

Stand-alone photoconversion of carbon dioxide on copper oxide wire arrays powered by tungsten trioxide/dye-sensitized solar cell dual absorbers



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ABSTRACT

A photoelectrochemical (PEC) cell composed of a WO₃/dye-sensitized solar cell (WO₃/DSSC) and copper oxide (Cu_xO, where $x=1$ and 2) wire arrays as a dual-absorber photoanode and cathode, respectively, is demonstrated as a stand-alone, durable device for CO₂ photoconversion. The Cu_xO wire arrays, which have high surface-to-volume ratios, exhibit promising electrocatalytic activity for CO₂ conversion to CO at Faradaic efficiencies of ~80% and ~60% at $E = -0.2$ and -0.4 V vs. RHE, respectively, and H₂ production is minimized at a Faradaic efficiency < ~20% in the potential range between -0.2 and -1.0 V vs. RHE. The single-absorber cell of a WO₃ photoanode and Cu_xO wire array cathode couple (WO₃-Cu_xO) requires a minimum overpotential of ~0.7 V to drive CO₂ conversion. For stand-alone CO₂ conversion, a DSSC is coupled to the WO₃-Cu_xO system. In the dual-absorber cell (WO₃/DSSC-Cu_xO), the long-wave band ($\lambda > ca. 450$ nm) passed through the semitransparent WO₃ film is absorbed by the dye-sensitized TiO₂ electrode of the DSSC. The WO₃/DSSC-Cu_xO shows a potential gain of ~0.7 V and is able to successfully drive CO₂ conversion on Cu_xO and simultaneously oxidize water on WO₃ without an external power supply. In this stand-alone system, the primary CO₂ conversion product is CO, with a solar-to-chemical energy efficiency of ~2.5%; H₂ and formate are obtained with energy efficiencies of 0.7% and 0.25%, respectively, in 5 h (overall efficiency ~3.45%). Neither CO₂ conversion product nor H₂ is found using the single-absorber system.

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1. Introduction

Artificial photosynthesis of value-added chemicals from CO₂ and water has attracted renewed attention, and diverse technical solutions for high efficiency and durability systems have been explored [1–6]. Conventional slurry-type photocatalysis has been shown to drive CO₂ conversion to CO, formate, and C1–C3 hydrocarbons with low conversion efficiency (< ~1%) [7]. Furthermore, the use of sacrificial organic compounds and carbon impurities inherently contained in materials often obscures the CO₂ reduction products [8,9]. Alternatively, photoelectrochemical (PEC) systems have been demonstrated to be

technically viable with a number of semiconductor photoanodes (e.g., WO₃ [10,11] and BiVO₄ [10,12,13]) coupled to metal (e.g., Cu, Au, and Ag) [14,15] or metal oxide electrodes (CuO and Cu₂O) [16] and photocathodes (e.g., Si [4], Cu₂O [5], CuO₂ [5], and CuFeO₂ [5,17]) coupled to metal/metal oxide anodes. Although they are promising, these single absorbers (photoanode or photocathode) exhibit significantly lower efficiencies than the solar conversion limit and require external biases [4,18], primarily because of energy losses arising from overpotentials in the O₂ evolution and CO₂ reduction reactions. Photo-voltaic (PV)-wired [19] and wireless monolithic [3,20,21] electrochemical CO₂ conversions are technically viable and highly efficient; however, their cost, complicated fabrication, and durability remain challenging.

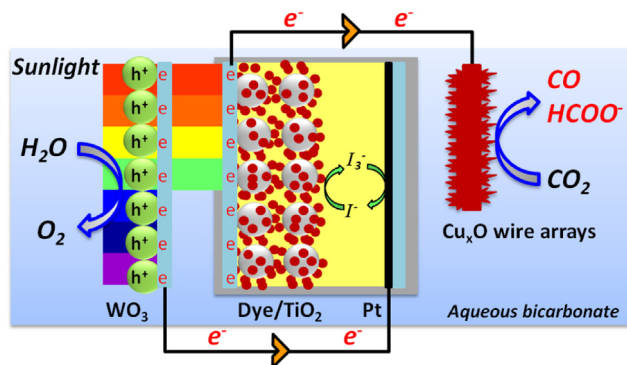
A dual-absorber approach utilizes four photons in tandem configurations (e.g., PV-PV, photoanode-photocathode, and photoanode-PV couples), similar to the mechanism of photosystems (PS) (specifically, PS-II and PS-I) [22]. The primary advantage of the

