

SUPPORTING INFORMATION

Anodic Cu₂S and CuS Nanorod and Nanowall Arrays: Preparation and Properties and Application in CO₂ Photoreduction

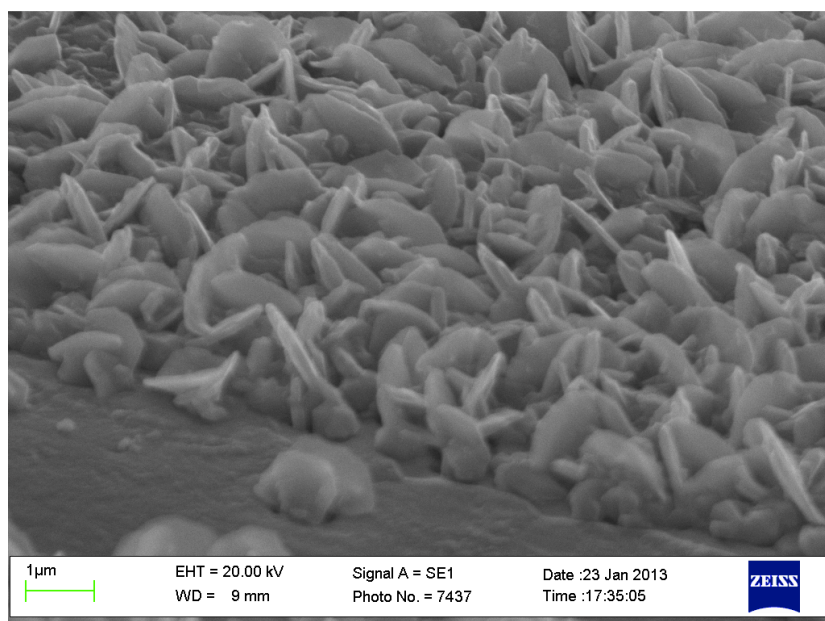
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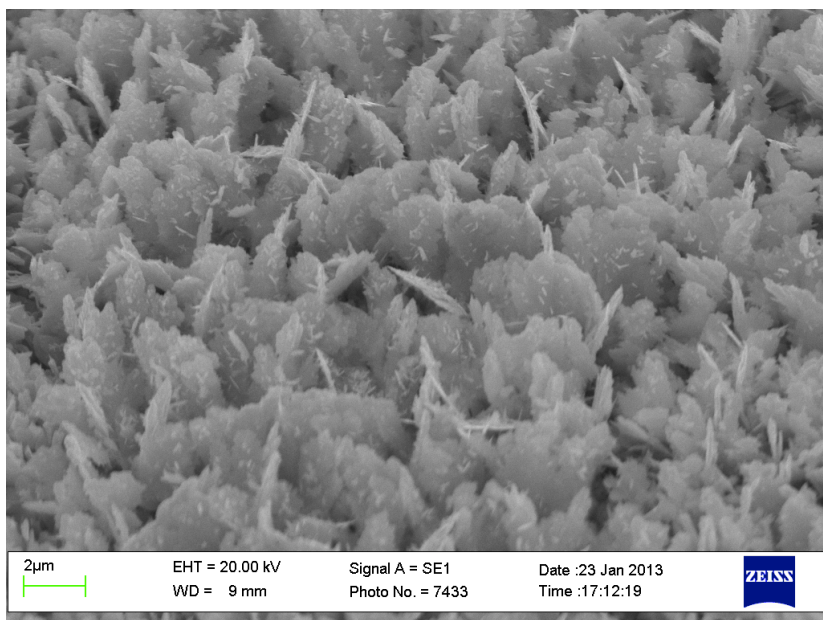
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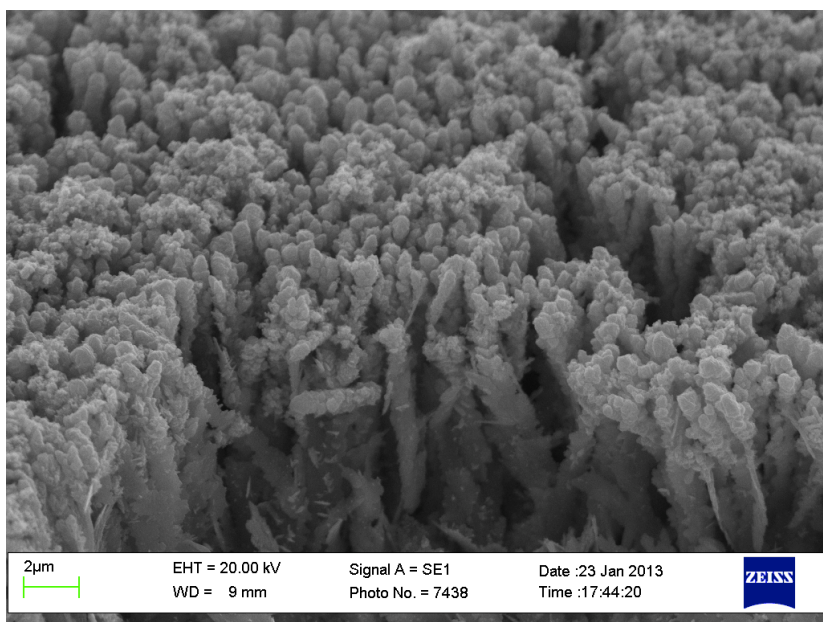
This document contains additional scanning electron micrographs, a representative anodization current transient, fully labelled X-ray diffractogram, HRTEM lattice images and GC spectra, presented in Figures S1 through S9.



