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Covalent Organic Frameworks: metal-free heterogeneous (photo)catalysts for green chemistry

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PURPOSE OF THE ABSTRACT

Covalent Organic Frameworks, first reported in 2005 by Omar Yaghi, and Covalent Triazine Frameworks, first reported in 2008 by Antonietti and Thomas, have recently emerged as highly versatile heterogeneous (photo)catalysts that can even operate in metal-free conditions. These materials are prepared by a controlled and reversible polymerization of one or two precursors into a highly porous and crystalline framework, quite similar to the synthesis of Metal-Organic Frameworks.

In thermal catalysis, the defects in CTFs have proven to be excellent catalytic centers, that can for instance activate oxygen gas. On the other hand, by a judicious choice of the precursors, one can create excellent photocatalysts and electrocatalysts. We can tune the bandgap, the conductivity, and many other properties of these semiconductors. It is important to understand the photophysics of these materials as well, to optimize them into highly selective photocatalysts for green applications. Photoluminescence, ultra fast spectroscopy, EPR, UV-VIS DRS, cyclovoltammetry are some of the techniques that allow a deeper insight in the reaction mechanism, the radicals and the lifetimes of the electron-hole pairs.

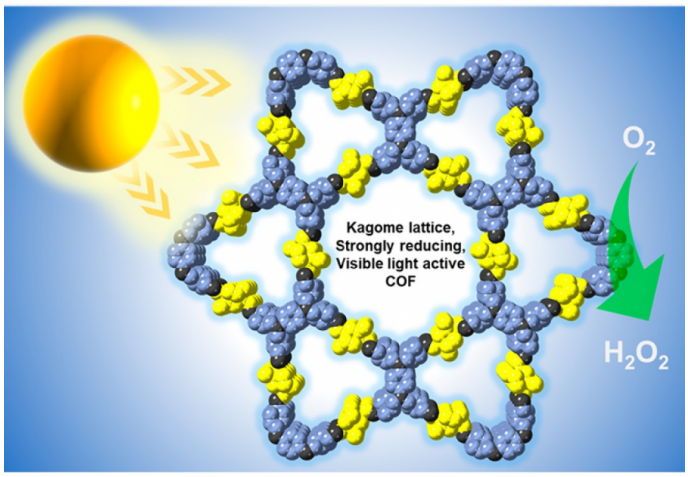
I will present several recent case-studies by our research group.

In a first example, we give an overview of the use of COFs in thermal catalysis[1]. In one specific example, we use CTF materials as a thermal catalyst in the oxidation of alcohols. We could elucidate the reaction mechanism and see that the CTF is able to activate oxygen into a superoxide radical. The reaction is 100% selective towards the aldehydes[2].

In the second example, we give an overview of the photocatalytic applications of COFs and CTFs[3]. In one specific example, we created strongly reducing (diarylamino)benzene functionalized Covalent Organic Framework for metal-free visible light photocatalytic H2O2 generation[4]. We were inspired by biological Würster systems, that created H2O2 from oxygen, just as our novel COF was able to do.

I will wrap up with some other yet unpublished examples: the photocatalytic reduction of nitro-compounds, the photocatalytic metal-free degradation of dyes and the use of COFs as sensors and adsorbents for pesticides[5].

FIGURES



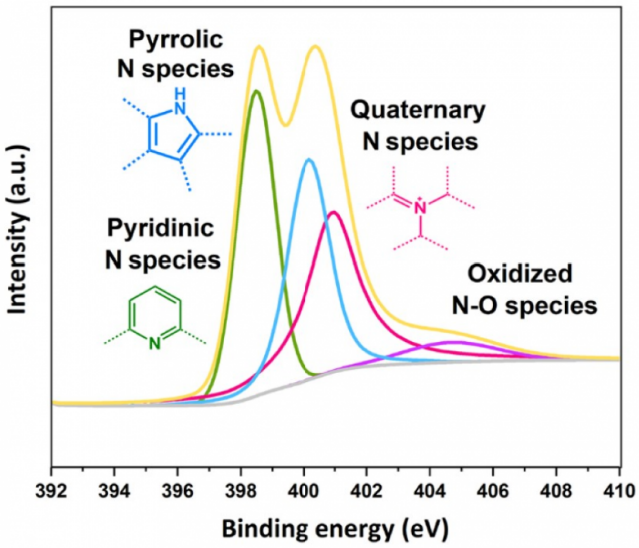


FIGURE 1

Strongly Reducing Covalent Organic Framework for photocatalytic H2O2 production

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FIGURE 2

XPS of defected CTF

Different Nitrogen Defects in Covalent Triazine Frameworks.

KEYWORDS

Covalent Organic Frameworks | Covalent Triazine Frameworks | photocatalyst | heterogeneous green catalysis

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