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Scheme 1. Schematic illustration of a stand-alone dual-absorber cell for CO₂ conversion. WO₃ was wired to the Pt-counter electrode of a dye-sensitized solar cell (DSSC), and dye-sensitized TiO₂ (Dye/TiO₂) of the DSSC was wired to copper oxide (i.e., Cu_xO, where $x=1$ and 2) wire arrays while WO₃ was placed in front of the Dye/TiO₂ in parallel. All electrodes were immersed in CO₂-purged 0.1 M bicarbonate aqueous solution, and WO₃ was irradiated with simulated sunlight (AM 1.5G; 100 mW cm⁻²).

dual absorber is that it can attain a higher efficiency limit than a single absorber, even though the bandgap is the same (e.g., 16.6% with $E_{g1}=E_{g2}=1.4$ eV; 11.6% with $E_{g1}=1.4$ eV) [23]. Recently, this dual-absorber approach has been explored for unassisted (stand-alone) water splitting, and a solar-to-hydrogen efficiency of $\sim 3\%$ was reported using the combination of a WO₃ and a dye-sensitized solar cell (DSSC) in a tandem configuration [24,25].

To achieve the stand-alone artificial photoconversion of CO₂, we applied a dual absorber, WO₃/DSSC, as described in Scheme 1. In contrast to water splitting, however, the following must be considered for the photoconversion of CO₂. First, the behavior of the WO₃ photoanode is dependent on the electrolyte composition. The typical electrolytes used for water splitting are highly acidic (e.g., 1 M H₂SO₄) which facilitates high-efficiency H₂ production and improves the durability of WO₃, whereas bicarbonate (0.1 M, pH 6–8) is favored in CO₂ conversion because of the high solubility of CO₂. The development of catalytically effective electrodes (i.e., cathodes) for CO₂ conversion is highly challenging. Pt, which is the most effective catalyst for the H₂ evolution reaction, is a poor catalyst for proton-coupled electron transfer to CO₂. However, some metals and oxides are able to efficiently reduce CO₂. For example, Cu and its oxides are capable of efficiently producing C1–C4 hydrocarbons, formate, and methanol in CO₂-purged bicarbonate solution [5,7,14], whereas Sn, Cd, Hg, and In have been shown to be effective in producing formate, and some noble metals (Au and Ag) are highly selective for CO production [4,14].

In this study, we synthesized wire arrays composed of Cu₂O and CuO (Cu_xO) with high surface-to-volume ratios and examined their electrochemical behavior and CO₂ conversion efficiency. Then, WO₃ thin films of varying thicknesses were coupled to the Cu_xO wire arrays for PEC CO₂ conversion in CO₂-purged bicarbonate solution. Finally, a dual-absorber WO₃/DSSC photoanode and a Cu_xO cathode couple were demonstrated as stand-alone, durable devices for CO₂ conversion and simultaneous water oxidation in bicarbonate electrolyte (Scheme 1). To the best of our knowledge, this is the first study investigating the stand-alone artificial photoconversion of CO₂ using a dual-absorber cell.

