

Solar H₂ production: using XAS to Boost the Efficiency of CuGa_{1-x}Fe_xO₂-Carbon Nitride p-n Heterojunction

Benjamin Martinez^{1,2,3}, Yu-Cheng Huang³, Chung-Li Dong^{3,4} and Chun-Hong Kuo^{1*}

¹Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan

²Sustainable Chemical Science and Technology, Taiwan International Graduate Program, Academia Sinica and National Chiao Tung University, Taiwan

³National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu, Taiwan

⁴Department of Physics, Tamkang University, New Taipei City 251, Taiwan
chunhong@gate.sinica.edu.tw

Abstract

Solar energy storage via H₂ evolution by photocatalytic water-splitting has focused scientific endeavors for five decades already. To enable a low cost, large scale and efficient production of H₂, photocatalysts must be selected and engineered meticulously, which makes new active materials as well as mechanistic insights highly sought-after. We report the facile fabrication of a CuGa_{1-x}Fe_xO₂-carbon nitride (CGFO_x-CN) p-n heterojunction and its 16h+ stable H₂ evolution under simulated solar light, without the use of cocatalysts. X-Ray Photoelectron Spectroscopy (XPS) and in-situ X-Ray Absorption Near Edge Structure (XANES) were employed as complementary and orbital-specific techniques to probe the changes caused by interfacing CGFO_x with CN and by light excitation. Moreover, the effect of Fe content on the photocatalyst's activity was explored, and the findings were applied to redesign CGO and double its efficiency.

Keywords – H₂ evolution, XAS, heterojunction, hole conductivity, charge transfer.

Introduction

Global energy demands being on the rise and expected to be met mainly by environmentally harmful fuels, an energy infrastructure based on renewably-made H₂ has been studied for decades.[1] Photocatalytic water-splitting is regarded as the most practical process for H₂ evolution. The light harvester (semi-conductors) and redox active sites are combined in a single photocatalyst system suspended in water. CuGaO₂ (CGO) is a metal oxide semiconductor with high p-type conductivity and stability in water make it an excellent candidate for water-splitting. Heterojunctions (HJ) are deemed to be the prime method to mitigate the problem of charge recombination in particulate photocatalysts.[3] Moreover, p-n HJ possess an extra driving force, an internal electric field to boost the photogenerated electron-hole separation. Therefore, carbon nitride (CN), a n-type semiconductor, has been combined with CGO to form CGO-CN p-n HJ. Then, CGO was modified by partial substitution of Ga atoms by Fe atoms. The bandgap of CuGa_{1-x}Fe_xO₂ (xCGFO) is drastically lowered and thus visible light absorption is enhanced. Absorptivity is a key parameter to be maximized in any photocatalysts. Besides, X-Ray Absorption Spectroscopy (XAS) is a powerful technique to probe both the empty electronic states near the conduction band minimum (CBM) and minute structural modifications in the catalyst. The insights gained from XAS are vital to design superior catalysts.

We report the efficient and stable H₂ evolution of CGO-CN under simulated solar light, without the addition of the common and expensive Pt cocatalyst. The efficiency is further enhanced in xCGFO-CN, but the HER trend versus x (Fe content) is unexpected. We used XANES to unravel the reasons behind the peculiar effect of Fe in CGFO_x and its influence on photocatalytic activity. This knowledge was used to redesign a Cu-poor version of CGO with double HER efficiency. Finally, we used *in-situ* XANES to track the electron migration pathway at the heterojunction and

obtain deep insights into the transfer mechanisms at the orbital level.

Experiments

CGO was prepared by hydrothermal method [4]. xCGFO was made by substituting x mmol of Ga precursor by x mmol of Fe precursor in the CGO protocol. CN was synthesized by thermal treatment of urea at 550°C. [5] Cu, Ga and Fe K-edges were obtained at beamline 17C-1 and N, C and O K-edges as well as Cu, Ga and Fe L-edges were obtained at 20A-1. Photocatalysis experiments were performed by dispersing 50 mg catalyst in 200 mL water with 10 vol% TEoA as sacrificial electron donor. The solution was then irradiated with simulated solar light and the H₂ evolved in the headspace was injected automatically and quantized with a GC equipped with thermal conductivity detector, using N₂ as carrier gas.