S1a.



S1b.



S1c.

Fig S1. With increasing anodization time, from 15 seconds to 5 minutes, the morphology is observed to evolve from nearly vertically oriented nanowalls (S1a, 15 s) to nanowalls with branches (S1b, 60 s) and finally to rods with dendritic nanobranches (S1c, 300 s).

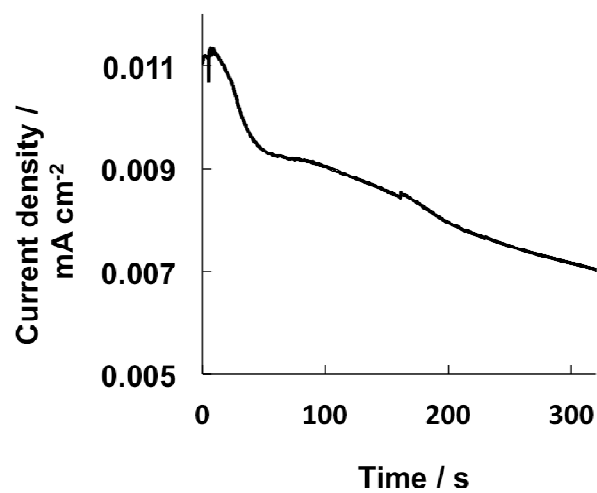


Fig. S2. Current time characteristics of the anodization process for formation of vertically oriented copper sulfide nanostructures. Data was recorded at constant anodization voltage, as indicated. Electrolyte was 0.1 M Na₂S (aqueous) solution.

