

Supporting Information

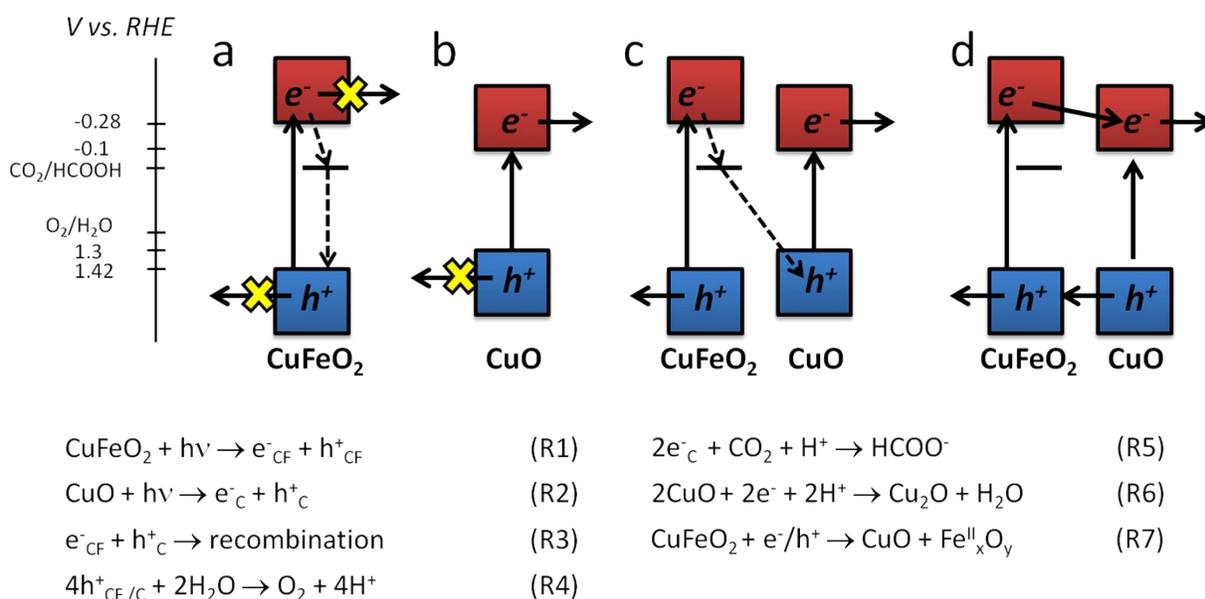
A facile synthesis of CuFeO₂ and CuO composite photocatalyst films for
production of liquid formate from CO₂ and water over a month

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Scheme S1. Illustration of CuFeO₂/CuO energetics (band gaps and band levels) and photoinduced charge transfer reactions (R1–R7). (a) CuFeO₂, (b) CuO, and (c and d) CuFeO₂/CuO. If the valence level of CuO is lower than that of CuFeO₂, then cascaded charge transfer can occur as depicted in (d). Subscripts CF and C refer to CuFeO₂ and CuO, respectively. In R7, Fe^{II}_xO_y refers to a family of ferrous oxides with stoichiometric (x = y) or non-stoichiometric (x < y; Fe-deficient) compositions.

