Enhanced photoelectrochemical performance of $CuBi_2O_4$ photocathode by CuI hole transport layer

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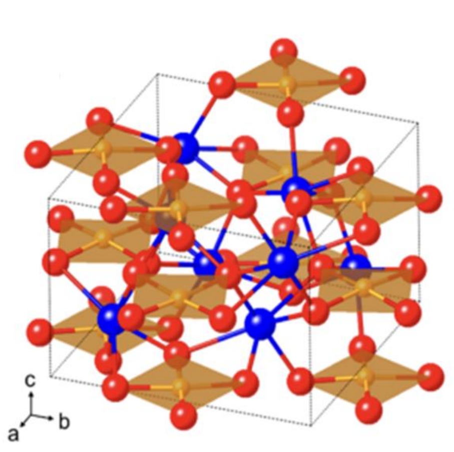
I. Abstract

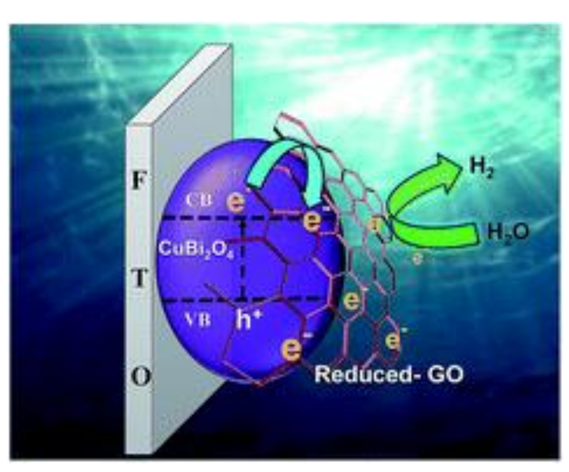
Photoelectrochemical (PEC) water splitting is one of the most promising strategies to produce green hydrogen fuels from solar energy. $CuBi_2O_4$ (CBO) is attracting p-type semiconductor materials as a photocathode because it has a suitable bandgap for water splitting (~1.8 eV) and exceptionally positive photocurrent onset potential (>1 V vs RHE), making it an ideal candidate for the top absorber in a dual absorber PEC device. However, the reported photocurrent for water reduction based on the CBO photocathode is still poor, far less than its theoretical photocurrent. The severe photocurrent loss of the CBO-based photocathode is mainly caused by the poor charge carrier transport properties and serious photo-corrosion phenomena. To tackle these issues, a CuI hole transport layer was adopted on the CBO photocathode to form a type-Ⅱ heterojunction (CBO/CuI) for accelerate charge mobility and the TiO2 passivation layer was encapsulated on as-prepared CBO/CuI film surface to suppress photo-corrosion. Herein, CBO/CuI thin films were fabricated by spin-coating method on fluorine tin oxide (FTO) glass substrate and TiO2 passivation layer was prepared by atomic layer deposition (ALD) technique. As a result, the CBO/CuI photocathode showed a photocurrent density of -0.707 mA cm-2 at 0.2 VRHE, which was more than four times higher than that of CBO photocathode (-0.123 mA cm-2 at 0.2VRHE). Also, the ALD-driven TiO2 passivation layer eliminates the partially located trap-states on the surface, resulting in increased bulk charge separation and improved interfacial charge transfer characteristics. This novel approach is feasible for fabricating a high-performance CBO photocathode for practical PEC water splitting.

II. Introduction

▪ Characteristics of $CuBi_2O_4$ (CBO) as photocathode



Chem. Mater. 2016, 28, 12, 4231–4242



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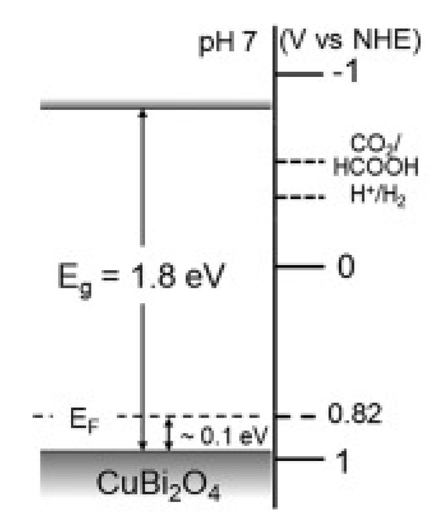