Results

While CGO and CN exhibit very limited H₂ production rate, CGO-CN achieved 80.0 μmol.g⁻¹.h⁻¹, more than a 200-fold increase (Fig. 1top). After modification of CGO with Fe, 10CGFO-CN has a H₂ production rate of 112 μmol.g⁻¹.h⁻¹. Although the visible light absorption of xCGFO increased drastically with increasing x (x=0 to 0.2), the HER only increased until x=10 before decreasing again (Fig. 1 bottom). The increase is bestowed by the bandgap decrease from 3.4 eV (CGO, x=0) to 1.7 eV (x=0.2). The subsequent HER decrease however is more intriguing. Cu L-edge spectra of xCGFO revealed that where Cu⁺ content remains constant, Cu²⁺ defects amount decrease as x increases (Fig. 2 left). This has been confirmed as well by XPS analysis. O K-edge shows clearly the appearance of a Fe-O bond, the decrease of Ga-O peak and the shift of Cu-O bonds as Fe content increases in xCGFO (Fig. 2 right). The synthesis of CGO was then modified to maximize the Cu²⁺ defect amount, turning the powder's color from yellow to deep blue-grey, and doubling the HER (Fig. 3).

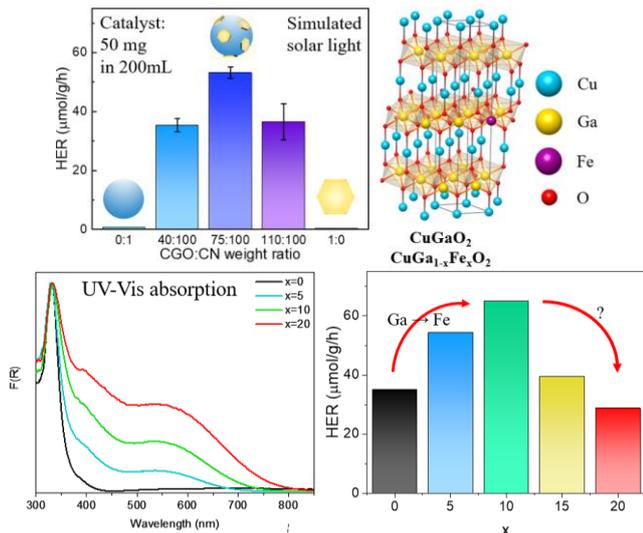


Fig. 1. Top-left: H_2 evolution rate of CN, CGO and CGO-CN, CGO-CN with different weight ratio. Top-right: crystal structure of CGO and x CGFO. Bottom: UV-Vis (DRS) absorption (left) and HER (right) of x CGFO-CN.

Discussion

The boost of HER in CGO-CN versus CGO and CN alone is due to the formation of a p-n HJ. First, the CBM and VBM of both CGO and CN are well-aligned so as to enable an e^- transfer from CGO's CBM to CN's CBM. Similarly, the photogenerated holes flow from CN's VBM to CGO's VBM. This inhibits the charge recombination which usually plagues photocatalysts. Furthermore, CGO and CN being respectively p- and n-type semiconductors, an extra internal electric field is acting as supplementary driving force to separate the e^-/h^+ pairs and enhance photocatalysis (clear B.E. shifts are observed in XPS spectra).

In x CGFO, the XAS study of Cu L-edge shows that higher x values are associated with lower Cu^{2+} content (Fig. 2 left), which in turn leads to lower p-type conductivity [6]. Indeed, more Cu^{2+} means that the material is e^- deficient, so holes have extended transport channels in the ab planes. The presence of Fe pins the VBM, and these localized states impair hole mobility, essential for the carrier transport in the heterojunction. Hall effect measurements confirmed this hypothesis. Therefore, higher light absorptivity in x CGFO is in competition with decreasing conductivity, which explains the non-linear HER trend.

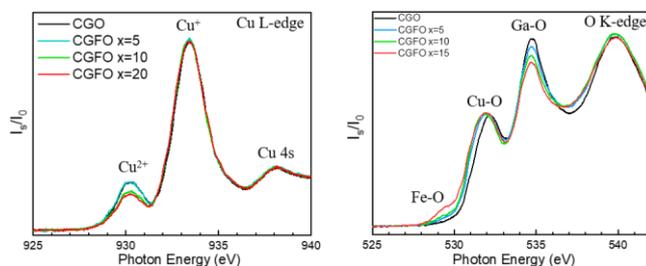


Fig. 2. XAS spectra Cu L-edge (left) and O K-edge (right) of x CGFO vs x (Fe content).

