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CEY-XANES Studies on Cu_xO/rGO/Cu Photoelectrocatalyst

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Abstract

For the reduction of CO_2, we have synthesized thin films of CuO on a Cu substrate (Cu_xO/rGO/Cu). To understand the chemical composition of Cu_xO in Cu_xO/rGO/Cu, CEY-XANES measurements were carried out at room temperature in air at the beamline BL14B2 of SPring-8. It was found that 10–20% was Cu metal and the rest was Cu oxides. Further studies are needed to understand the composition of the Cu oxides.

Keywords: Photocatalysts, Cu_xO/rGO/Cu, CEY-XANES, oxidation states

Background and Purpose of Research:

Reduction of CO_2 by photocatalytic methods is gaining extensive attentions, change CO_2 into hydrocarbon fuels such as alcohols, carbon monoxide, and other gas and liquid products using solar energy. Cuprous oxide (Cu_2O), with a direct band gap (2.0 eV) has green characteristics: non-toxic and compatible with environment. The promising band gap and relevant arrangement of the conduction and valence bands, make it an excellent photocatalyst for CO_2 photoreduction. A chemical compound of sp^2 hybridized carbon atoms, graphene, a two-dimensional monolayer, has drawn attentions in recent years because of its attractive physical and chemical properties. In general, graphene is a zero band gap semiconductor with asymmetric band structure.

Only few researches have been carried out in relation to the integration of CuO with carbonaceous materials. We have synthesized thin films of CuO on a Cu substrate [1, 2]. A *p*-type reduced graphene (rGO) layer was introduced to cover the CuO layer through a simple hydrothermal method. Through photoelectrochemical measurements, the superior properties of our Cu_xO/rGO/Cu photocatalyst: significant high photocurrent up to 9.6 mA cm^{-3} at 0.8 V vs. Ag/AgCl. From the preparation in one-pot hydrothermal approach, the film can directly use as photoelectrodes in photoelectrochemical cell. Therefore, the study to understand the nature of CuO/rGO/Cu will gives insight on implications on the overall photoconversion efficiency.

From the XRD spectra, when the hydrothermal reaction time is increased from 1 hour to 3 hours, the intensity of the CuO peaks is negligible. Due to the low amount and amorphous nature of CuO, the peak was not recognized in the XRD analysis. We extended the analysis using XPS to examine the existence of CuO element, and the presence of CuO was affirm from the two main peaks at 932.52 and 952.53 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. Although, this technique provides information regarding the oxidation state of copper in the certain thin samples, the bulk composition could not be obtained. Therefore, CEY-XANES measurements were carried out to understand the bulk composition.

Experimental:

Four samples were prepared in Fuel Cell Institute in UKM, Malaysia as listed below:

Sample A: Cu foil in DMF solvent (3-hour reaction time)
Sample B: Cu foil in DMF with hydrazine as reduction agent (3-hour reaction time)
Sample C: Cu foil with Graphene Oxide (GO) in DMF with hydrazine (3-hour reaction time)
Sample D: Cu foil with GO in DMF with hydrazine (24-hour reaction time)

The sample size was 2 cm × 2 cm with the thickness of 0.25 mm. The thickness of the Cu_xO/rGO layer was estimated as 6 μm

On those samples, CEY-XANES of Cu (K-edge, 9.0 keV) in Cu_xO/rGO/Cu photoelectrocatalyst was carried out at the beamline BL14B2 of SPring-8 in air at room temperature.

Results

Figure 1 shows the XANES spectra of Samples A to D and references of Cu_2O, CuO, and Cu. The white lines of Samples A to D were very different. The linear combination of the data from Sample A to D using those of Cu_2O, CuO, and Cu had some ambiguities, probably because of the existence of trace amounts of other components, such as CuOH and $Cu(OH)_2$. As a first approximation, the fitting was done with the spectra of Cu and CuO as a representative of Cu oxides. The ratios were obtained as:

Sample A	Cu metal : Cu oxides = 10 : 0
Sample B	Cu metal : Cu oxides = 2 : 8
Sample C	Cu metal : Cu oxides = 2 : 8
Sample D	Cu metal : Cu oxides = 1 : 9

The details of the composition of the Cu oxides are still unknown. A combination of Rietveld refinement on X-ray diffraction patterns and EXAFS is expected to understand the chemical compositions, as well as structures.

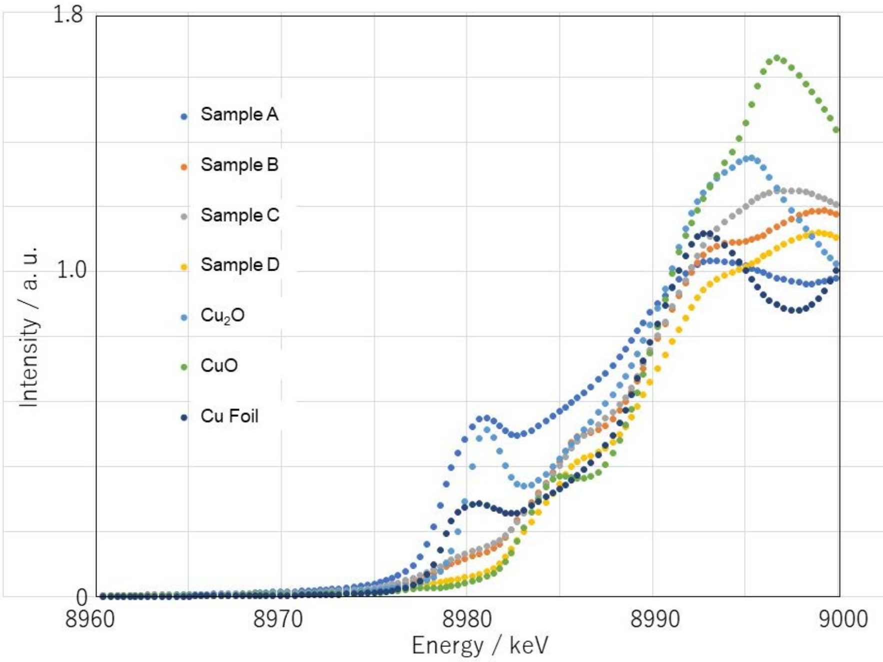

Fig. 1 XANES spectra of Samples A to D and reference samples of Cu_2O, CuO, and Cu.

References

[1] R. M. Shah, R. M. Yunus, M. S. Masdar Mastar, L. J. Minggu, W. Y. Wong and A. A. H. Kadhum, *Sains Malaysiana*, **48 (6)**, 1233 (2019).

[2] R. M. Shah, R. M. Yunus, M. S. Masdar Mastar, L. J. Minggu, W. Y. Wong and A. A. H. Kadhum, *International Journal of Energy Research*, submitted.