

Investigation of Nanostructure and Photocatalytic Stability of Mesoporous CuCrO₂ 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 (H₂). Novel catalyst compounds, which meet all the essential criteria for a PEC system, i.e. a small energy band gap (E_g) 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⁺X³⁺O₂ 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 CuCrO₂ 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 CuCrO₂ delafossite is a *p*-type semiconductor with a small band gap of ~1.38 eV. However, the most efficient H₂ 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 CuCrO₂, a combination of STEM and EELS was used.

A C_s-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 CuCrO₂ 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 CuCrO₂ 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 CuCrO₂ to understand how dopants affect the microstructure and photoactivity.

The as-synthesized mesoporous CuCrO₂ microstructure is characterized by pore sizes of ~10 nm and an inter-pore spacing of ~17 nm (Figure 1). The mesoporous CuCrO₂ 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 CuCrO₂ nanoparticles. The hydrogen-generating efficiency of

the mesoporous 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 ~ 18.5 h in both the bulk and mesoporous CuCrO_2 particles, which is likely a consequence of the reduction of dissolved Cu^{2+} resulting from the photo-corrosion of Cu^+ from the 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 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 CuCrO_2 were improved significantly. Studies comparing the microstructure and photoactivity of Cu(X)O_2 with other Cu(X)O_2 systems will continue [4].

References

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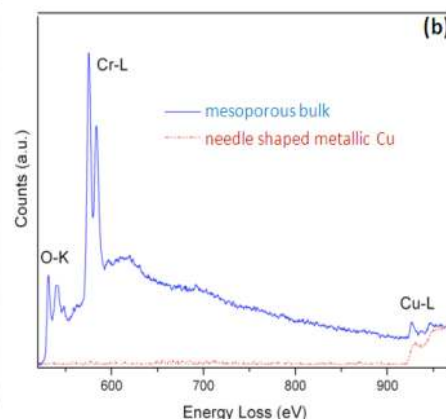
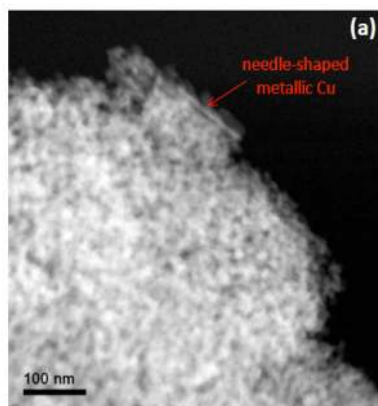
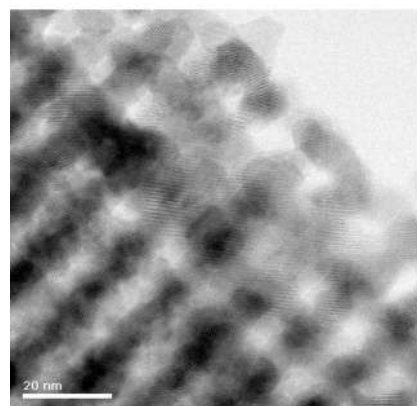


Figure 1. Typical BF-STEM images of mesoporous structured Cu(X)O_2 ($x = \text{Cr}$).

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