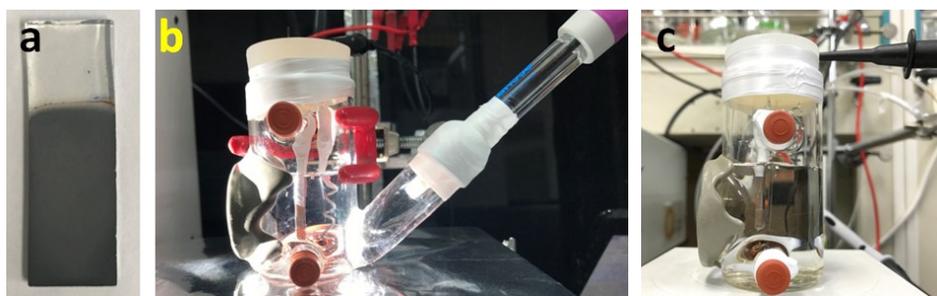


Figure S1. Photos of (a) CuFeO₂/CuO (coated on FTO), (b) three-electrode setup (CuFeO₂/CuO, Pt wire, and reference electrode from left), and (c) two-electrode setup (CuFeO₂/CuO and Pt foil from left). The photocurrent onset potentials of DMSO- and water-based samples were +0.85 and +0.93 V vs. RHE, respectively (Figure 1). These values refer to half-reaction potentials of working electrodes (versus reference electrode, as shown in Figure S1b). In the three-electrode setup for photoelectrochemical reaction, the photocurrent onset potentials are often (*but not always*) designated as the flatband potentials (E_{fb}) (H.O. Finklea, *Semiconductor Electrodes*, Elsevier, 1988). Accordingly, the onset potential of +0.93 V vs. RHE for the water-based CuFeO₂/CuO sample indicates the approximate position of E_{fb} , 0.93 V more positive than that of HER ($2H^+ + 2e^- \rightarrow H_2$) under given experimental conditions.

In addition, photovoltages (difference between the photocurrent onset voltage and the standard potential for the redox process taking place at the electrode) can be estimated using the two-electrode setup. The cell voltage (E_{cell}) of this study refers to the tandem voltage of two half-reactions (CO₂ reduction and OER) and obtained in the two-electrode setup under operation (Figure S1c). For example, the equilibrium cell voltage (E°) for the reaction ($CO_2 + H_2O \rightarrow HCO_2H + 1/2O_2$) is estimated to be ~ 1.4 V ($\Delta_r G^\circ = \sim 270$ kJ/mol; $\Delta_r G^\circ = -nFE^\circ$). The bandgap energies of CuFeO₂ and CuO were estimated to be ~ 1.7 and 1.4 eV (see Scheme S1). They are comparable to the E° value, driving the overall reaction with the CuFeO₂/CuO semiconductors alone.

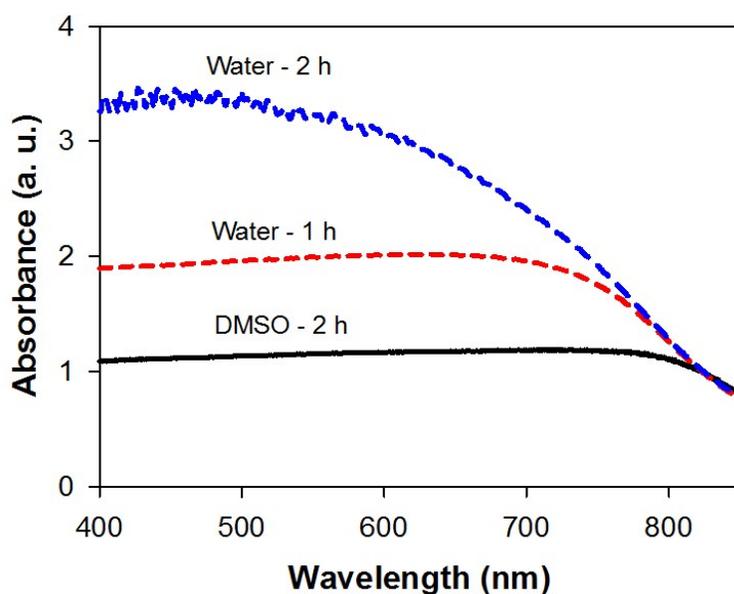


Figure S2. UV-vis absorption spectra of as-synthesized $\text{CuFeO}_2/\text{CuO}$ films via electrodeposition (1 and 2 h) in DMSO and water-based solutions containing Cu and Fe.