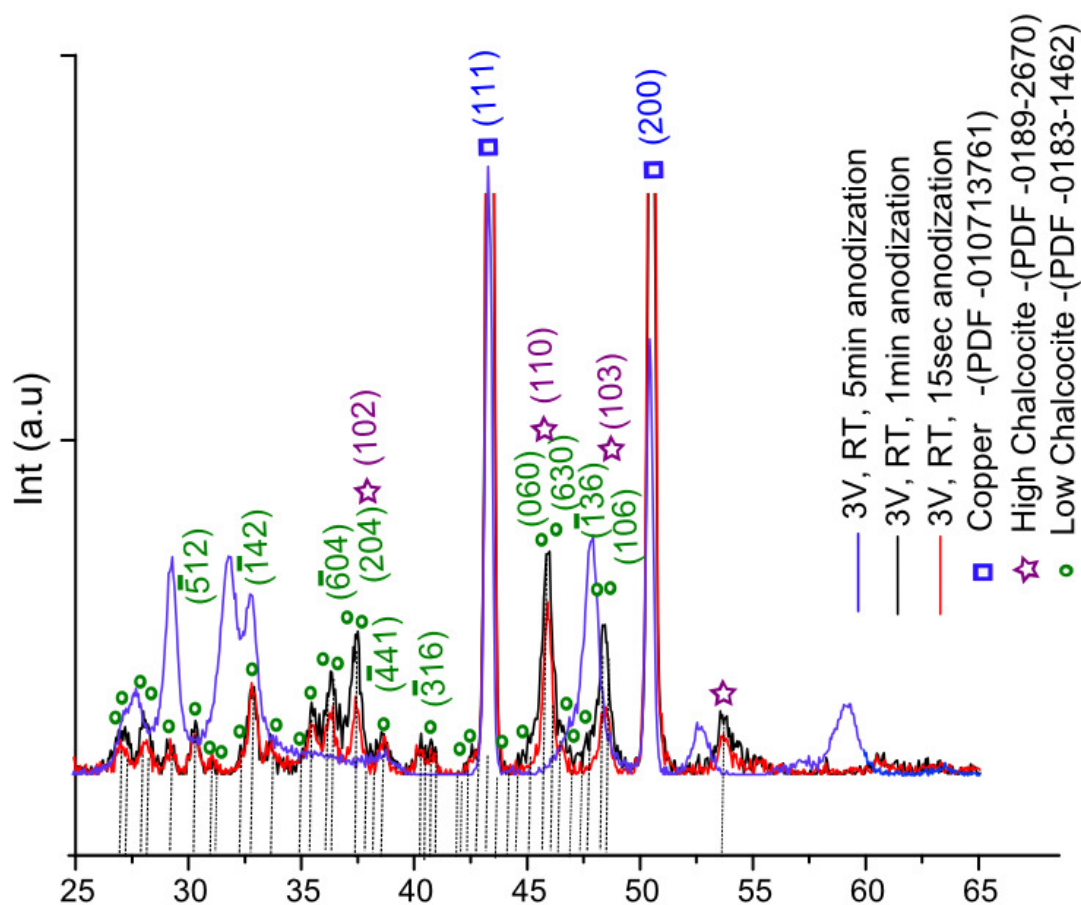
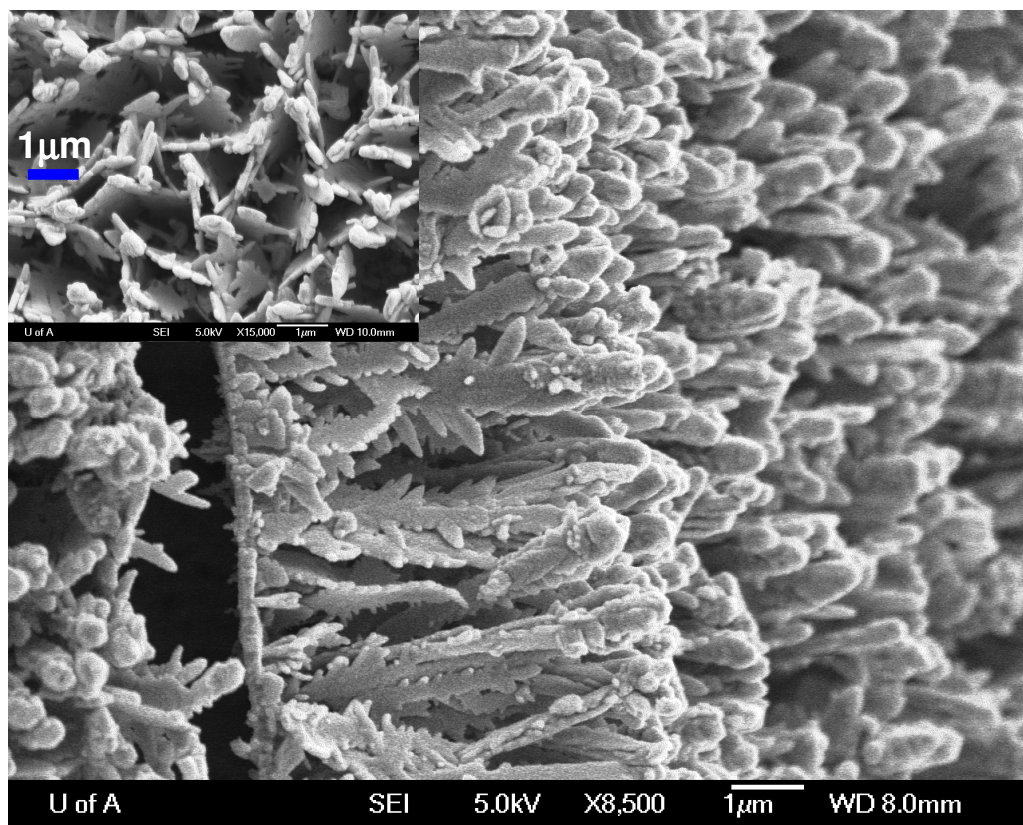