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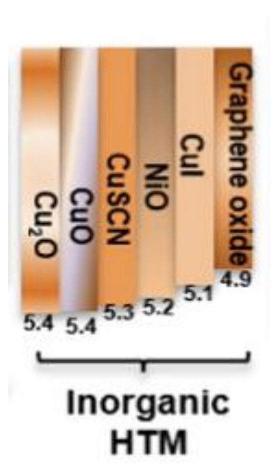
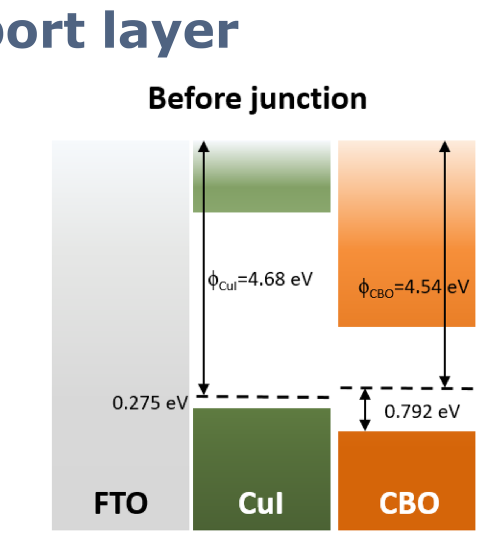
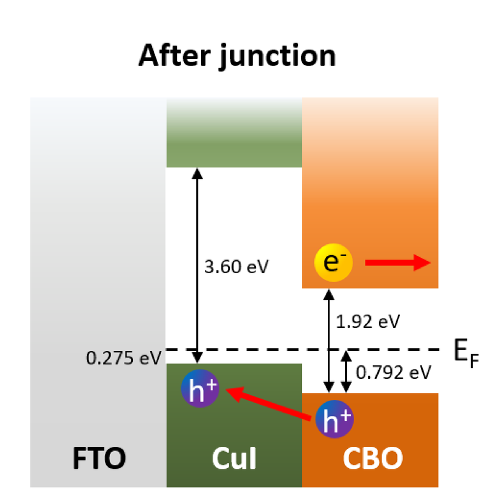
- ❑ CBO is a p-type semiconductor, as a promising candidate material for photocathode.
- ❑ CBO is composed of earth-abundant, inexpensive, and non-toxic elements. It has also a favorable band position for photoelectrochemical water splitting.
- ❑ CBO has a relatively narrow bandgap of about 1.8 eV and a highly positive onset potential (>1 V vs RHE), which can generate a large internal photo-voltage and is advantageous as a top absorber of tandem cell.
- ❑ However, CBO photocathode still show low photocurrent density due to the low carrier transportation, which leads to high surface recombination, and photo instability in the CBO photocathode.