2. Experimental section

2.1. Materials and preparation of electrodes

Reagents and solvents of analytical grades were purchased from Sigma-Aldrich and used without further purification, unless otherwise mentioned. To fabricate WO₃ film electrodes, tungsten

(W, 1 g) was dissolved in aqueous H₂O₂ (30%, 4 mL) to obtain peroxytungstic acid. Then, 2-propanol (3 mL) was dropped into the peroxytungstic acid solution, followed by the addition of poly (ethylene glycol) 300 (PEG 300, 10 mL) as an organic stabilizer and a structure-controlling agent [26,27]. The W:PEG weight ratio was 1:10. Then, the precursor (1 mL) was spin-coated onto a fluorine-doped tin oxide substrate (F-SnO₂: FTO, 20 mm × 15 mm, 8 Ω/sq, Pilkington Co., Ltd.) and then dried at 150 °C for 30 min (one cycle). This cycle was repeated two, three, and four times; then, the as-obtained samples were annealed at 550 °C for 30 min. To create the Cu_xO electrodes, polycrystalline Cu foils (99.999%, 1 mm thick) were first treated with HCl (1 M); then, ultrasonically cleaned in 2-propanol, acetone, and deionized water; and finally, dried under a N₂ gas stream. Then, the treated Cu foils were subjected to thermal oxidation at 450 °C for 4 h in the atmospheric air to grow Cu_xO on the Cu [28]. For comparison, CuO samples were also prepared by coating CuO powder on Cu.

2.2. Electrochemical characterization of electrodes and tandem cells

The electrochemical behavior and performance of the electrodes (WO₃, Cu, and Cu_xO) were examined in a typical three-electrode configuration with Ag/AgCl (3 M KCl) or a saturated calomel electrode (SCE) as a reference electrode and Pt foil as a counter electrode using an electrochemical workstation (CompactStat, IVIUM). These working electrodes were immersed in sodium bicarbonate solution (NaHCO₃, 0.1 M) prepurged with Ar or CO₂ for over 1 h in an air-tight single cell; then, the potential was swept at a scan rate of 10 mV s⁻¹. To investigate the PEC characteristics of WO₃, three different electrolytes were used: bicarbonate (0.1 M NaHCO₃), perchloric acid (0.1 M HClO₄), and perchlorate (0.1 M LiClO₄).

To fabricate the DSSC, thin films of TiO₂ with a thickness of ca. 12 μm and an active area of ca. 0.25 cm² were prepared on FTO (20 mm × 15 mm) using TiO₂ paste (TTP-20N, ENBKOREA Co. Ltd., Korea) through a repeated screen-printing technique [29,30]. The detailed fabrication procedure is described in the Supporting information (SI). Then, a DSSC was immersed in bicarbonate solution, and a WO₃ electrode (0.25 cm²) was placed in front of the dye-sensitized TiO₂ electrode (Dye/TiO₂) of the DSSC. WO₃ was wired to the Pt electrode of the DSSC, and Cu_xO (or Cu) was wired to the Dye/TiO₂. Hereafter, the dual-absorbers coupled with the Cu_xO and Cu cathodes are denoted as WO₃/DSSC-Cu_xO and WO₃/DSSC-Cu, respectively. For comparison, WO₃ and Cu_xO were also directly wired (WO₃-Cu_xO).

The power of a solar simulator (Polaronix K201, McScience) equipped with a 200-W Xenon lamp and an air mass 1.5 (AM 1.5) filter was calibrated to be 1 sun (100 mW cm⁻²) using a standard mono-Si solar cell (PVM-396, PV Measurements Inc.) certified by the National Renewable Energy Laboratory (United States). The linear-sweep voltammograms (LSVs) of the cells were obtained using the electrochemical workstation.

2.3. Product analysis

Aqueous formate (HCOO⁻) was identified and quantified using liquid chromatography (IC, Dionex ICS-1100). A mixed eluent of Na₂CO₃ (3.5 mM) and NaHCO₃ (1 mM) was flowed through a Dionex IonPac AS 14 (4 mm × 250 mm) column. H₂ and CO gases were monitored by gas chromatography (GC) (Agilent 7820) with a thermal conductivity detector (TCD) and a 5-Å molecular sieve column. N₂ was used as the carrier gas for H₂, whereas helium (He) was used for CO analysis. For quantification, each standard gas (Fluka) was allowed to flow through the GC-TCD, and standard curves of each gas concentration and the corresponding spectral area were obtained.

The Faradaic efficiencies of the products (H₂, CO, and formate)

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