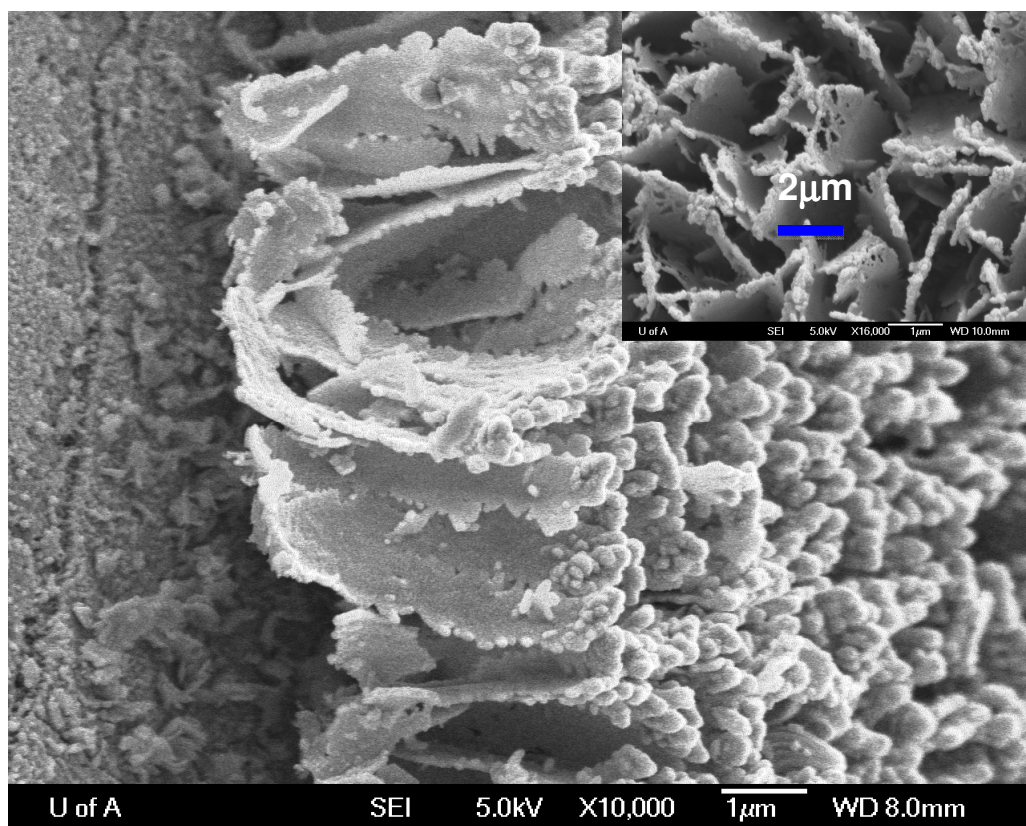


