Single-Layered Two-Dimensional Covalent Organic Frameworks Boost the Electrochemical CO_2 Reduction Reaction

Dr. Nicolás Arisnabarreta
Yansong Hao, Enquan Jin, Aude Salamé, Klaus Muellen, Marc Robert, Roberto Lazzaroni, Sandra Van Aert, Kunal Mali, and Steven De Feyter
Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven Leuven (3001), Belgium
Nicolas.arisnabarreta@kuleuven.be

The appropriate conversion of carbon dioxide (CO_2) into value-added chemicals is a key step in the management of global warming. To do so, different catalysts can be employed, which impacts the product formation. Two-dimensional covalent organic frameworks (2D-COFs) are a rational choice since their structures, and hence properties, can be tuned on-demand. Metal complexes of porphyrins and phthalocyanines can be incorporated into 2D-COFs and are considered the next generation of electrocatalysts due to their outstanding efficiencies in the electrochemical CO_2 reduction reaction (CO_2RR).[1,2] Such 2D-COFs may be either fabricated as a bulk powder and immobilized at the electrode surface or grown directly on them as a thin (thickness >200 nm) or even single-layered (s2D-COF, ~ 0.5 nm thickness) film. However, powder immobilization process on the electrode can largely affect their targeted application i.e., efficiency/selectivity of CO_2RR. Thus, substrate-supported s2D-COFs can be advantageous over the immobilization of 2D-COF powder due to: (i) availability of most of the active sites at the surface maximizing the efficiency; (ii) better charge transport; and (iii) higher gas diffusion. However, given the complexity, there is a lack of protocols for the successful and fast on-surface synthesis of 2D-COF monolayers.

In this work, [3] we demonstrate a fast and straightforward fabrication method of porphyrin-containing s2D-COFs, which allowed their extensive high-resolution visualization *via* scanning tunneling microscopy (STM, Fig. 1a-c) in liquid conditions with the support of STM simulations. The as-prepared single-layered film was then employed as a cathode for the electrochemical reduction of CO_2 (Fig. 1d-e). Fe porphyrin-containing s2D-COF@graphite used as a single-layered catalyst provided moderate-to-high carbon monoxide selectivity (82%) and partial CO current density (5.1 mA/cm^2). This work establishes the value of using single-layered films as heterogeneous catalysts and demonstrates the possibility of achieving high performance in CO2 reduction even with extremely low catalyst loadings.

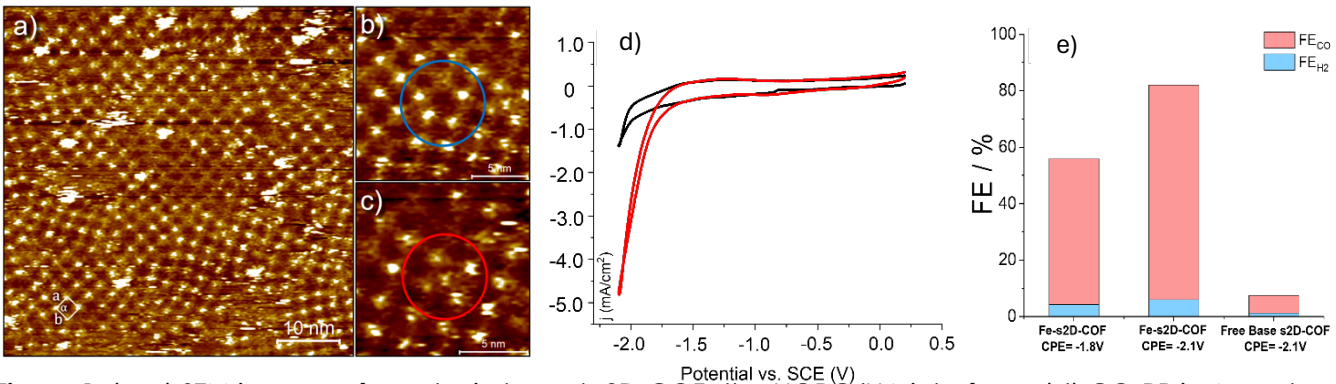

Figure 1: (a-c) STM images of porphyrin-based s2D-COFs the HOPG/HA interface. (d) CO_2RR in Ar and CO_2 (black and red curve).(e Faradaic efficiencies (FEs) obtained for the CO and H_2 production.

References

[1] Christian S Diercks, Yuzhong Liu, K. E. Cordova, O. Yaghi. **Nature Materials Volume 17, pages301–307 (2018).**
[2] Nam, DH., De Luna, P., Rosas-Hernández, A. *et al.* ***Nature Mater.* 19, 266–276 (2020).**
[3] Nicolás Arisnabarreta Yansong Hao, Enquan Jin, Aude Salamé, Klaus Muellen, Marc Robert, Roberto Lazzaroni, Sandra Van Aert, Kunal S. Mali, Steven De Feyter. **Adv. Energy Mater. (2024), 14, 230437.**