▪ CuI hole transport layer



Z.H. Bakr et al., Nano Energy 34 (2017) 271

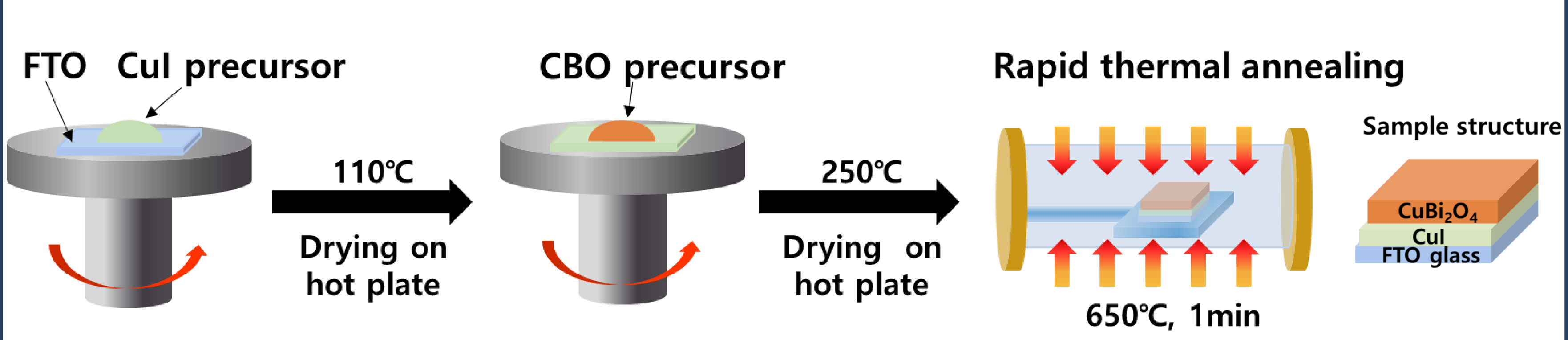




- ❑ CuI, which is a kind of inorganic hole transport layer, has high carrier mobility and defect free interface with the absorbing layer to minimize carrier recombination.
- ❑ It can be confirmed that CBO and CuI are type-II hetero-junctioned. Therefore, CuI can be used as a hole transport layer for CBO.

II. Experimental

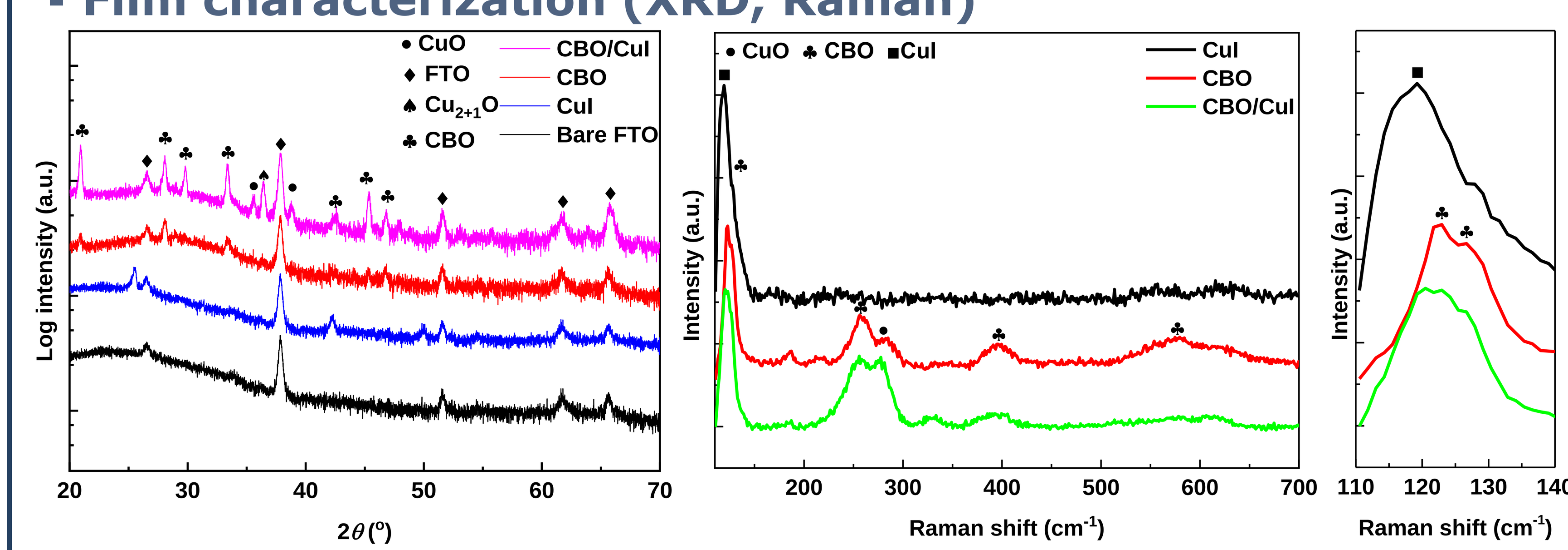
▪ Film fabrication – Spin coating



- ❑ Spin coating is widely used in microfabrication of functional oxide layers on glass or single crystal substrates using sol-gel precursors, where it can be used to create uniform thin films with nanoscale thicknesses.
- ❑ Spin coating process has the advantages of being reproducible, very easy, and cheap. It can be carried out in a low temperature process and thus can be produced without significantly damaging the CuI in an air atmosphere.
- ❑ During spin coating process of CBO and CuI, Drying was carried out at 250 °C and 110 °C, respectively. After drying, it was annealed at 650 °C for 1 minute in an oxygen atmosphere.