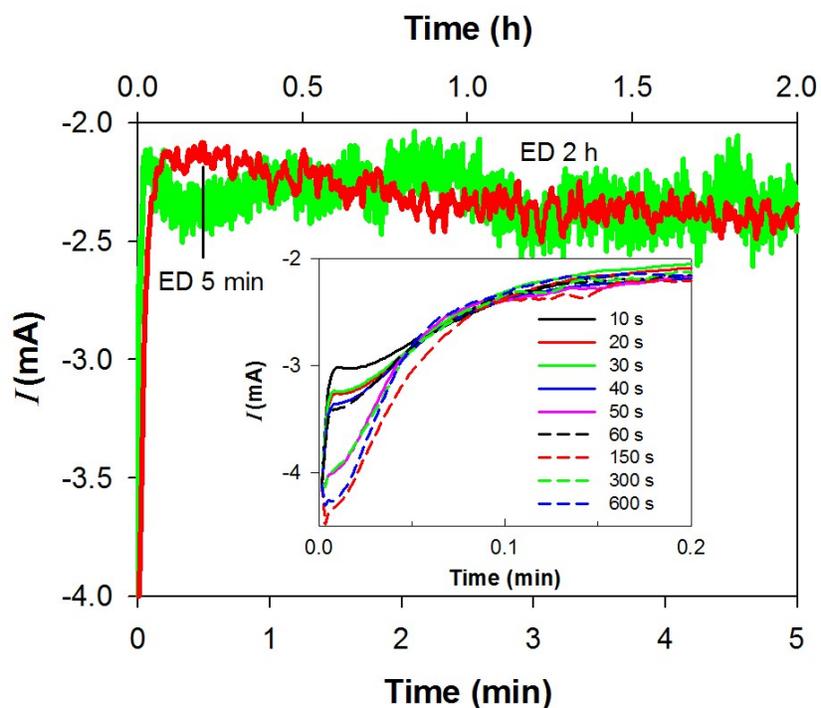
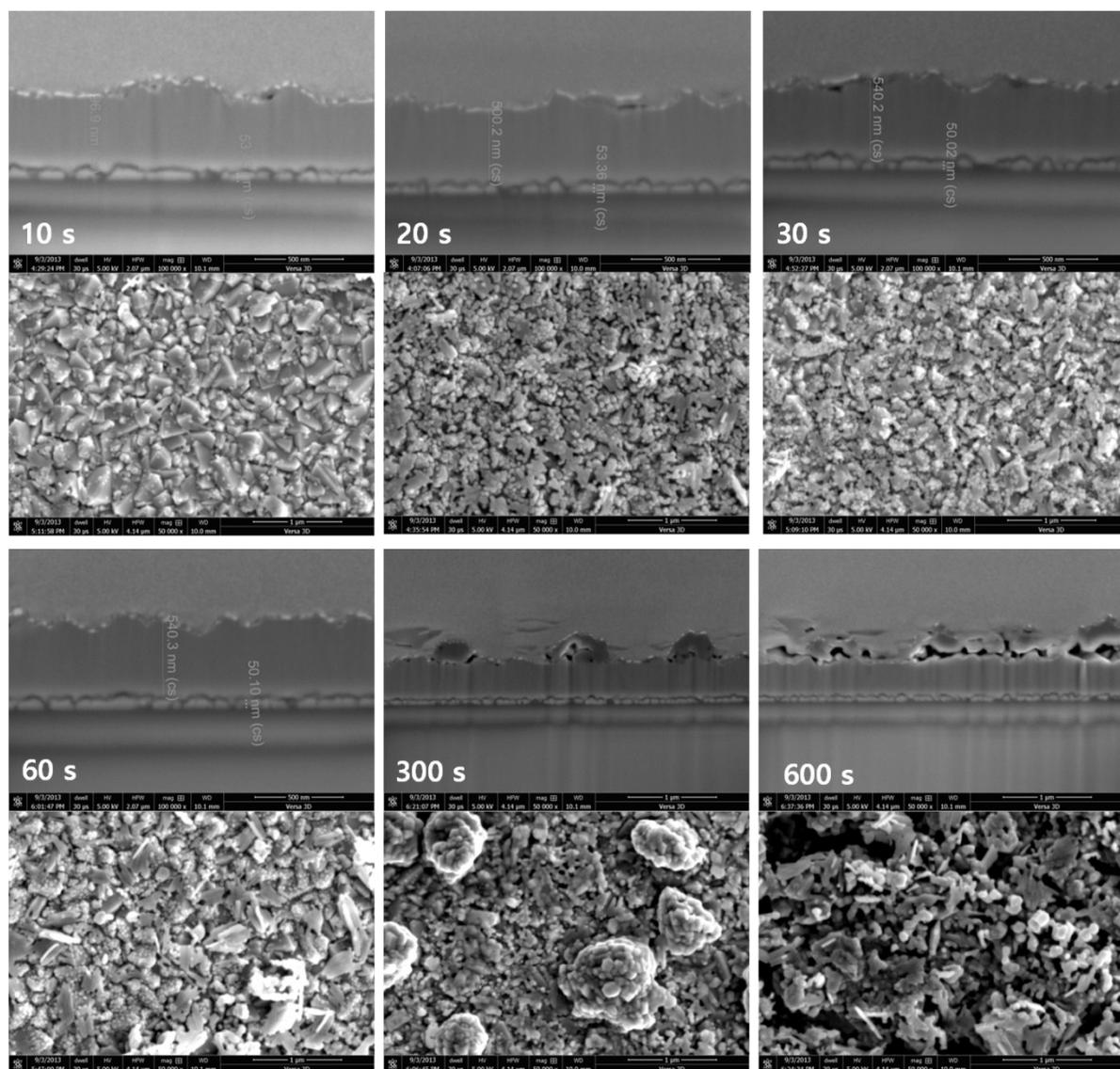


