase in the semiconductor film thickness can create a different morphology and usually enhances the light absorption, whereas at the same time the minority carrier (electrons in a p-type semiconductor) must travel farther [22–24]. The trade-off between the absorption and the charge carrier transfer in thick films often leads to unexpected results, requiring an elaborate design for the materials and systems. The surface of the as-synthesized CFO samples was characterized using surface analysis techniques, including X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Their PEC activities were evaluated by measuring the degree of reduction of Cr(VI) to Cr(III) in aqueous solutions under simulated sunlight (AM 1.5G; 100 mW cm⁻²). Hexavalent chromium is a well-known carcinogenic aquatic contaminant, and the World Health Organization recommends a Cr(VI) concentration below 50 ppb in drinking water, whereas water insoluble Cr(III) is often used for dietary supplements. This application of the CFO has not been previously reported and should expand its viability and practicality.

2. Experimental

Mixed CuO and CuFeO₂ films were synthesized by a modified electrochemical deposition method [10,18,19]. In brief, pieces of fluorine-doped SnO₂ (FTO)-coated glass (Pilkington, ~500 nm thick FTO layer, 1.5 cm × 3.5 cm) were ultrasonically pretreated in an ethanol solution for 10 min to remove any possible contaminant. They were washed with deionized water (>18 MΩ cm) and dried naturally in the air. Then, a clean FTO-coated glass electrode (working electrode), SCE (reference electrode), and Pt wire (counter electrode) were immersed in aqueous solutions containing KClO₄ (50 mM, Aldrich), hydrous Cu(NO₃)₂ (4 mM, Aldrich), and hydrous Fe(ClO₄)₃ (12 mM, Aldrich). A constant potential (-0.36 or -0.66 V vs. SCE; denoted as ED-1 and ED-2, respectively) was applied to the working electrode for 2 h using a potentiostat (Gamry Instrument), followed by annealing at 650 °C for 3 h in the atmospheric air.

The surfaces of the as-synthesized CFO samples were characterized using XRD (Bruker) to examine the crystalline structure (CuO and CuFeO₂). Also, the morphologies and spatial compositions were determined using SEM/EDS (FEI Quanta 400). The elemental information (C 1s, O 1s, Cu 2p, and Fe 2p) and oxidation states over the film depth of the synthesized film electrodes were collected using an etching technique with XPS (Kratos AXIS UltraDLD). A single etching cycle was conducted for 1 min by sputtering with Ar gas (99.99%) on the focused surface area (1 mm × 1 mm) under a vacuum condition of 10⁻⁶ torr in the sample transfer chamber (STC) and <10⁻⁹ torr in the sample analysis chamber (SAC) to ensure that the ion gun was fully activated. At the end of each etching cycle, the high-resolution XPS spectra of each targeted element were collected using a monochromatic Al K_α (1486 eV) X-ray source at 20 eV of pass energy with three sweeps and then calibrated using a 483.5 eV of the C 1s spectra. A 1 min etching process was found to etch ~5 nm of a Ta standard specimen. Despite the use of a different sample composition, the etching rate (i.e., ~5 nm min⁻¹) was presumed to be similar to each other.

AFM images were obtained using a Dimension Icon AFM system (Bruker, CA, USA) equipped with a Nanoscope (Version 9.1) controller and analyzed by Nanoscope analysis software (Version 1.5). To obtain topographical and phase images of the samples, a standard tapping mode was applied in air using a silicon-etched TESPA-V2 AFM probe with a ~10 nm tip radius under a 319 kHz resonant frequency. During the analysis, a 20 μm × 20 μm area of each sample was scanned with a scan rate of 0.5 Hz and resolution of 512 × 512 pixels.

The CFO energetics were investigated by measuring the optical bandgap energy using a UV-VIS-NIR spectrometer (Shimadzu) with a diffuse reflectance mode and estimating the flat band potential based on an electrochemical impedance study (i.e., Mott–Schottky measurement) in a 1 M NaCl solution in the range of 1.0 V and -0.2 V vs SCE at a scan rate of 10 mV s⁻¹.

The time-resolved photoluminescence (TRPL) emission decay curves for the as-synthesized samples were obtained using a confocal microscope (MicroTime-200, Picoquant, Germany) with a 20× objective at the Korea Basic Science Institute (KBSI), Daegu Center, Korea. A single-mode pulsed diode laser (wavelength λ = 379 nm with a pulse width of ~30 ps and ~30 μW of laser power) was used as the excitation source. The details of this analytical protocol are found elsewhere [14,19,22,25].

The photoelectrochemical behaviors of the CFO samples (ED-1 and ED-2) were examined in an aqueous NaCl solution (1 M, Sigma Aldrich) in the absence and presence of Cr(VI) (1 mg L⁻¹ for K₂Cr₂O₇, Sigma Aldrich; equivalent to 6.8 μM for Cr(VI)). The light-chopped linear sweep voltammograms (LSVs) of the CFO samples were obtained at a potential range of +0.6 V to -0.6 V vs SCE with a scan rate of 5 mV s⁻¹ under simulated solar light (AM 1.5G; 100 mW cm⁻²) using a 150 W Xe arc lamp (ABET solar simulator). For the PEC reduction of Cr(VI) with an initial concentration of 6.8 μM, an as-synthesized CFO electrode (0.25 cm²) and a Pt counter electrode were simply wired, and they were placed in two different cells separated by a proton-exchange membrane (Nafion 117). Both cells were filled with the aqueous NaCl solution (1 M), and Cr(VI) was spiked into the CFO cell just before initiating PEC experiment. After 30 min, the back side of the CFO (i.e., the uncoated side) was irradiated with the simulated solar light. During the PEC test, aliquots were intermittently collected from the CFO cell. If necessary, an SCE reference electrode was also placed in the CFO cell, where a constant potential of -0.5 V vs SCE was applied to the CFO electrode under irradiation. To quantify Cr(VI) concentration, chemical reagents mixed with H₃PO₄ (10 μL), H₂SO₄ (20 μL), and diphenyl benzenaide (80 μL) solutions were added

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