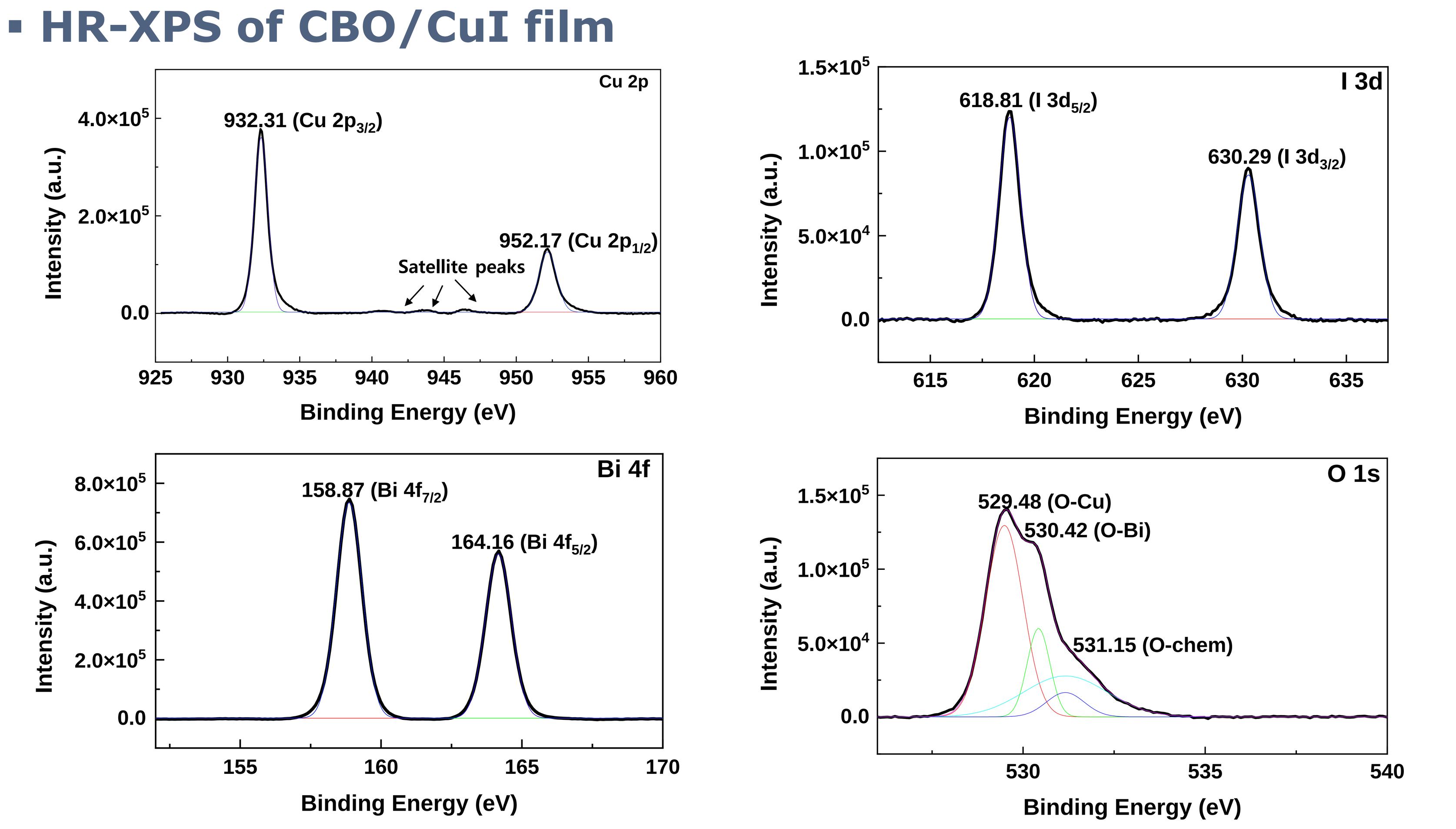
III. Results & discussion

▪ Film characterization (XRD, Raman)



