

Standardizing photocatalytic CO₂ reduction

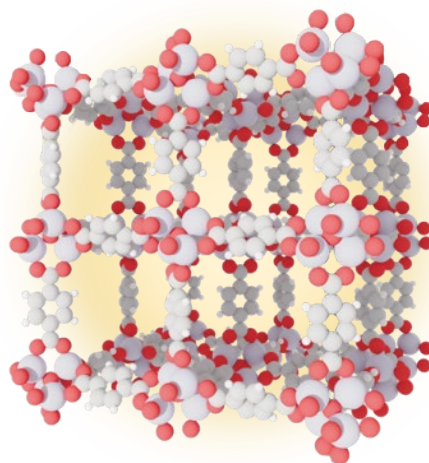


Metal–organic frameworks are important catalysts for photocatalytic CO₂ reduction but if the field is to continue to advance, then reporting of photocatalytic metrics and practices must be standardized.

Photocatalytic CO₂ reduction (CO₂R) uses light energy to convert CO₂ into high energy density chemicals such as carbon monoxide and methanol. Whilst photocatalytic CO₂R has been extensively researched in the past few decades, the use of metal–organic frameworks (MOFs) as photocatalysts for CO₂R is a relatively young area of research in comparison, with the first reports appearing approximately 15 years ago. MOFs are constructed from metal nodes and organic linkers which coordinate to form 3D frameworks and are ideal catalysts owing to their large specific surface areas, multiple active sites and ease of functionalization^{1,2}.

For any field to evolve, process performance must be benchmarked against the state-of-the-art standard such as a specific material or device. Standardizing metrics ensures consistency and reliability across experiments and allows for comparisons between different laboratories. Several efforts have been made to standardize reporting across a range of application spaces, including photocatalysis, but inconsistencies remain in the reporting of materials and devices^{3,4}. In the case of photocatalytic CO₂R on MOFs, there is a complex interplay between materials, reaction conditions and environmental factors and therefore there are many considerations when establishing standards.

Writing in a [Perspective](#) in this issue, Warnan and co-authors extensively examine the published literature on MOFs for photocatalytic CO₂R and draw conclusions about the state-of-the-art of the field and discuss potential improvements in reporting. While the diversity in composition of MOF-based photocatalysts for CO₂R has widened in the past decade, inconsistencies in the reporting of catalytic metrics, carbon sources, electron sources and experimental set-ups are evident.



For example, maximum product evolution rates should be documented via catalyst content screening. Although inherent to the experimental set-up (which should be fully documented, as discussed later), product evolution rates also correlate to photocatalyst loading. The impact of MOF photocatalyst loading can be removed by changing MOF content in the reaction until a maximized product evolution rate is achieved (the optimal rate), therefore allowing for better comparisons between catalysts. This form of analysis is currently rare in the CO₂R MOF literature.

Apparent quantum yield (AQY) gives an indication of light utilization and sensitivity of the photocatalyst. However, Warnan and co-authors determine that in approximately 70% of publications on MOFs for CO₂R, this metric is not reported and that even when given, it is rarely determined at different wavelengths. A suggestion is that the maximum attainable AQY under various loadings is reported, alongside the optimal product evolution rate.

Carbon and electron sources also need strong verification. MOFs contain a large amount of carbon which could be decomposing giving misleading results, and also, many experiments are carried out in solvents which contain carbon. Isotope labelling experiments can verify the source of carbon, oxygen, and hydrogen in the final products. Only 55% of publications currently

report some form of isotope labelling. For full redox systems, where sacrificial electron donors are not used, quantification of both oxidation and reduction products should be performed and the number of electrons transferred should match.

Warnan and co-authors examine the reported conditions under which photocatalysis is examined. In 20% of publications, the irradiation wavelength range is not stated which makes comparison across literature difficult. Only 8% of reports use air mass filters which are designed to replicate solar spectrum wavelength distribution. In most reports (70%), irradiance is not specified.

The accurate reporting of electron sources is essential for comparison across materials. The MOF photocatalysis community is reliant on sacrificial electron donors which readily donate electrons under photocatalytic conditions. Coupling the reduction of CO₂ to a sustainable oxidation reaction is closer to artificial photosynthesis, but this is only done in around 26% of publications, and only in 50% of these papers are there adequate data to verify product stoichiometry. Around 66% of the photocatalytic reactions with MOF photocatalysts are carried out in organic solvents which is likely a result of the low water stability of MOFs. This is not ideal, and water would be a more sustainable, potentially electron-providing solvent. Therefore, increasing water stability of MOF photocatalysts is one key area of focus.

In summary, full reporting of testing conditions is recommended so that accurate benchmarking can take place, allowing researchers to accurately determine key successes and shortcomings of MOF photocatalysts. Reporting of catalytic metrics should be carefully considered, to give as accurate as possible a picture of how the MOF photocatalyst performs under varied conditions.

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