MOF-based Photocatalytic Reduction of CO_2

Yishu Zhang Literature Seminar April 16th, 2019

The increased emission of CO_2 from burning fossil fuels has been causing serious issues such as global warming, and great efforts have been made on solving these problems.[1,2] One potential methods is direct conversion solar energy to chemical fuels, which is also known as artificial photosynthesis. With this method, the transformation of carbon dioxide to fuel and chemical feed stocks can be achieved.[3] The great challenge for this process lies in optimizing efficiency, activity and selectivity. A number of catalytic systems have been designed, however, the combination of all three properties in one system is still absent.[4] For example semiconductor-based photocatalysts have been used to accomplish the photocatalytic reduction with high performance, yet still suffer from weak CO_2 adsorption and activation.

Metal-organic frameworks (MOFs) are ideal platforms for achieve the combination of three properties in one system.[5,6] Highly selective molecular catalysts within the backbone give the system high selectivity.[7,8] With the extensive surface area and tunable pore sizes, active sites are easily accessible for substrates which leads to outstanding activity.[9,10] Optoelectronic properties such as bandgaps and intrinsic charge carrier mobility have been engineered to achieve higher efficiency.[11,12] In addition, high degree of stability in solution and tolerance to a wide range of pH condition, give MOF-based photocatalyst great potential.

$\{Cu_3(TCA)_2(dpe)_3(H_2O)_3\}_n$(MOF-Cu), $\{Co_3(TCA)_2(dpe)_3(H_2O)_6\}_n$(MOF-Co), and $\{Ni_3(TCA)_2(dpe)_3(H_2O)_6\}_n$ (MOF-Ni), are isomorphic MOFs with different transition-metal centers with same organic linkages 4,4',4''-nitrilotribenzoic acid ligands (TCA) and 1,2-di(4-pyridyl)ethylene (dpe).[13] These MOFs only contain a single active metal center, which makes them perfect models to study the influence of the different transition-metal involved in the catalytic reaction. Three MOFs showed very different performance in the photocatalytic reduction, and MOF-Ni stood out for its high specificity over two isomorphic MOFs. Furthermore, more insights about the mechanism (Figure 1) of the photocatalytic reduction were discovered.

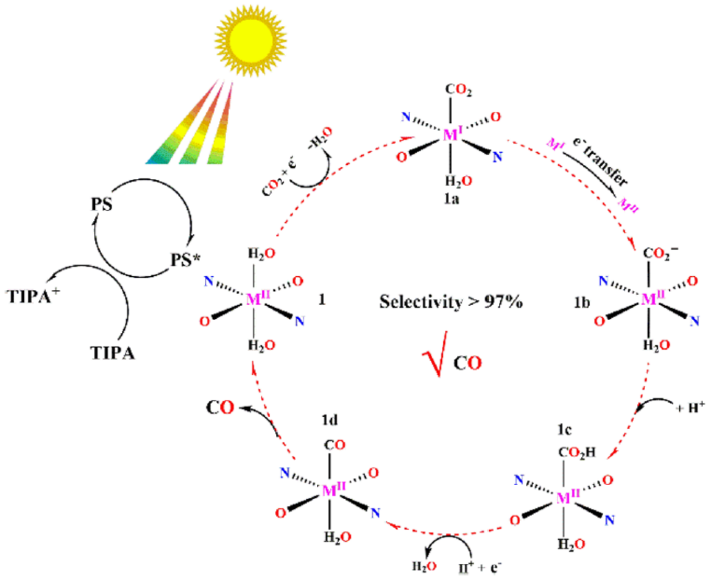

Figure 1. Proposed photocatalytic mechanism of MOFs for the CO_2 to CO conversion.[13]

BIF-20 (BIF = boron imidazolate framework), is constructed with porous boron imidazolate coordinated to tetrahedral Zn^{2+}. Just like other other member from zeolite-like frameworks, BIF-20 has shown great ability for CO_2 storage and separation. With a rational combination of BIF-20 and a proper photosensitizer could not only tune the optical adsorption to desirable wavelength but also enhance the photocatalytic performance. Graphitic carbon nitride (g-C_3N_4) has been widely explored as photocatalyst for CO_2 reduction and it can be coupled with a porous structure to achieve higher performance. Thus g-C_3N_4 was integrated with BIF-20 and the new system has been proven to possess a much enhanced photocatalytic activity compare to g-C_3N_4 nanosheet (Figure 2).[14]