Fig S3. Glancing incidence X-ray diffractograms (GIXRD) of the samples corresponding to the SEM images in Fig. S1 (15 seconds, 1 minute and 5 minutes anodization times). Anodization durations of 15 seconds and 1 minute results in the formation of the low chalcocite (Cu_2S , JCPDS 01-0831462) phase while the 5 minute anodized sample forms the covellite (CuS , JCPDS 01-078-2121) phase. (The X-axis represents values of 2-theta, in degrees)



S4a.



S4b.

Fig. S4. Cross-sectional FESEM micrographs of copper sulfide nanostructures grown on Kapton by anodization at 2.5 V (Fig. S3a) and 3 V (Fig. S3b). In each case, the Insets show the top view. Anodization at 2.5 V forms vertically dendritic nanowire-like morphology and at 3 V, forms a dendritic nanowall-like morphology.

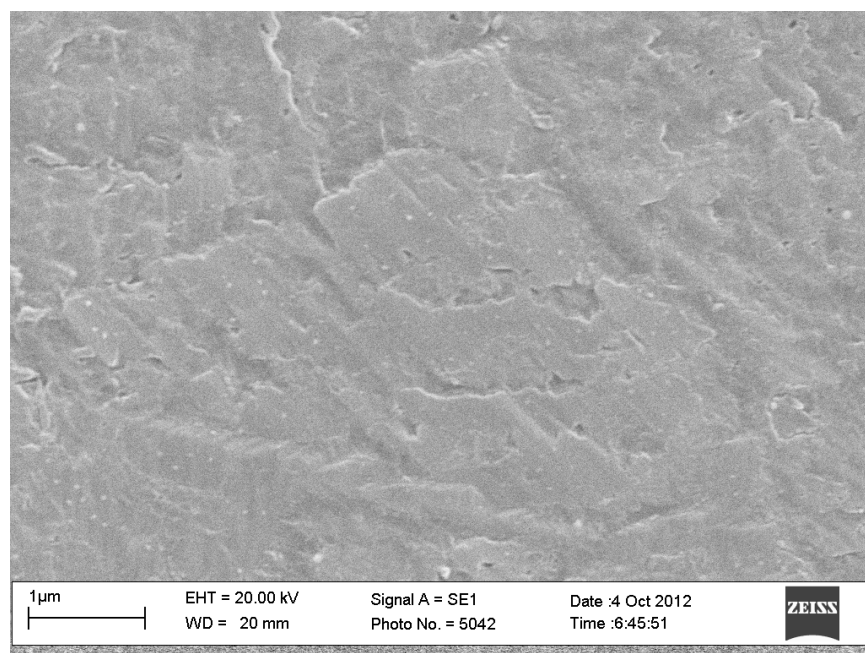


Fig. S5. Top View SEM image of a planar copper sulfide film formed by anodization at 0.3 V for 30 min in 0.2 M Na₂S (aq.)

