

Photoelectrochemical Carbon Dioxide Reduction Using a Perovskite Photoelectrode with an Organic Modifier

Sehun Seo¹, Sizhou Yang², Ayush Agrawal³, Qiang Zhang¹, Haiyan Mao⁴, Hojoong Choi¹, Tim Kodalle², Woong Choi⁵, Keon-Han Kim⁵, Adman Webber⁵, Alexis T. Bell⁵, Carolin M. Sutter-Fella², Jeffrey A. Reimer⁴, Matthias Heuchel¹, Aditya Mohite³, Yi Liu², Francesca M. Toma^{1*}

¹ Institute of Functional Materials for Sustainability, Helmholtz-Zentrum Hereon, Teltow, Germany

² Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

³ Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX, USA

⁴ Department of Chemical and Biomolecular Engineering, University of California Berkeley, Berkeley, CA US

⁵ Liquid Sunlight Alliance, Lawrence Berkeley National Laboratory, Berkeley, CA 94710, USA, Universität



Helmholtz-Zentrum
hereon

Introduction

Photoelectrochemical (PEC) carbon dioxide reduction (CO₂R), the direct conversion of CO₂ into energy-dense multi-carbon-based hydrocarbons (C₂+), using sunlight, represents a promising avenue towards achieving a carbon-neutral society. However, the production of C₂+ via PEC CO₂R presents considerable challenges due to (1) the limited photophysical performance of photoelectrodes and (2) the high overpotential with low selectivity for C₂+ production. Therefore, the rational design of photoelectrodes with catalysts is essential, considering the compatibility between suitable active materials and catalytic factors such as the microenvironment and internal catalytic characteristics.

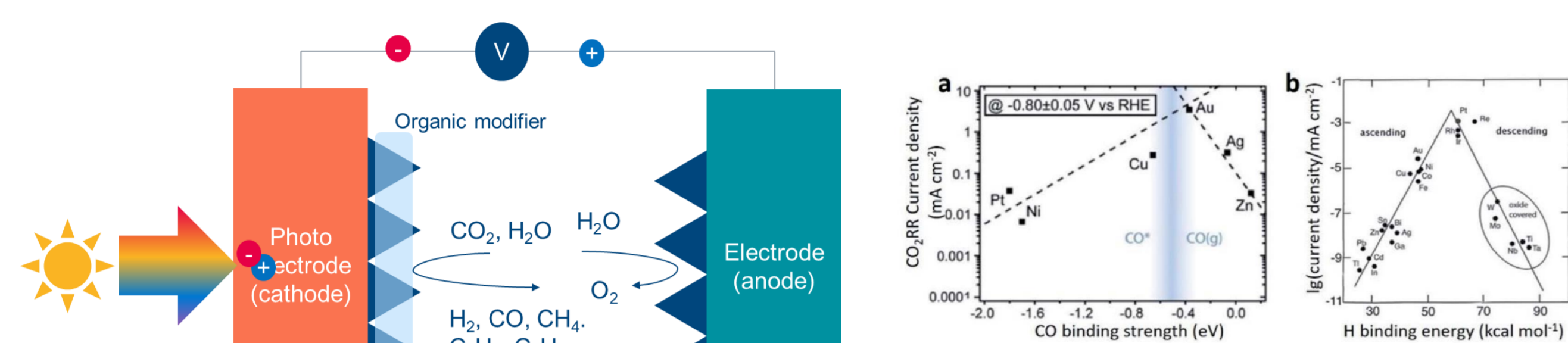


Figure 1. Schematic of PEC CO₂R

- The PEC CO₂R is the conversion of CO₂ to more reduced chemical species using solar energy. (Figure 1)
- Photoelectrode generates charges, hole and electron, by absorbing solar energy.

Organometal halide perovskites (OHPs) is Promising photoactive material for PEC CO₂R due to its excellent properties.

