



# Screen-printed Hole Transport Material-free perovskite solar cell for water splitting incorporating Cu-NiCo<sub>2</sub>O<sub>4</sub> catalyst

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## ABSTRACT

Water splitting has gained significant attention in recent years as a greener alternative for harvesting energy. In this report, we utilize screen-printed Hole Transport Material (HTM) free single junction perovskite solar cell with an open circuit voltage ( $V_{oc}$ ) of 0.9 V for direct water splitting. Further, we extend this concept to incorporate three different earth-abundant materials: copper, copper-nickel, and copper-nickel-cobalt oxide, as catalysts in a 1 M Potassium hydroxide (KOH) electrolyte solution, along with a perovskite solar cell for water splitting. Among these, the perovskite solar cell with a copper-nickel-cobalt oxide catalyst shows the best performance with 0.98 mA/cm<sup>2</sup> photocurrent density and 1.2% solar to hydrogen efficiency at no applied bias, i.e., 0 V vs Reverse Hydrogen Electrode (RHE).

## 1. Introduction

Global warming is causing irreversible damage to the earth and human social life [1]. CO<sub>2</sub> is one of the main reasons for climate change. Sustainable hydrogen energy could be an excellent eco-friendly alternative. Hydrogen energy is clean and cheap compared to other natural products. Moreover, it can be saved for future use, carried, and consumed without harmful side effects [2]. Currently available methods to produce hydrogen, such as steam methane reformation (SMR) of natural gas, are expensive [3]. Compared to the SMR method, photo-electrochemical cell (PEC) and photovoltaic (PV)-electrolysis systems are advantageous and can facilitate the production of hydrogen for large-scale applications with eco-friendliness [4–5].

Among the solar cells studied, perovskite-PEC is gaining significant attention despite its limitations, such as etching and fast degradation in the electrolyte. Apart from this, issues such as ineluctable illumination through electrolyte and the need for convoluted mechanical structures need to be resolved [6]. To overcome the challenges mentioned above,

PV-electrolysis structure design is employed. Only one solar cell is exposed to the sun, while the catalyst is immersed in the electrolyte with the combination of HTM for oxygen or Electron Transport Material (ETM) hydrogen evolution catalyst on the backside of ohmic contact [7]. In the case of single-junction perovskite solar cells, higher efficiencies are attained by using Fe<sub>2</sub>O<sub>3</sub> as an oxygen evolution catalyst [8]. However, very few researchers have focused on utilizing cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) for these applications. Natural oxygen vacancies in Co<sub>3</sub>O<sub>4</sub> provide lots of opportunities for oxygen evolution [9]. When Co<sub>3</sub>O<sub>4</sub> is incorporated with metals like nickel or cerium, better performance is attained compared to normal Co<sub>3</sub>O<sub>4</sub>. Even in the case of low doping levels, good stability results are reported [10].

In the current work, we have employed a single-junction screen-printed HTM-free mesoscopic carbon (C)-based perovskite solar cell for water splitting. By integrating with a Cu-NiCo<sub>2</sub>O<sub>4</sub> oxygen evolution catalyst, we have achieved 1.2% solar to hydrogen efficiency, which is much better than the methods without a catalyst. Once the catalyst degrades, we can replace it with a new one without damaging the solar

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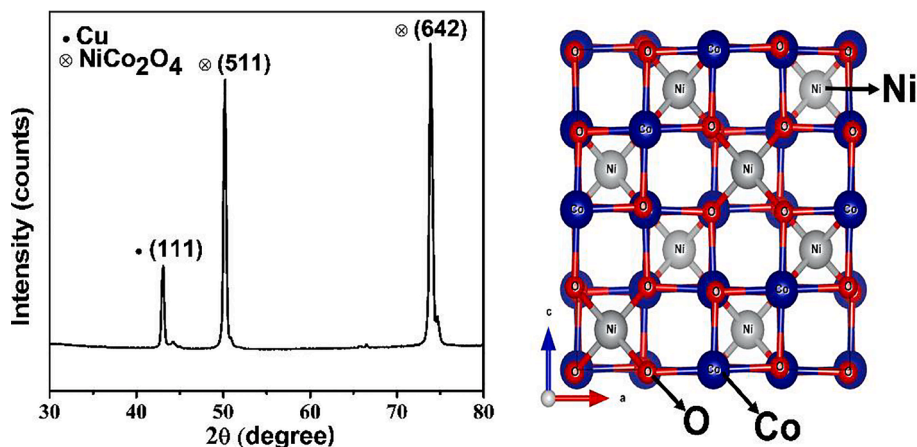


Fig. 1. XRD pattern of Cu-NiCo<sub>2</sub>O<sub>4</sub> film with Ni, Co and O atoms.

