57072-DNI10. **FACILE SYNTHESIS OF METAL ORGANIC FRAMEWORK-BASED HETEROJUNCTION PHOTOCATALYSTS FOR CO_2 PHOTOCONVERSION INTO HYDROCARBON FUELS**

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OBJECTIVE

The ultimate objective of the project is to develop metal-organic frameworks (MOFs)-based heterojunction photocatalysts to address environmental issues, such as CO_2 emission, indoor air quality, and water pollution. In the last funding period, we have successfully synthesized various MOFs-based nanocomposites and iron oxide nanowires to address the above mentioned issues.

PROGRESS AND RESULTS

1. <u>Synthesis of Novel MOFs-based Nanocomposites</u>

We have developed novel synthetic strategies to synthesize several unique MOFs-based nanocomposites for the first time, including $Cu_3(BTC)_2/TiO_2/Cu_2O$ ternary structure, Au@ZnO@ZIF-8 Janus nanoparticles, highly oriented 1D MIL-100(Fe)/TiO_2 nanoarrays, and iron mesh-based MIL-100(Fe) filters.

To further understand the charge transfer mechanisms in CO_2 photoreduction, a ternary nanocomposite was synthesized through self-assembly of TiO_2/Cu_2O heterojunctions via a microdroplet approach followed by *in situ* growth of $Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylate) (see **Fig. 1**). With increased charge carrier density and efficient CO_2 activation, the ternary nanocomposite exhibits a high CO_2 conversion efficiency and preferential formation of CH_4. Systematic measurements by using gas chromatography, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, and time-resolved *in situ* diffuse reflectance infrared Fourier transform spectroscopy reveal that the semiconductor heterojunction and the coordinatively unsaturated copper sites within the hybrid nanostructure are attributable to the performance enhancements.

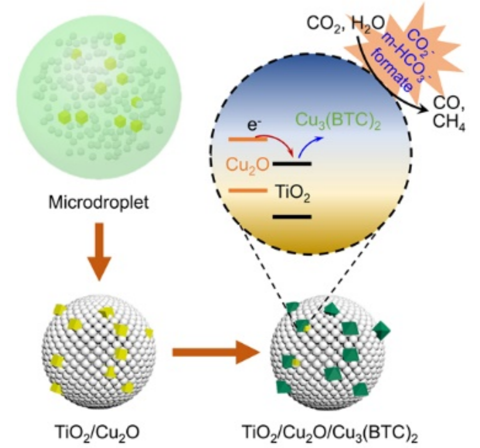

Fig. 1. Schematic of the synthesis of MOF-based ternary nanocomposites.

To address indoor air quality issues, such as efficient detection of volatile organic compounds (VOCs), a Janus nanostructure was synthesized via an anisotropic growth method, composed of plasmonic gold nanoparticles, semiconductors, and MOFs (i.e., Au@ZnO@ZIF-8; ZIF: zeolitic imidazolate framework; see **Fig. 2** for the synthesis process and detection mechanism). The Janus nanostructure exhibits excellent selective detection to formaldehyde (HCHO, as a representative VOC) at room temperature over a wide range of concentrations (from 0.25 to 100 ppm), even in the presence of water and toluene molecules as interferences. In addition, HCHO was also found to be partially oxidized into non-toxic formic acid simultaneously with detection. The mechanism underlying this technology was unraveled by both experimental measurements and theoretical calculations: ZnO maintains the conductivity, while ZIF-8 improves the selective gas adsorption; the plasmonic effect of Au nanorods enhances the visible-light-driven photocatalysis of ZnO at room temperature.

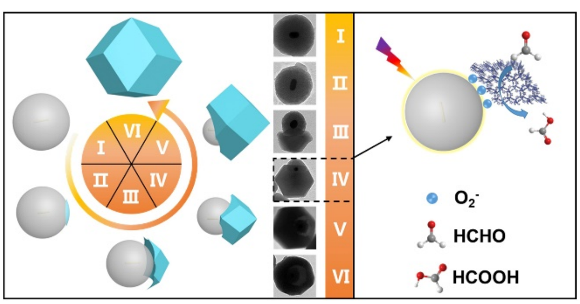

Fig. 2. Schematic of MOF-based Janus structure evolution (left) and possible mechanism of HCHO detection.

