

## Investigation of Nanostructure and Photocatalytic Stability of Mesoporous CuCrO<sub>2</sub> Delafossite using Analytical Electron Microscopy

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Investigating new sources of renewable energy has been a major focus in the scientific community during the last decade and continues to attract much attention [1]. Photovoltaics — used in the conversion of solar energy to electrical power — are considered a promising technology to meet the requirements of a clean, non-fossil fuel in the future. The photoelectrochemical cell (PEC), utilizing semiconducting surfaces for catalysis, has been intensively studied as a method to generate hydrogen (H<sub>2</sub>). Novel catalyst compounds, which meet all the essential criteria for a PEC system, i.e. a small energy band gap (E<sub>g</sub>) for absorption of visible light, chemical stability for reuse and storage, a negative conduction band potential and an efficient conversion rate, are being investigated. Cu<sup>+</sup>X<sup>3+</sup>O<sub>2</sub> oxides, where X denotes a transition metal, crystallize in the delafossite structure, have been reported as leading candidates to meet these PEC requirements, primarily as a result of their interesting band-gap modulation, long-term chemical stability, and low-cost [2,3].

Mesoporous CuCrO<sub>2</sub> delafossite structures were successfully synthesized by nanocasting methods using KIT-6 as a template. Copper nitrate and chromium nitrate precursors were melted together at 60°C or dissolved in methanol before impregnation into the silica KIT-6 template. After calcination at ~1000°C in Ar, delafossite nanostructures were obtained after removal of the silica template by treatment in a NaOH solution. The synthesized mesoporous CuCrO<sub>2</sub> delafossite is a *p*-type semiconductor with a small band gap of ~1.38 eV. However, the most efficient H<sub>2</sub> generation for this material takes place under irradiation with a wavelength of ~400nm, which is shorter than the expected value (~900 nm). Two potential explanations for this controversial result include (1) the existence of surface defects and (2) a low electronic conductivity in the bulk delafossite, both of which could result in the recombination of photo-generated electrons and holes. To investigate the surface structure and electronic structure of the mesoporous CuCrO<sub>2</sub>, a combination of STEM and EELS was used.

A C<sub>s</sub>-corrected FEI Titan 80/300 TEM/STEM equipped with a Gatan Imaging Filter was used for this study. Bright-field (BF) and dark-field (DF) STEM images were recorded simultaneously to study the crystal structure of the CuCrO<sub>2</sub> delafossite. The fine structures of Cr-L, Cu-L, and O-K edges have been studied to reveal the electronic structure of the material. The oxidation states of Cu and Cr were investigated by EELS. Mesoporous CuCrO<sub>2</sub> samples exposed for different periods of light illumination were evaluated to understand the catalytic stability. In addition, we have also studied bi-metallic-doped mesoporous CuCrO<sub>2</sub> to understand how dopants affect the microstructure and photoactivity.

The as-synthesized mesoporous CuCrO<sub>2</sub> microstructure is characterized by pore sizes of ~10 nm and an inter-pore spacing of ~17 nm (Figure 1). The mesoporous CuCrO<sub>2</sub> morphology maximizes the solar-to-chemical conversion efficiency as a result of a very high surface/volume ratio and an enhanced degree of crystallinity of the CuCrO<sub>2</sub> nanoparticles. The hydrogen-generating efficiency of

the mesoporous  $\text{CuCrO}_2$  materials is at around 20 times higher than that of the bulk materials. A small amount of “excess” metallic Cu is observed after light illumination of  $\sim 18.5$ h in both the bulk and mesoporous  $\text{CuCrO}_2$  particles, which is likely a consequence of the reduction of dissolved  $\text{Cu}^{2+}$  resulting from the photo-corrosion of  $\text{Cu}^+$  from the  $\text{CuCrO}_2$  lattice during water splitting. The mesoporous sample exhibited some collapse of the mesoporous structure. EELS data shows these regions to be locally Cu-deficient, but were surrounded by Cu metal, needle-shaped particles (Figure 2). In the regions where the mesoporous structures were maintained, Cu ions kept the valence of  $1^+$  regardless of illumination time (up to 173 h). Doping the mesoporous  $\text{CuCrO}_2$  with a Mg not only stabilized the oxidation state of Cu during illumination, but also stabilized the mesoporous morphology. As a result, both the conversion rate and photocatalytic stability of the Mg-doped mesoporous  $\text{CuCrO}_2$  were improved significantly. Studies comparing the microstructure and photoactivity of  $\text{Cu(X)O}_2$  with other  $\text{Cu(X)O}_2$  systems will continue [4].

### References

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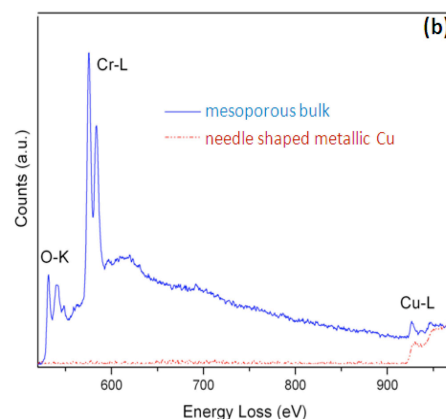
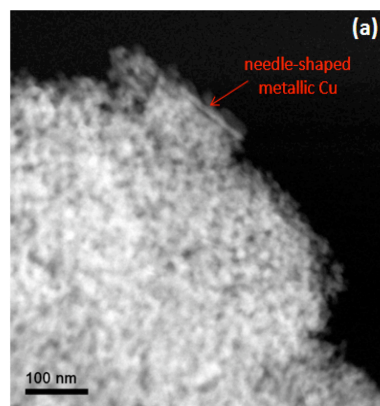
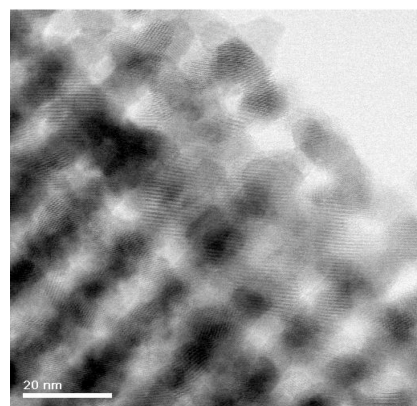


Figure 1. Typical BF-STEM images of mesoporous structured  $\text{Cu(X)O}_2$  ( $x = \text{Cr}$ ).

Figure 2. (a) Needle shaped particles were observed in the samples after 48h light illumination (b) EELS spectra reveal these particles are metallic Cu.