Figure S3. Time-profiled electrodeposition (ED) currents at $E = -0.36$ V vs. SCE for ED times of 5 min (red line, bottom y-axis) and 2 h (green line, top y-axis). Inset further shows the current profiles for 12 sec right after the ED initiation (total ED times of 10 - 600 sec).



Figures S4. FIB-TEM images for cross-sectional views and SEM images for top views of $\text{CuFeO}_2/\text{CuO}$ samples synthesized in aqueous solutions for varying electrodeposition times (10 – 600 s) at $E = -0.36 \text{ V vs. SCE}$.

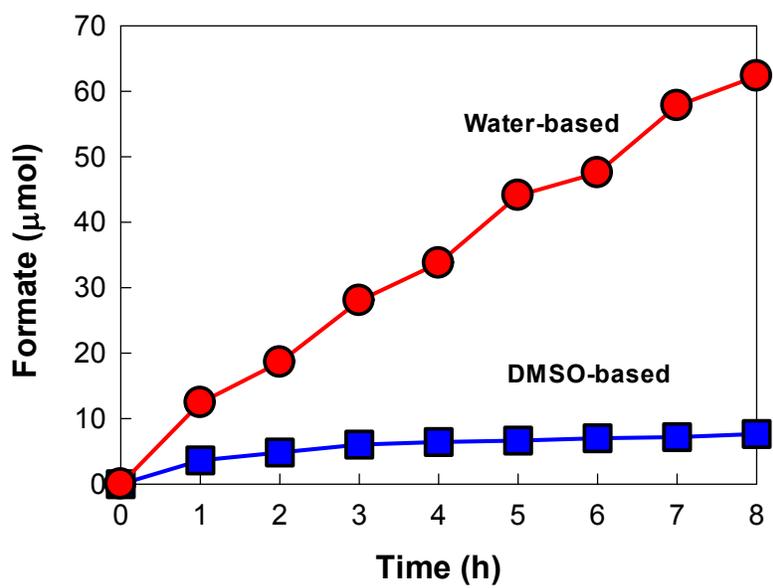


Figure S5. Comparison of $\text{CuFe}_2\text{O}_2/\text{CuO}$ samples synthesized in DMSO and water solvents for photoelectrochemical formate production in aqueous bicarbonate (0.1 M) solutions purged with CO_2 . $E = +0.15$ V vs. RHE.