The highly oriented 1D nanoarrays (i.e., MIL-100(Fe)/TiO_2, see **Fig. 3**) were developed as photocatalysts for the first time (MIL = Materials Institute Lavoisier). The 1D structured TiO_2 nanoarrays not only enable the direct and enhanced charge transport, but also permit easy recycling. With the *in situ* growth of MIL-100(Fe) on the TiO_2 nanoarrays, the composite exhibits enhanced light absorption, electron/hole separation, and accessibility of active sites. As a result, up to 90.79% photodegradation efficiency of tetracycline, a representative antibiotic, by the MIL-100(Fe)/TiO_2 composite nanoarrays was achieved, which is much higher than that of pristine TiO_2 nanoarrays (35.22%). It is also worth mentioning that the composite nanoarrays demonstrate high stability and still exhibit high efficiency twice that of the pristine TiO_2 nanoarrays even in the 5^{th} run. This study offers a new strategy for the degradation of antibiotics by using 1D MOF-based nanocomposite nanoarrays.

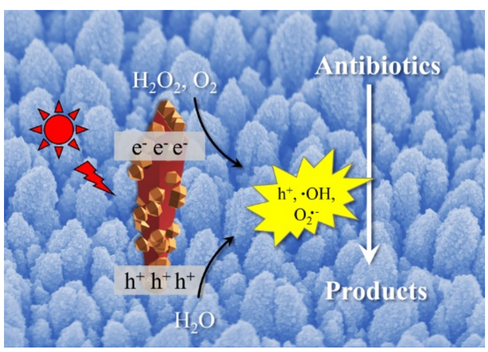

Fig. 3. Schematic of MOF-based 1D nanoarrays for efficient photodegradation of antibiotics.

Efficient oxidation from arsenite [As(III)] to arsenate [As(V)], which is less toxic and more readily to be adsorbed by adsorbents, is important for the remediation of arsenic pollution. Towards addressing this issue, we have designed and synthesized a metal organic framework (MIL-100(Fe)) filter to efficiently remove As(III) from groundwater. With commercially available iron mesh as a substrate, MIL-100(Fe) is implanted through an *in situ* growth method (**Fig. 4**). MIL-100(Fe) is able to capture As(III) due to its microporous structure, superior surface area, and ample active sites for As adsorption. This approach increases the localized As concentration around the filter, where Fenton-like reactions are initiated by the Fe^{2+}/Fe^{3+} sites within the MIL-100(Fe) framework to oxidize As(III) to As(V). The mechanism was confirmed by colorimetric detection of H_2O_2, fluorescence, and electron paramagnetic resonance detection of ·OH. With the aid of oxygen bubbling and Joule heating, the removal efficiency of As(III) can be further boosted. The MIL-100(Fe)-based filter also exhibits satisfactory structural stability and recyclability. Notably, the adsorption capacity of the filter can be regenerated satisfactorily. Our results demonstrate the potential of this filter for the efficient remediation of As contamination in groundwater.

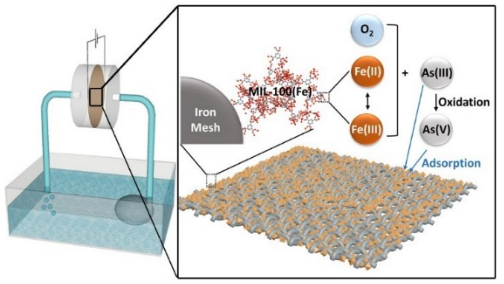

Fig. 4. Schematic of iron mesh-based MOF filter for efficient As(III)/As(V) removal from groundwater.