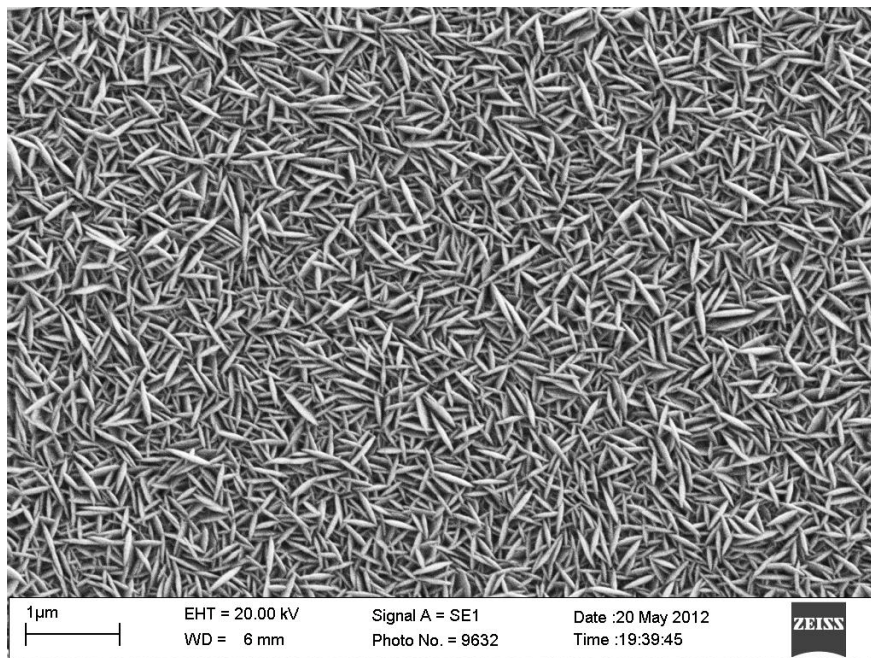
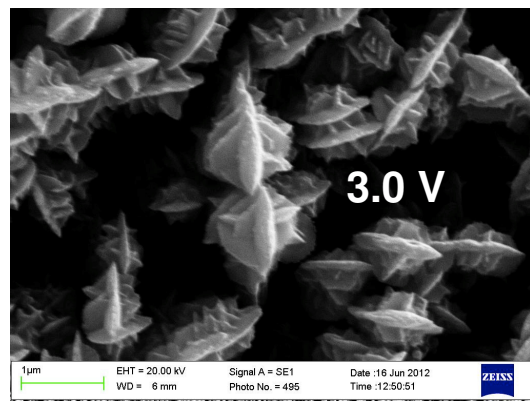
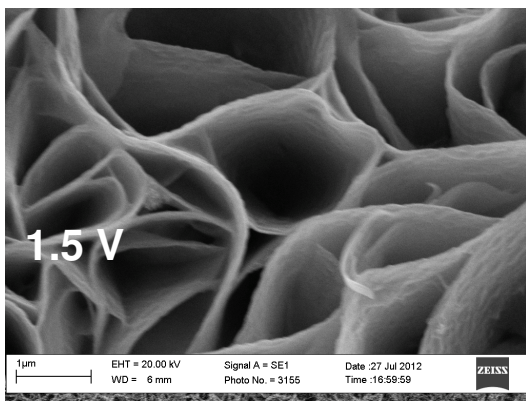
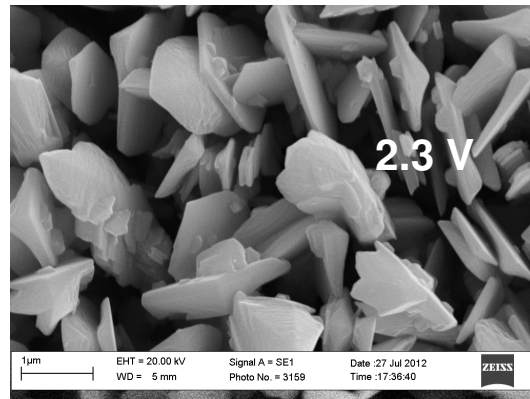
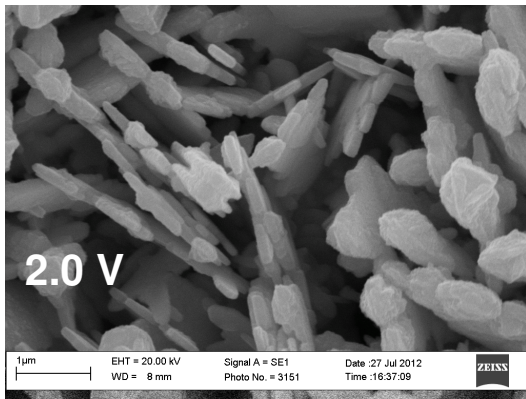


Fig S6. Evolution of morphology for copper sulfide nanostructures with anodization voltage is illustrated this figure. Anodization voltages are indicated on the figures. It can be observed that at 0 V (or simple immersion of copper foils in Na_2S solution) nanostructures are observed but these are neither vertically oriented, nor do they contain dendritic characteristics. When voltage is applied and vertically orientation and dentrite formation is observed.