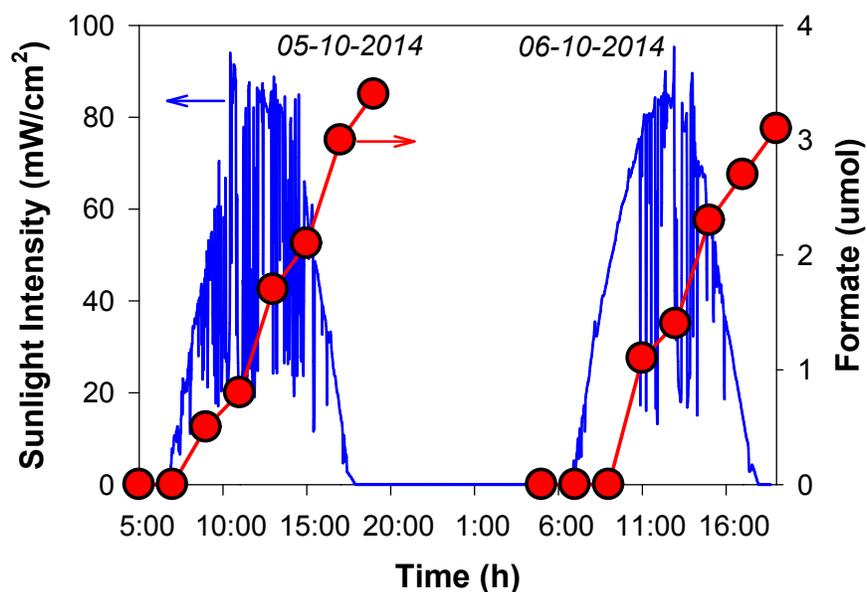


Figure S6. Outdoor field test for photocatalytic production of formate on $\text{CuFeO}_2/\text{CuO}$ film (wired to a Pt foil) in CO_2 -purged aqueous bicarbonate (0.1 M) solution. The experiment was performed in Kyungpook National University, Daegu, Korea (Longitude 128.60°; Latitude 35.88°) on October 5 – 6, 2014.

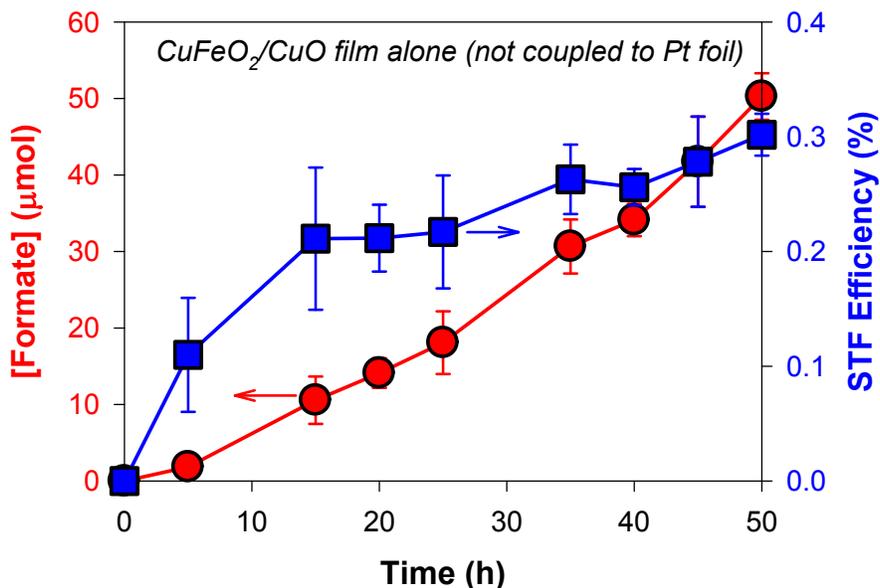


Figure S7. Photocatalytic production of formate on $\text{CuFeO}_2/\text{CuO}$ film immersed in CO_2 -purged bicarbonate (0.1 M) solution upon irradiation of AM 1.5 (100 mW/cm^2). $\text{CuFeO}_2/\text{CuO}$ was not wired to a Pt foil.

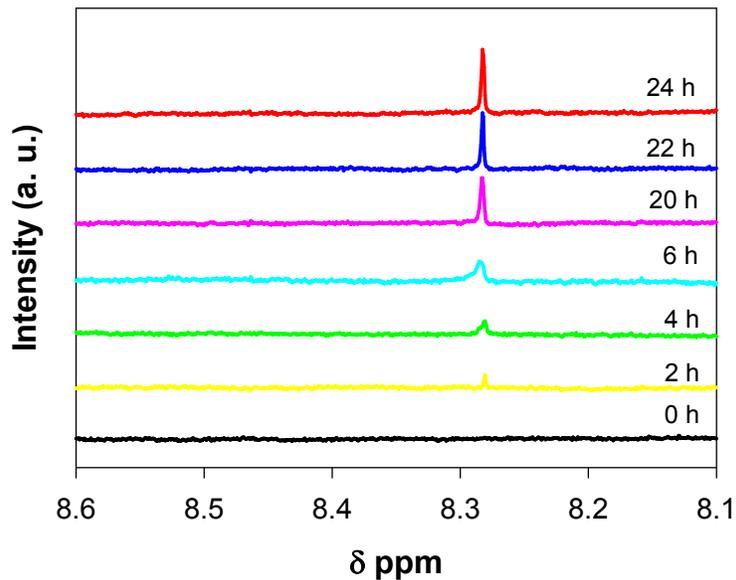


Figure S8. ^1H -NMR spectra of formate produced in CO_2 -purged ^{13}C -bicarbonate ($\text{H}^{13}\text{CO}_3^-$) solution during 24-h photocatalysis. See Figure 3 and experimental section for detailed experimental procedure.