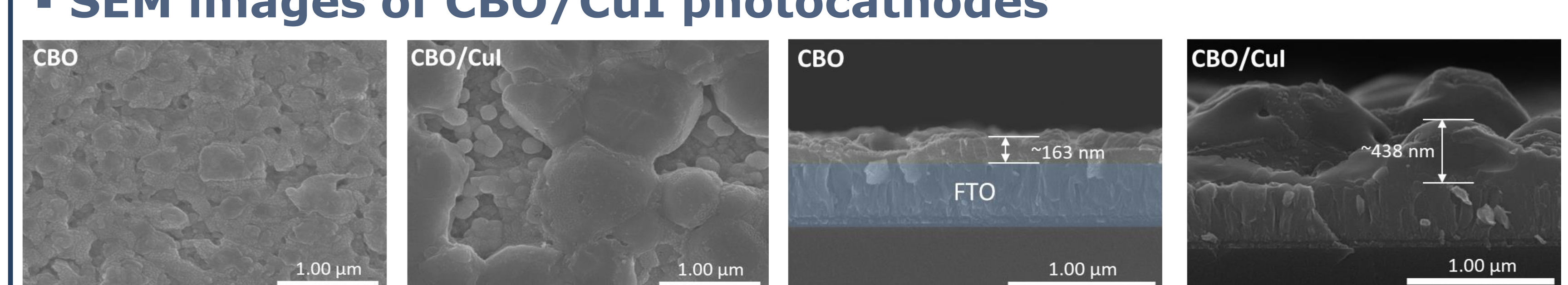
❑ The XRD pattern and Raman peaks show that CBO was synthesized on CuI .

▪ HR-XPS of CBO/CuI film



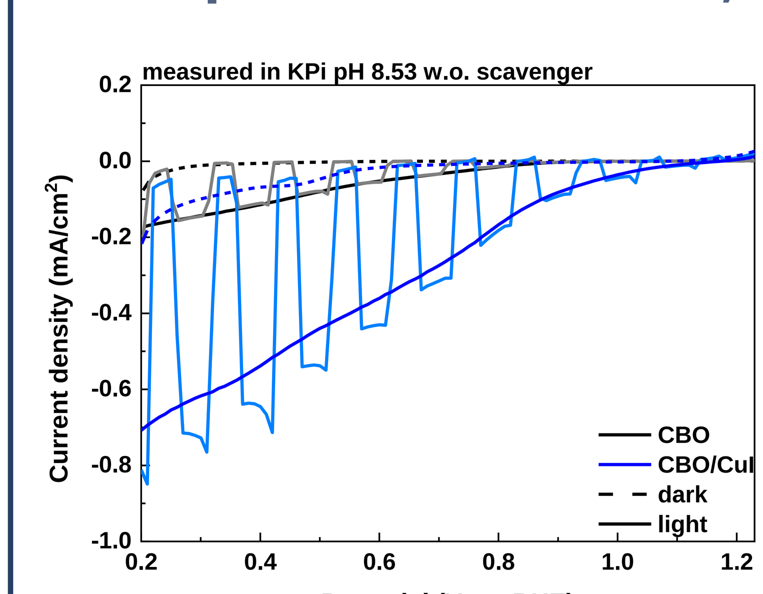
- ❑ Iodine was detected in HR-XPS data. In addition, it was confirmed that satellite peaks appeared in Cu 2p spectra except for two strong peaks.
- ❑ Satellite peaks imply the presence of Cu^{+1} ions and consequently confirmed the formation of copper iodide.

