Investigation of Nanostructured $Cu(X)O_2$ Delafossite by Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS)

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Introduction

The investigation of renewable energy has been a major focus of both research and industry during the last decade and continues to attract much attention [1]. Photovoltaics — the conversion of sunlight to electrical power — is considered a promising technology to meet the requirements of a clean non-fossil fuel in the future. The photoelectrochemical (PEC) conversion over semiconductors has been intensively studied as one of photovoltaic methods to generate Hydrogen (H_2) though water-splitting by the process of sun-light absorption of catalysts. This method is now being challenged by fabricating novel catalysis compounds which meet the essential criteria for PEC system, i.e. a small E_g for absorption of visible sunlight, chemical stability for reusing and storage, a negative flat band potential and an efficient conversion rate. $Cu^+(X^{3+})O_2$ oxides, crystallizing in the delafossite structure, where X denotes a first-row transition metal, has been recently reported as candidates to meet these requirements [2,3]. We have synthesized $Cu(X)O_2$ delafossites with different transition metals X, X = Cr, Fe, Mn, In, La. It has been found that the catalytic activity and stability of this material system varies significantly with their morphologies and different transition metal elements X. To investigate the mechanism behind these phenomena, scanning transmission electron microscopy (STEM) including Z-contrast imaging and electron energy loss spectroscopy (EELS) have been applied to characterize the microstructure, chemical distribution, and electronic structure of these materials.

Materials and Methods

$Cu(X)O_2$ (X = Cr, Fe, Mn, In, La) mesoporous structures are synthesized by nanocasting methods using KIT-6 as template. Cupper nitrate and X metal nitrate precursors were melted together at 60°C or dissolved in methanol before impregantion into silica KIT-6 template. After calcination at ~1000°C in Ar, delafossite nanostrutcures were obtained after removal of silica template by treatment of hot NaOH solution. .

We have used a probe aberration-corrected electron microscope (FEI Titan 80/300) equipped with a Gatan EELS spectrometer to carry out the microstructural and chemical analysis on these materials. Bright field and dark field STEM images have been recorded simultaneously to study the detailed crystal structures of these materials. Energy filtered TEM (EFTEM) has been performed to map the distribution of transition metal elements after illuminations. Electron energy loss spectroscopy (EELS) has been used for chemical analysis, phase determination, and electronic structural analysis. The possible oxidation state change of Cu has been investigated by analyzing the fine structures of O-K edge and Cu-L edge of EELS spectra.

Results and Discussion

The synthesized $Cu(X)O_2$ has a mesoporous structure with pore sizes of ~10 nm and interpore spacings of ~7 nm (Figure 1). The mesoporous morphology maximizes solar-to-chemical conversion efficiency by taking advantage of the bandgap ~1.3 eV and minimizing the charge transfer distances. A small amount of metal Cu has been observed after illumination in both bulk and mesoporous $Cu(X)O_2$ particles. This can be explained to be a result of the reduction of the dissolved Cu^{2+} which resulted from the photocorroded Cu^+ from $Cu(X)O_2$ lattice during water splitting. In the mesoporous $Cu(X)O_2$ samples, Cu ions keep their valence of 1+ as long as the mesoporous structure is well preserved. The local regions with a collapsed mesostructure, on the other hand, are observed to be Cu-deficient. Metal Cu particles are always seen at their surroundings. Doping with bi-valence metal was found to not only stabilize the oxidation state of Cu after illumination, but also was found to steady the mesostructure morphology. As a result, both the conversion rate and the life time of the bivalent element doped mesoporous $Cu(X)O_2$ are improved significantly.

Significance

This work provides guidance of improving the conversion efficiency and the life time of $Cu(X)O_2$ nanostructure as photoelectrocatalysts for solar-to-chemical energy conversion.

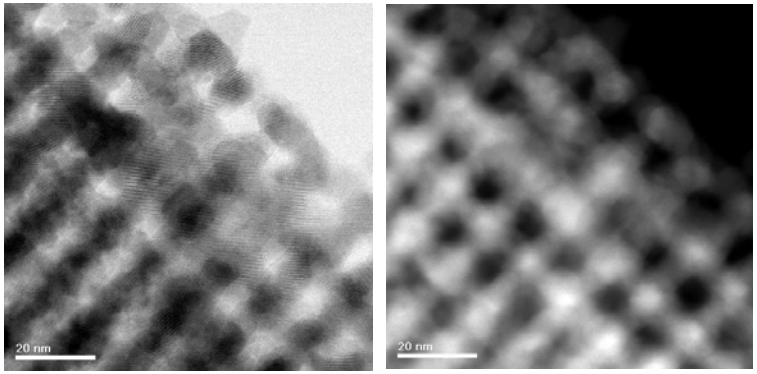

Figure 1. Typical BF- (left) and ADF- (right) STEM images of mesoporous structured $Cu(X)O_2$ (x = Cr).

References

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