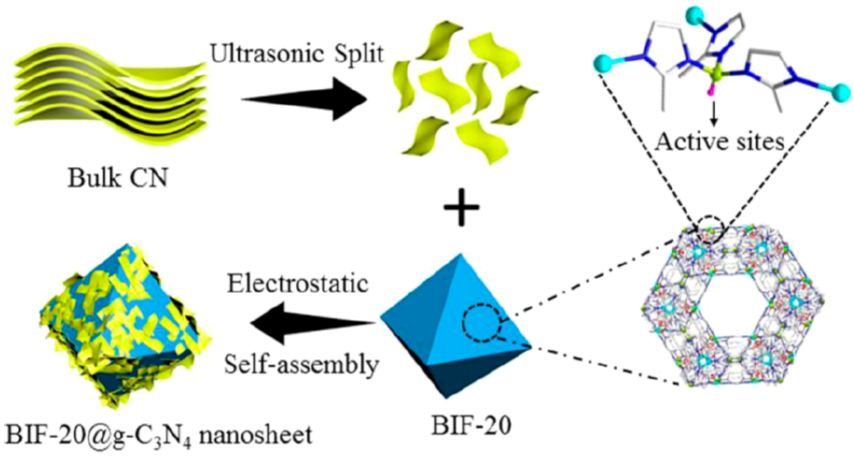

Figure 2. Schematic description of the preparation of the BIF-20@ g-C3N4 nanosheet photocatalyst[14].

Halide peroskites (PVK) are optoelectronic materials featuring excellent optoelectronic properties such as large extinction coefficient and tunable absorption range, which allows them to be potential photocatalyts for CO_2 reduction. However, problems like low CO_2 capturing ability lead to low conversion efficiency. A PVK@MOF composite photocatalytic wad designed and synthesis through a direct grow of zinc/cobalt-based zeolitic imidazolate framework (ZIF) on the surface of $CsPbBr_3$ quantum dots (Figure 3). This system has achieved better CO_2 capture ability and higher charge separation efficiency further lead to improved photocatalytic activity.[15]

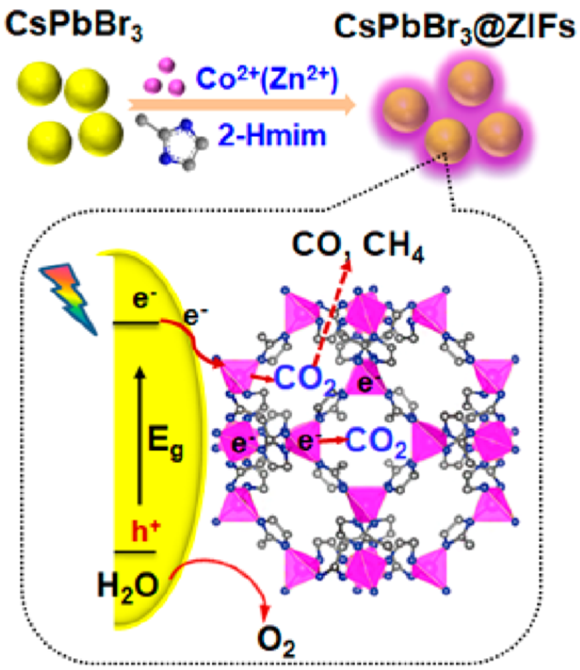

Figure 3. Schematic illustration of the synthesis process and CO2 photoreduction process of CsPbBr3/ZIFs[15].

These examples show that MOFs can serve as a great platform to support known photocatalysts. Due to their structural and optoelectronic properties, the photocatalytic activity can be strongly enhanced compared to the catalyst alone. Quantum yield was barely mentioned in these papers, which might be the next step in developing MOF-based photocatalyst. Catalytic efficiency is one way to evaluate a catalyst, on the other hand, how effectively is energy input being used for the reduction is another concern.

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