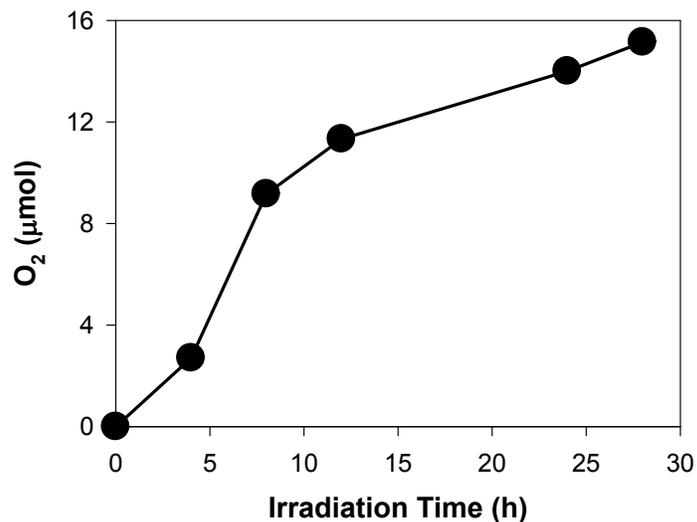


Figure S9. Time-profiled O_2 evolutions on Pt foil wired to $\text{CuFeO}_2/\text{CuO}$ film in CO_2 -purged aqueous bicarbonate (0.1 M) solution under irradiation of AM 1.5 light ($100 \text{ mW}\cdot\text{cm}^{-2}$).

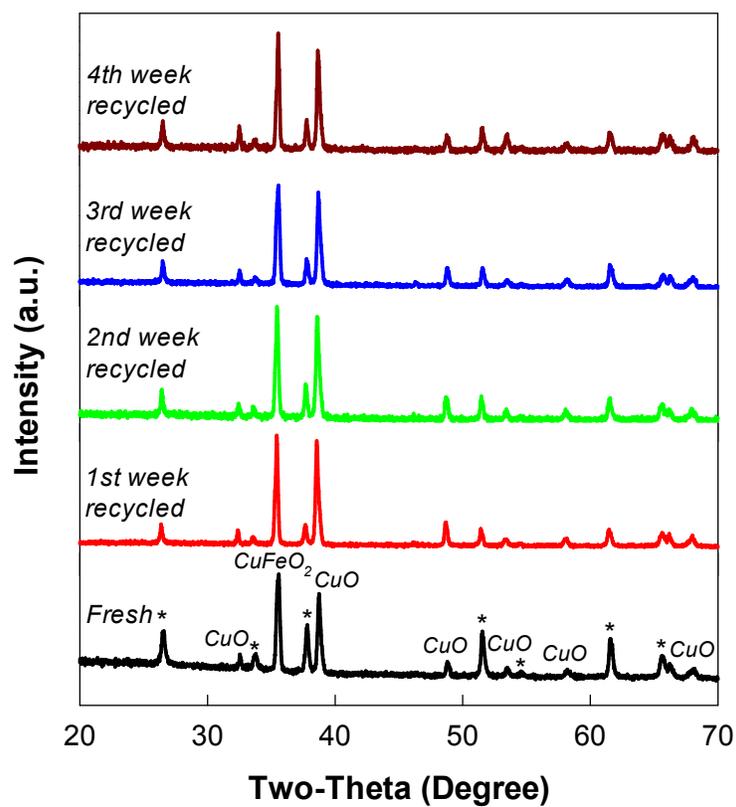


Figure S10. XRD spectra of as-synthesized and recycled $\text{CuFeO}_2/\text{CuO}$ samples.