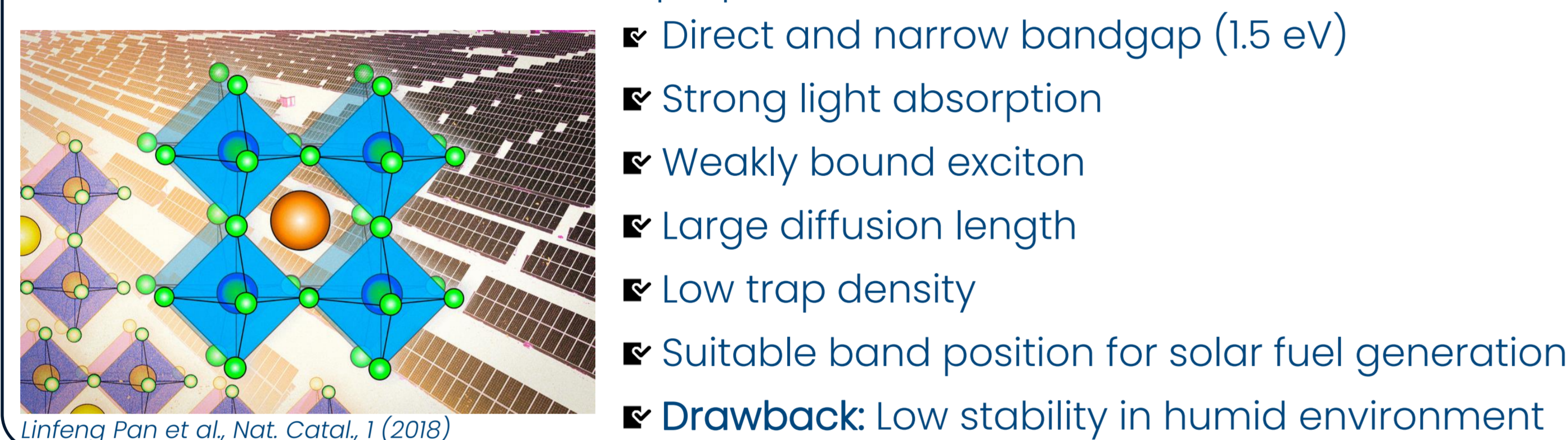


Figure 2. volcano plots showing binding energy of (a) the CO intermediate and (b) hydrogen
Choi, W. et al., J. Mater. Chem. A 2020, 8 (31), 15341–15357.

- Direct and narrow bandgap (1.5 eV)
- Strong light absorption
- Weakly bound exciton
- Large diffusion length
- Low trap density
- Suitable band position for solar fuel generation
- Drawback: Low stability in humid environment

- Catalyst determine product selectivity by control of reaction pathway depending on their internal characteristics.

- Copper is the suitable catalyst to produce C₂+ products due to its suitable binding energy for absorbed CO*, which is an important intermediate with low hydrogen production. (Figure 2)
- Oxide-derived copper (Ox-Cu): Defective Cu surface enhances C-C coupling for ethylene production with suppression of Methane production

- Organic modifier controls the microenvironment of catalyst surface.

- Covalent organic frameworks (COFs) are a class of material characterized by two- or three-dimensional (2D or 3D) porous crystalline structures that are connected by strong covalent bonds formed by reacting organic monomers with precise control enabling defined composition and porosity within the structures.
- COFs is suitable and stable organic modifier to control the wettability, CO₂ capturing, pH etc on the catalyst surface due to its unique structure.
- Nafion is usually used to bind between COF and Ox-Cu and to control of pH at catalyst surface as an organic modifier.

Results

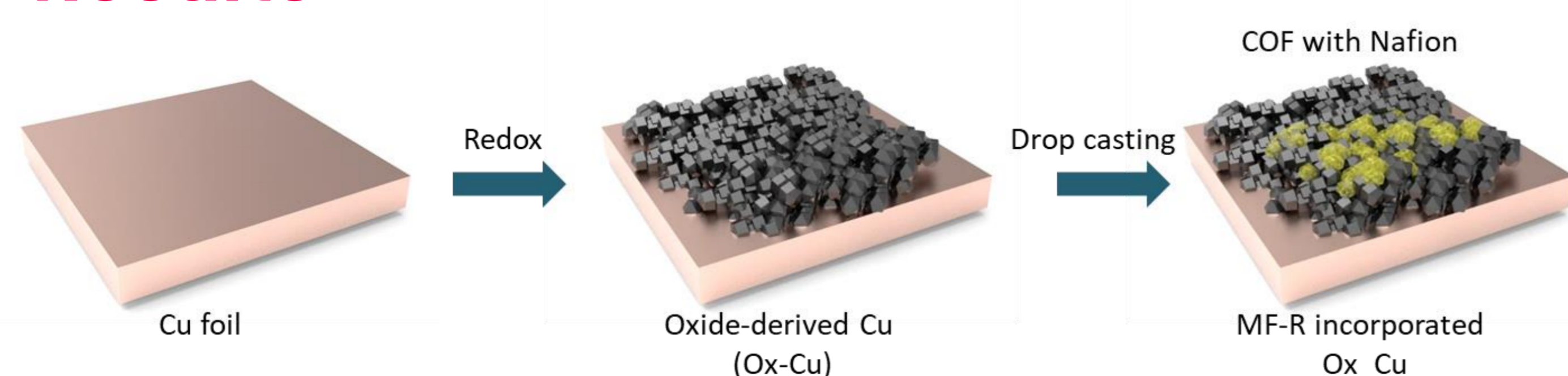


Figure 3. Schematic of procedure for catalyst preparation

We first synthesized Ox-Cu on Cu foil to enhance C-C coupling. The COF with Nafion was decorated on the Ox-Cu to improve the microenvironment on Ox-Cu surface