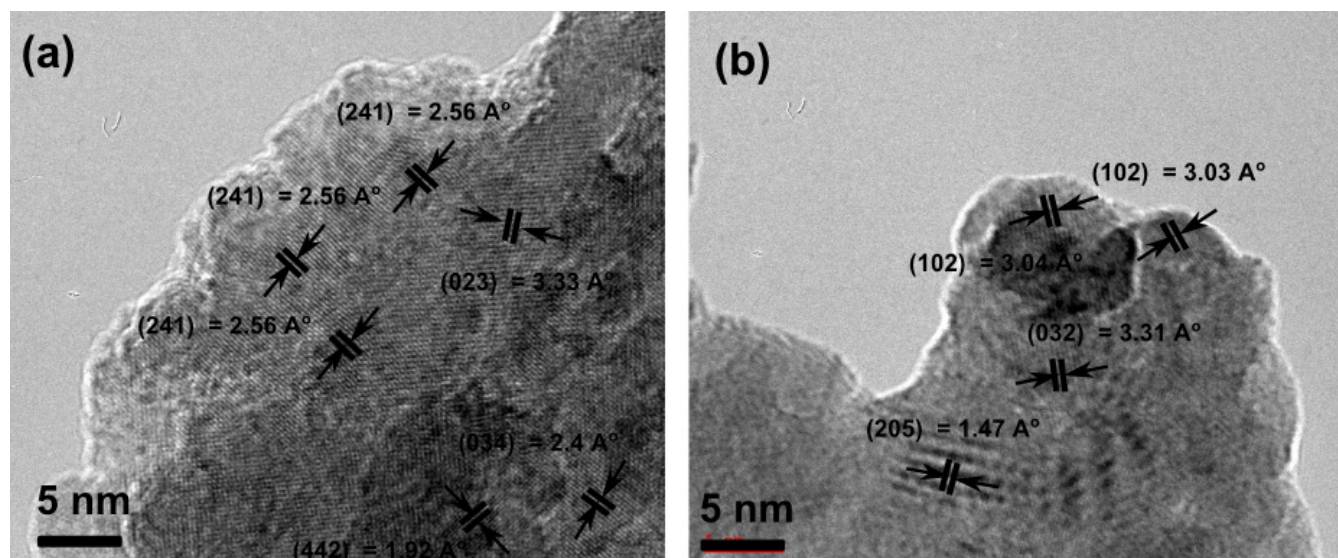


Fig. S7. HRTEM lattice images of Cu foil anodized at 5°C at (a) 1.5 V and (b) 3V

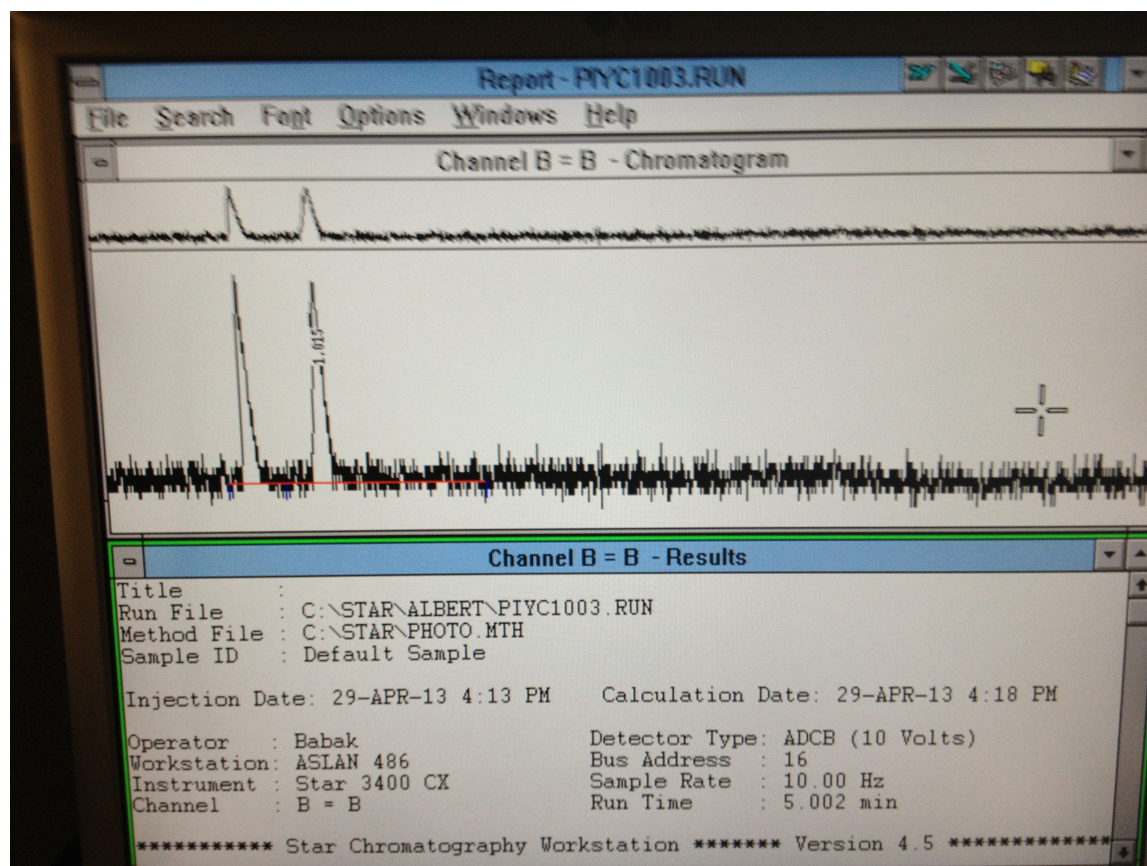


Fig. S8. Results of the CO₂ photoreduction reaction, Cu foil anodized at 1.5 V at 5°C. The first peak corresponds to air and is present even when no sample is present