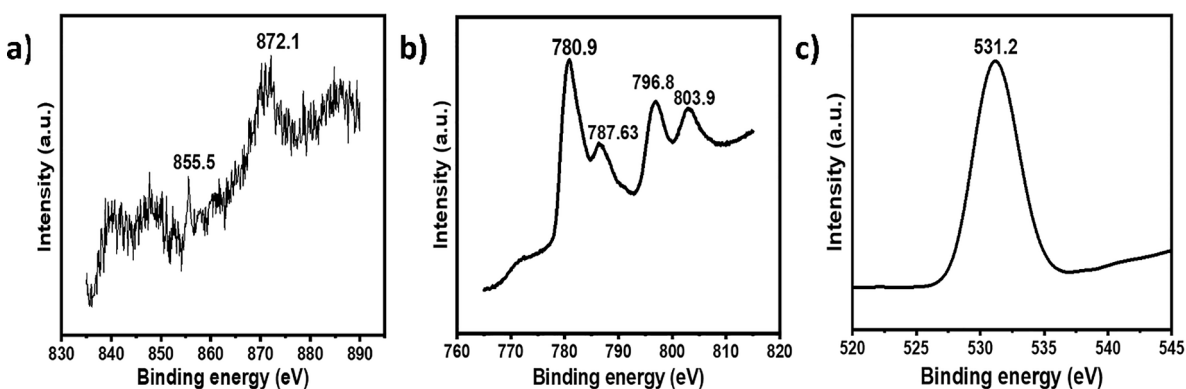


Fig. 2. XPS spectra of (a) Ni 2p, (b) Co 2p, and (c) O 1s for the Cu-NiCo<sub>2</sub>O<sub>4</sub> film.

cell, until the solar cell's lifetime is over. This approach can reduce the time of fabrication and cost.

## 2. Experimental details

A Pure copper substrate is cleaned with acetic acid at 70 °C to remove the residuals on the surface. Nickel is first deposited over copper with 0.5 Å/sec for about 100 nm, and then 40–50 nm of Co<sub>3</sub>O<sub>4</sub> is deposited by electron-gun evaporation at room temperature

## 3. Results and discussion

The X-ray diffraction (XRD) pattern of grown Cu-NiCo<sub>2</sub>O<sub>4</sub> film on copper substrate is shown in Fig. 1 with peaks corresponding to Cu-NiCo<sub>2</sub>O<sub>4</sub> and Cu phases. The grown film is polycrystalline in nature revealing (511) and (642) planes of cubic crystal structure. The XRD pattern also exhibits a small peak at 43.04°, representing the (111) plane of cubic Cu structure. The presence of Cu-NiCo<sub>2</sub>O<sub>4</sub> is mainly due to the incorporation of oxygen into Ni lattice, which can be confirmed by X-ray photoelectron spectroscopy (XPS) analysis.

The chemical composition and valance state of Cu-NiCo<sub>2</sub>O<sub>4</sub> film are

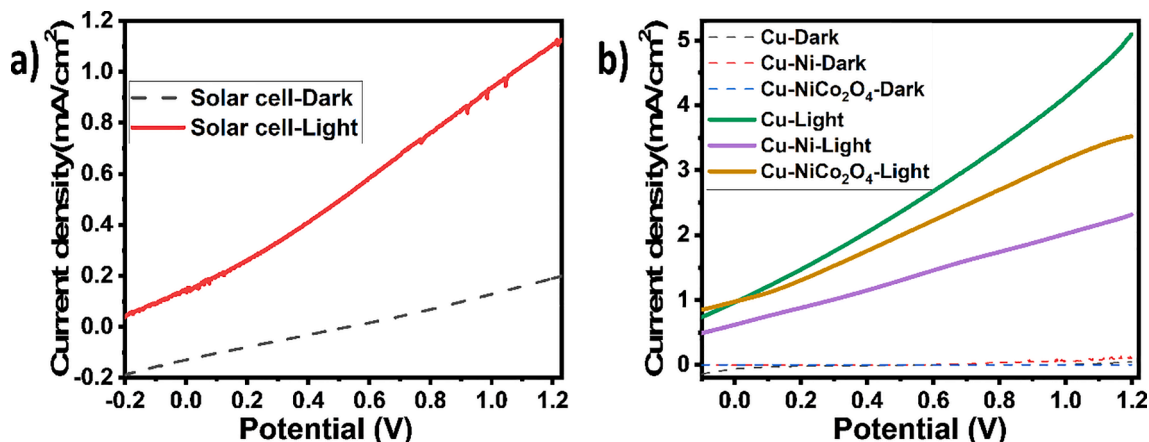


Fig. 3. Photocatalytic efficiencies (a) only with the solar cell efficiency and (b) with catalysts.