Catalytic performance of MF

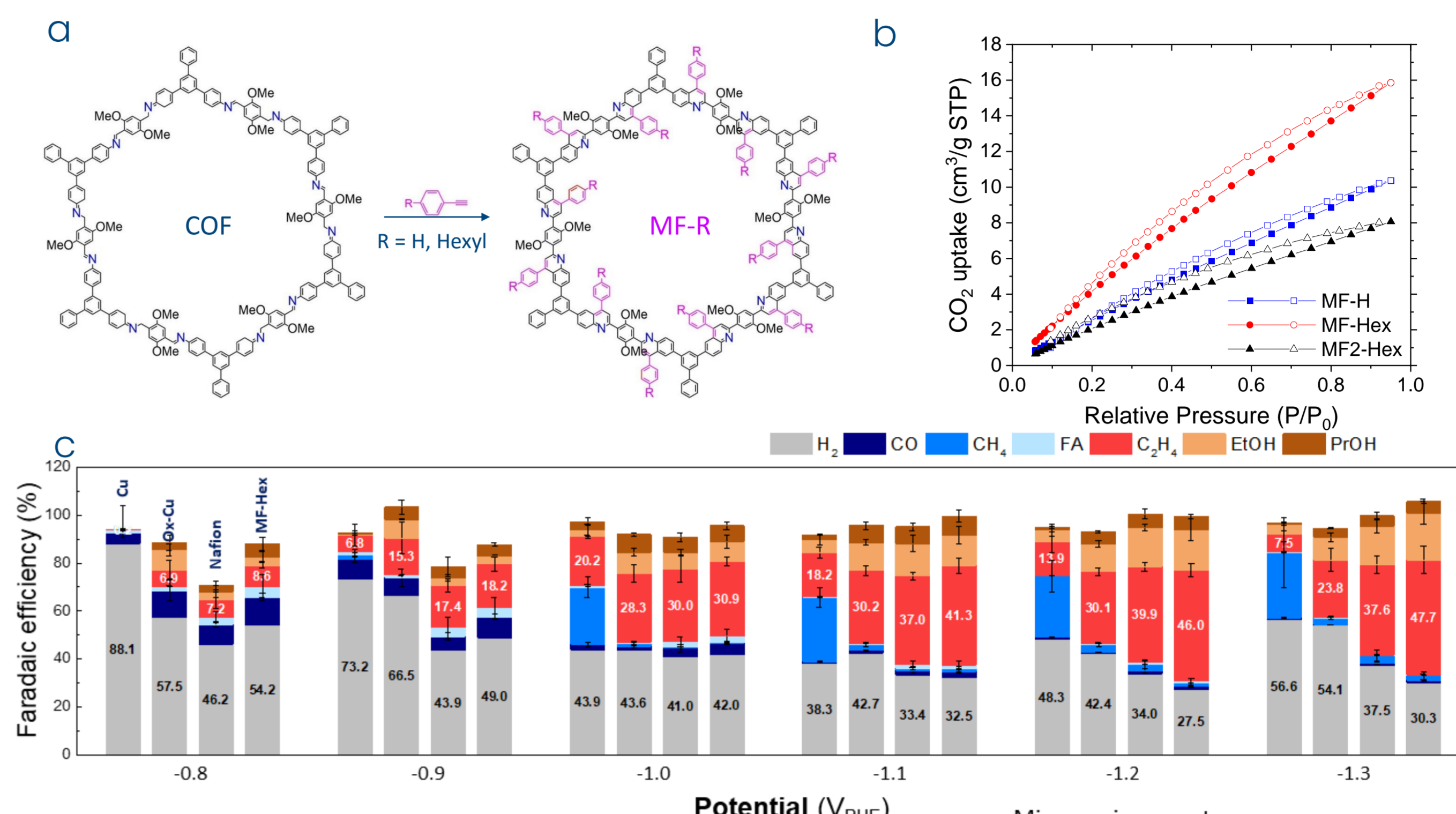


Figure 4: (a) Schematic of MF. (b) CO₂ uptake of MF. (c) Faradaic efficiency of CO₂R for bare Cu, Ox-Cu, Nafion-Cu, MF-Cu. (d) Mechanism of the enhanced selectivity of CO₂R due to catalyst and organic modifier

- We synthesized modified COF (MF) with different substituents to control the CO₂ capture characteristic. MF-HEX shows the best CO₂ uptake.
- MF-HEX shows the best C₂+ selectivity of c.a. 70 % at -1.3 V_{RHE}. This improved selectivity was caused by the increased local CO₂ concentration due to CO₂ physisorption of MF on the catalyst surface.