We exploited this finding by engineering a highly defective $Cu^{1+\delta}GaO_2$, where Cu^{2+} amount is maximized, granting it a boosted conductivity and double HER. The morphology and size, as well as XRD pattern is unchanged.

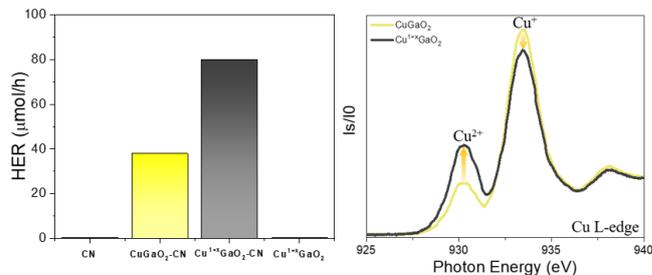


Fig. 3. HER and Cu L-edge of CGO and $Cu^{1+\delta}GaO_2$

Finally, XANES analysis with *in-situ* illumination of x CGFO-CN enables the study of the elusive charge migration mechanism in HJ photocatalysts, one of the crucial areas of study in the field [3]. In brief, the Fe L-edge signal shows that the Fe 2p-3d transition intensity drops under light in 10CGFO (no CN), and that the C K-edge spectrum for CN (no x CGFO) is unchanged. However, for 10CGFO-CN, the Fe L-edge is unchanged by light irradiation and the C 1s- π^* (C=N) transition intensity drops. This indicates that in 10CGFO-CN, photogenerated e^- don't accumulate in Fe 3d empty states (CBM) but are transferred efficiently to CN's CBM (aromatic rings). Thus, the quantity of e^- available in CN for photocatalysis is augmented, increasing the catalytic rates. Thereby, we have showcased the heterojunction-type charge transfer mechanism in this photocatalyst.

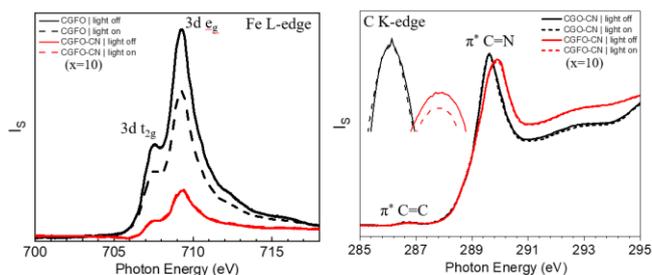


Fig. 4. *In-situ* XANES N K-edge of CN and CGO-CN in dark versus under simulated solar light.

References

- [1] J. M. Ogden, Annual Review of Energy and the Environment 1999, 24, 227-279
- [2] Z. Hua, W. Huan, C. Wei, J. A. K.-Y., "CuGaO₂: A Promising Inorganic Hole-Transporting Material for Highly Efficient and Stable Perovskite Solar Cells," Advanced Materials 2017, 29, 1604984.
- [3] L. Jingxiang, Y. Jiaguo, J. Mietek, W. Swelm, A.-G. A. A., "Heterojunction Photocatalysts," Advanced Materials 2017, 29, 1601694.
- [4] R. Srinivasan, B. Chavillon, C. Doussier-Brochard, L. Cario, M. Paris, E. Gautron, P. Deniard, F. Odobel, S. Jobic, "Tuning the size and color of the p-type wide band gap delafossite semiconductor CuGaO₂ with ethylene glycol assisted hydrothermal synthesis" Journal of Materials Chemistry 2008, 18, 5647-5653.
- [5] S.-C. Lee, H. O. Lintang, L. Yuliati "A Urea Precursor to Synthesize Carbon Nitride with Mesoporosity for Enhanced Activity in the Photocatalytic Removal of Phenol" Chem. Asian J. 2012, 7, 2139 – 2144
- [6] T. Senty, B. Haycock, J. Lekse, C. Matranga, H. Wang, G. Panapitiya, A. D. Bristow, J.-P. Lewis, "Optical absorption and disorder in delafossites" Applied Physics Letters 2017, 111, 012102.