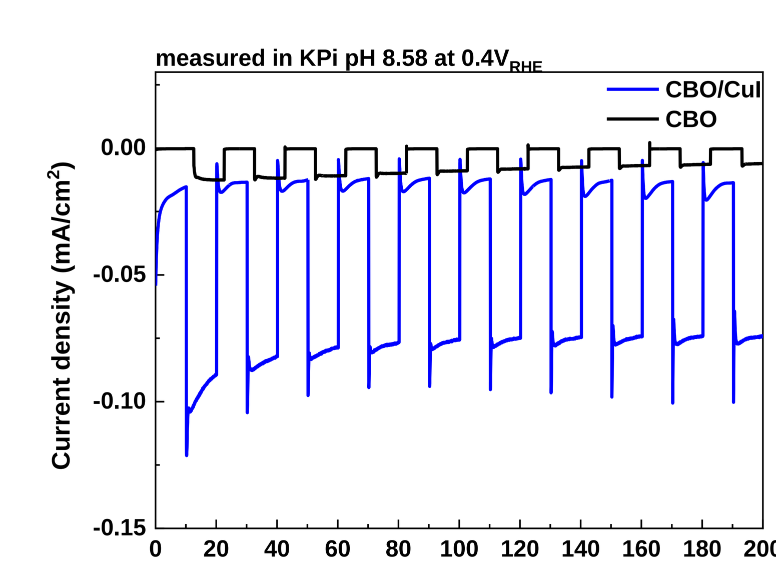
▪ SEM images of CBO/CuI photocathodes

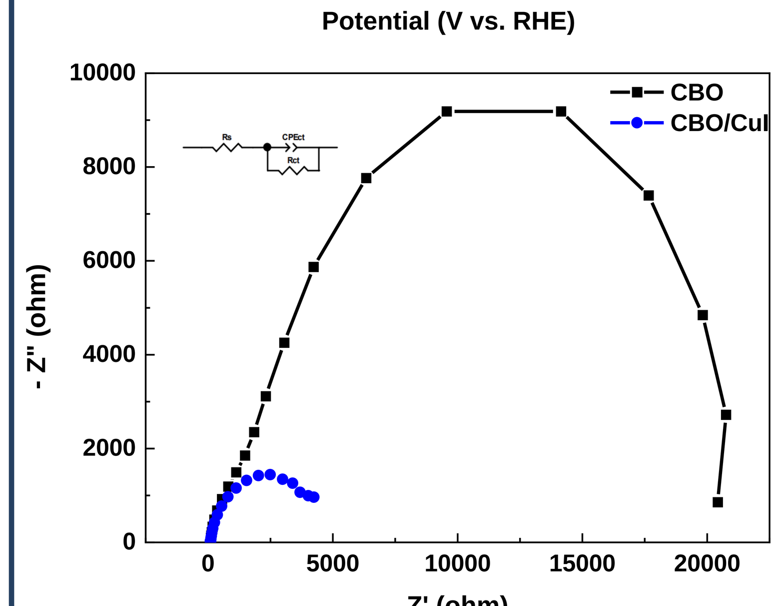


- ❑ Top SEM images show that each sample has different morphologies and thickness.
- ❑ SEM images show that the CBO thin films layer with ~163 nm thick is deposited and the CBO/CuI film with ~438 nm is deposited.

▪ PEC performance – LSV, EIS, stability







- ❑ The photocurrent density of CBO/CuI photocathode was improved 3 times than that of CBO photocathode at 0.2 VRHE.
- ❑ Charge transfer kinetics from the CBO/CuI photocathode to the electrolyte solution was improved.
- ❑ Onset potential moves in a positive direction. This shows that copper iodide transferred the generated charge as a hole transport layer to the cathodes and anodes surfaces faster.

IV. Summary

- ❑ We fabricated CBO/CuI photocathode on FTO substrate.
- ❑ The charge transport properties were improved by the formation of type-II heterojunction in the CBO/CuI.
- ❑ The photocurrent density of CBO/CuI photocathode is about 3 times higher than that of CBO photocathode.

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