PEC performance of MF/OHP photocathode

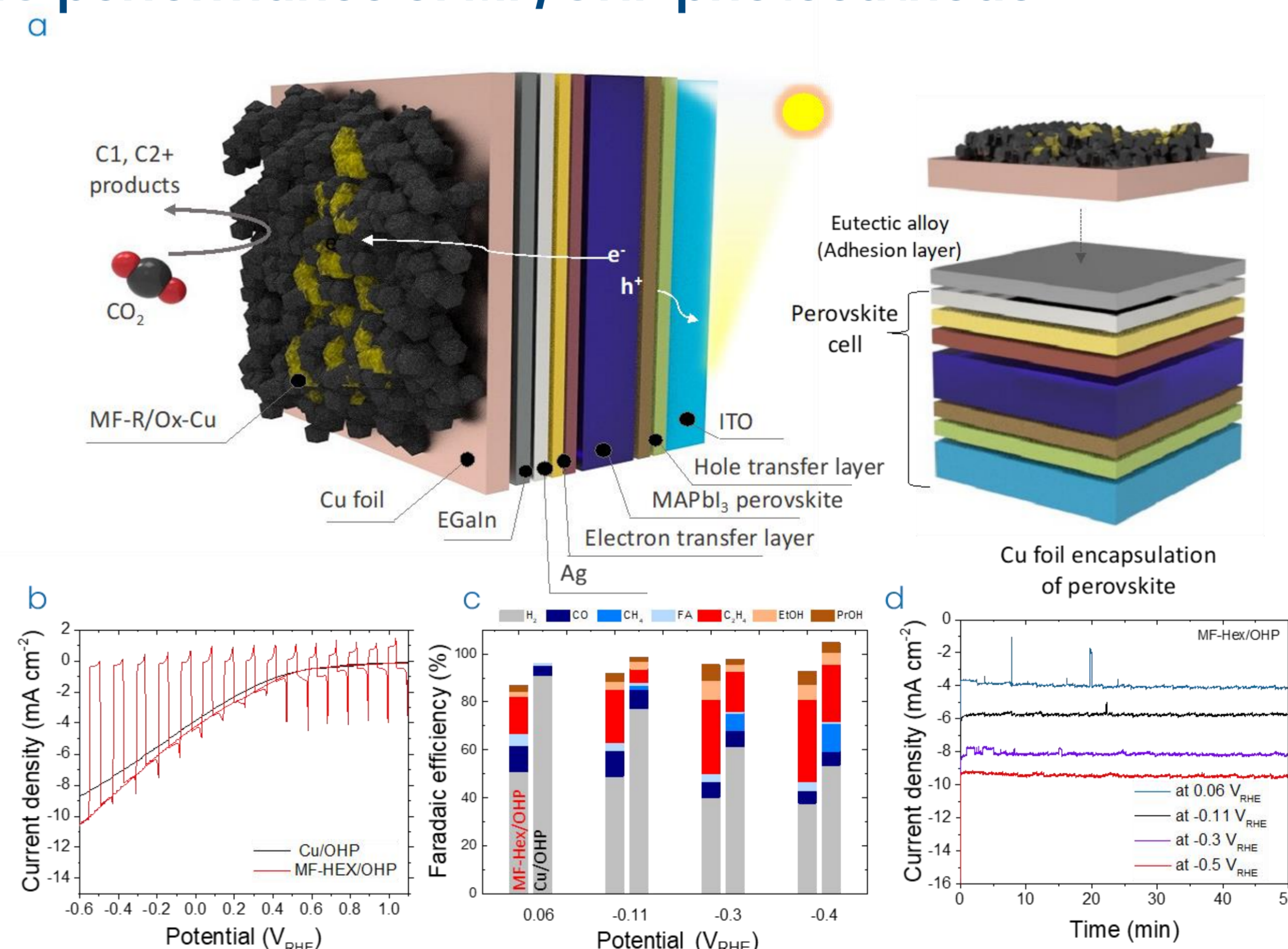


Figure 5 (a) Schematic of MF-decorated OHP photocathode. (b) LSV curves for Cu/OHP and MF/OHP. (c) Faradaic efficiency of CO₂R for Cu/OHP and MF/OHP. (d) CA measurements of MF/OHP at different potential

- MF-HEX was decorated on the OHP photocathode.
- Photocurrent density of MF/OHP is 10 mA/cm² at -0.4 V_{RHE}, -4 mA/cm² at 0.06 V_{RHE}
- MF/OHP photocathode exhibited a remarkable C₂+ selectivity, with over 15% faradaic efficiency (FE) at 0.06 V_{RHE} and over 34% FE at -0.4 V_{RHE} under 1 sun AM 1.5G, as compared to bare-Cu/OHP photocathode.

Summary

- MF Catalyst improves local CO₂ concentration by CO₂ physisorption, which improves selectivity of C₂+ production.
- High C₂+ productivity at high potential in MF-HEX/OHP photocathode