analysed using XPS, through which we confirm the oxidization state of the transition metal ion. The shift of the binding energy due to relative surface charging is corrected using the C 1 s level at 284.8 eV as an internal standard. The XPS spectra of Ni, Co, and O elements are shown in Fig. 2(a)–(c). For the Ni 2p spectrum, the peaks at 855.5 and 872.1 eV assigned to Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> binding energy levels indicate Ni<sup>2+</sup>. For the Co 2p spectrum, the distinct peaks of 2p<sub>3/2</sub> state at 780.9 and 787.6 eV are assigned to Co<sup>2+</sup> oxide band and satellite peak in Co<sub>3</sub>O<sub>4</sub>. The Co<sup>2+</sup> and satellite 2p<sub>1/2</sub> peaks are also observed at 796.8 and 803.9 eV respectively. The O 1s spectrum with a peak at 531.2 eV corresponds to the Ni oxide binding of incorporated oxygen into Ni lattice mentioned above. The energy-dispersive X-ray spectroscopy (EDS) analysis results shown in Fig. S3 reveal the existence of oxide on the surface of nickel after Co<sub>3</sub>O<sub>4</sub> is deposited on the surface of nickel. In order to check the band structure and Density of States(DOS) are illustrated in Fig. (supplementary information) S7 (a) & 7(b). Based on DFT-PBE calculations performed in the QUANTUM ESPRESSO software, we determined a bandgap of 1.87 eV. The valence band maximum (VBM) and conduction band minimum (CBM) coexist in the G-K direction, resulting in a direct bandgap. The DOS findings indicate that CBM is mostly caused by Co and O atoms, while VBM is caused by Ni and O atoms.

The photo-electrolysis is carried out under xenon lamp using 1 M KOH solution as electrolyte to distinguish the performance of solar cell with and without a catalyst. The solar cell with an active area of 0.4 cm<sup>2</sup> generates a potential around 0.9 V after illumination to drive the water splitting. However, the minimum thermodynamic value generally needed for water splitting is around 1.23 V. As we increase the bias of solar cell, the photocurrent density increases as well as shown in Fig. 3. In Fig. 3(a), the solar cell is tested without a catalyst. Photocurrent density of 0.14 mA/cm<sup>2</sup> and STH efficiency of 0.17% assuming 100 % faradic efficiency are obtained, and they degrade quickly due to high corrosion rate. Next, the solar cell is protected and kept on the surface of electrolyte. Only catalyst is immersed as shown in Fig. S1(b). This configuration shows tremendous performance enhancement. The PEC performances of devices with three different catalysts Cu, Cu-Ni, and Cu-NiCo<sub>2</sub>O<sub>4</sub> are studied. Among these, device with Cu catalyst exhibits better result with photocurrent density around 0.91 mA/cm<sup>2</sup> and STH of 1.13%. But oxide layer is formed because pure Cu is highly unstable in KOH solution. To overcome this problem, nickel is first deposited on the surface of the copper substrate and then Co<sub>3</sub>O<sub>4</sub> is deposited, which may lead to the formation of NiCo<sub>2</sub>O<sub>4</sub> due to incorporation of oxygen into Ni lattice. For the device with Cu-Ni co-catalyst, lower values of photocurrent density of 0.61 mA/cm<sup>2</sup> and STH efficiency of 0.75% is recorded. This may due to dislocations at the interface of nickel and copper and also influence of compositions percentage of copper and nickel [11]. But in terms of stability, better performance is observed as shown in Fig. S8(a) & S8(b). The device with Cu-NiCo<sub>2</sub>O<sub>4</sub> co-catalyst showed photocurrent density of 0.98 mA/cm<sup>2</sup>, STH efficiency of 1.2%, and good stability. This may due to influence of oxygen vacancies formed in semiconductors, leading better performance for OEC when compared to metals.

#### 4. Comparison of results with other solar cells

Solar cell with co-catalyst	Area of the solar cell	Applied voltage	Photocurrent	Reference
Units	cm <sup>2</sup>	(V)	mA/cm <sup>2</sup>	
Perovskite Solar Cell with BiVO <sub>4</sub>	1	0 V	0.45	[12]
Perovskite Solar Cell with Co(OH) <sub>2</sub> /BiVO <sub>4</sub>	1	1.23 V	4.52	[7]
perovskite solar cell-TiO <sub>2</sub> /BiVO <sub>4</sub>	1	0 V	1.3	[13]
Perovskite Solar Cell with Cu	0.40	1.23 V	4.80	This work
Perovskite Solar Cell with Cu-NiCo <sub>2</sub> O <sub>4</sub>	0.40	0 V	0.98	This work

#### 5. Conclusion

We have employed a Cu-NiCo<sub>2</sub>O<sub>4</sub> oxygen evolution catalyst and a single junction screen-printed HTM-free mesoscopic C-based perovskite solar cell with an efficiency of 13.90% for solar cell electrolysis applications, resulting in a solar to hydrogen efficiency of 1.2%. When the solar cell is used with the catalyst, it performs better. Moreover, we can remove the catalyst and replace a new one without damaging the solar cell, showing the versatility of this approach. This approach will reduce the time and fabrication costs. The proposed approach can greatly improve the efficiencies of STH.

#### CRedit authorship contribution statement

**K. Poshan Kumar Reddy:** Conceptualization, Methodology. **Mohammad Rameez:** Data curation, Writing – original draft. **Tsai-Te Wang:** Data curation, Writing – original draft. **Kuangye Wang:** Data curation, Writing – original draft. **Eric Yan-Ru Lin:** Visualization, Investigation. **Ming-Chang Lin:** Visualization, Investigation. **Eric Wei-Guang Diao:** Visualization, Investigation. **Chen-Hsiung Hung:** Writing – review & editing. **Yun-Lun Chueh:** Writing – review & editing. **Krishna P. Pande:** Supervision. **Po-Tsung Lee:** Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2022.131838>.

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