2. Development of Iron Oxide Nanowires

In addition to the MOFs-based nanocomposites, we have also developed novel iron oxide nanowires (IO NWs) for efficient indoor air quality control (see **Fig. 5**). Heating, ventilation, and air conditioning (HVAC) systems are among the most common methods to improve indoor air quality. However, after long-term operation, the HVAC filter can result in a proliferation of bacteria, which may be released into the filtered air subsequently. This issue can be addressed by designing antibacterial filters. In this study, we reported an iron oxide nanowire-based filter fabricated from commercially available iron mesh through a thermal treatment. Under optimal conditions, the filter demonstrated a log inactivation efficiency of >7 within 10 seconds towards *S. epidermidis* (Gram-positive), a common bacterial species of indoor bioaerosol. 52% of bioaerosol cells can be captured by a single filter, which can be further improved to 98.7% by connecting five filters in tandem. The capture and inactivation capacity of the reported filter did not degrade over long-term use. The inactivation of bacteria is attributed to the synergic effects of hydroxyl radicals, electroporation, and Joule heating, which disrupt the cell wall and nucleoid of *S. epidermidis*, as verified by model simulations, fluorescence microscopy, electron microscopy, and infrared spectroscopy. The relative humidity plays an important role in the inactivation process. The filter also exhibited satisfactory inactivation efficiency towards *E. coli* (Gram-negative). The robust synthesis, low cost, and satisfactory inactivation performance towards both Gram-positive and Gram-negative bacteria make the filter demonstrated here suitable to be assembled into HVAC filters as an antibacterial layer for efficient control of indoor bioaerosols.

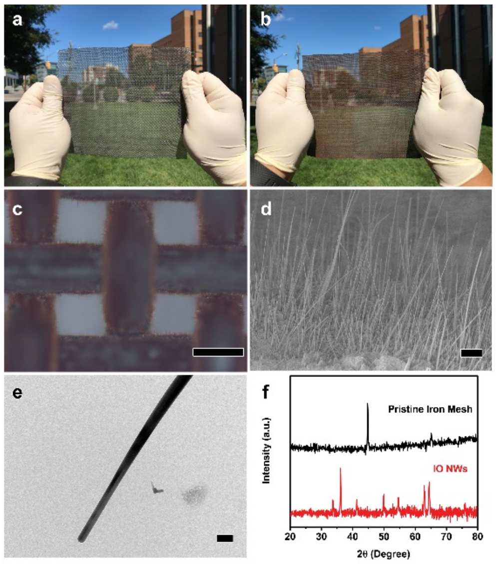

Fig. 5. Digital images of the pristine iron mesh (a) and iron mesh with IO NWs (b). Optical microscopy image (c), SEM image (d), and TEM image of the IO NWs on the iron mesh (e). (f) XRD patterns. Scale bars in (c)–(e) represent 200 μm, 5 μm, and 200 nm, respectively.

IMPACT OF RESEARCH

The research supported by ACS-PRF has resulted in one provisional patent and eight articles published/accepted in high impact and reputable journals, such as *Journal of Materials Chemistry A (IF = 9.931), ACS Applied Materials & Interfaces (IF = 8.097), Nano-Micro Letters (IF = 7.381), Environmental Science & Technology (IF = 6.653), Environmental Science: Nano (IF = 6.087),* and *Catalysis Science & Technology (IF = 5.773)*. The results were also disseminated in several national and international conferences. The project has trained one postdoc and one graduate student. The graduate student has been selected as the winner for the **2018 Outstanding Graduate Research Assistant Award** from the College of Engineering at VCU, the inaugural **Mechanical and Nuclear Engineering Fellowship** from the department, and one of the 60 students from American universities to attend the 20th National School on Neutron and X-ray Scattering supported by the United States Department of Energy. This grant has served as an important seed funding for the PI to secure several other grants, such as a grant from the National Science Foundation, another one from the Virginia state, and four user proposals from Argonne National Laboratory and Oak Ridge national laboratory.