in the reaction chamber. The air peak appears 0.6 minutes after sample injection. The second peak appearing at ~1 minute after injection corresponds to methane, as established from calibration experiments.

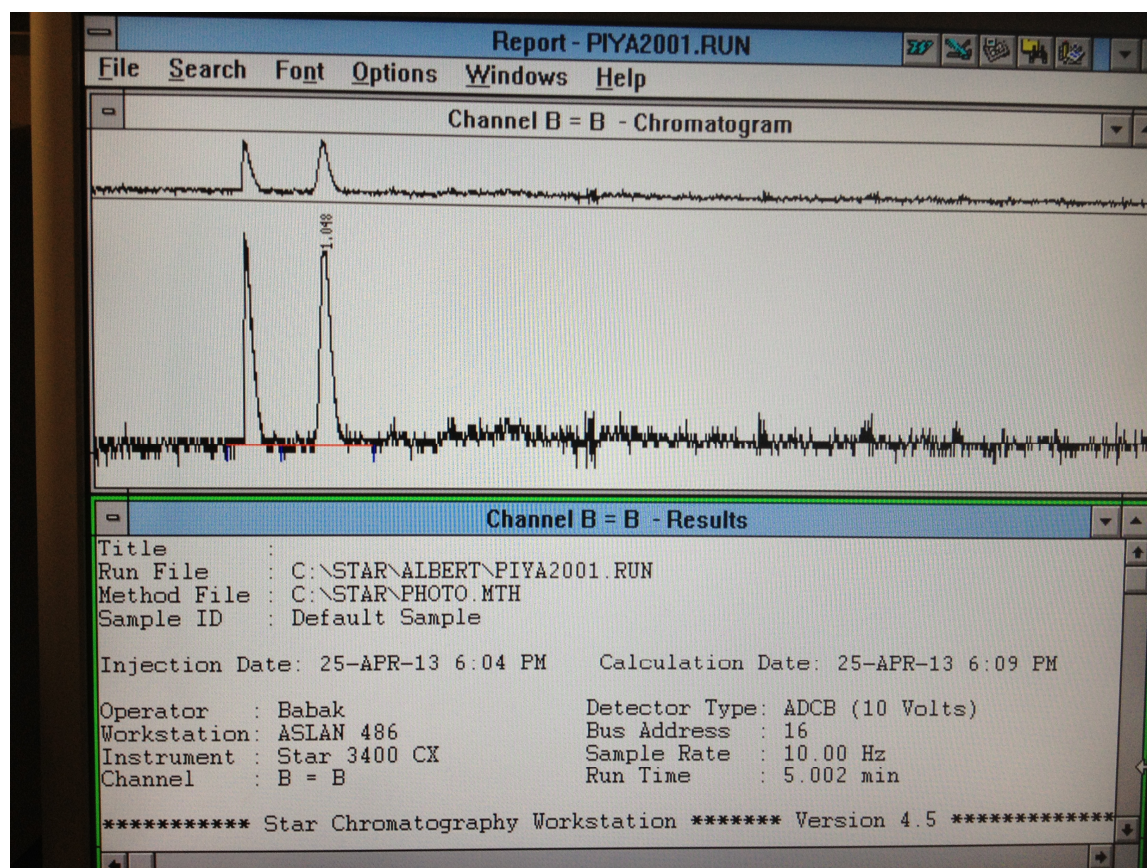


Fig. S9. Results of the CO₂ photoreduction reaction, Cu foil anodized at 1.5 V at 5°C