## **Supporting Information**

# State of Art and Prospective of the Heterogeneous Photocatalysts Based on Metal Organic Frameworks (MOFs): Design, Modification Strategies, and Their Applications and Mechanisms in Photodegradation, Water Splitting and CO<sub>2</sub> Reduction

Zeren Ma, Bin Guan\*, Jiangfeng Guo, Xingze Wu, Yujun Chen, Jinhe Zhang, Xing

Jiang, Shibo Bao, Lei Chen, Kaiyou Shu, Hongtao Dang, Zelong Guo, Zekai Li,

Shunyu Yao, Zhen Huang

Key Laboratory for Power Machinery and Engineering of Ministry of Education, Shanghai Jiao Tong University, Shanghai 200240, China

\*Corresponding author: Bin Guan

Dongchuan Road No.800, Min Hang District, Shanghai, P.R.China 200240

Tel.: +86 21 34206859; fax: +86 21 34205553.

E-mail: guanbin@sjtu.edu.cn

# **Supporting Figures**



Figure S1 MOFs material was used in  $H_2S$  gas detector to evaluate meat freshness. Cited with permission from reference <sup>1</sup>.



**Supporting Figure S2** 

**Figure S2** Mechanism of hydrogen production by UiO-6-NH<sub>2</sub> and Au/UiO-6-NH<sub>2</sub> photocatalytic water splitting. Cited with permission from reference  $^{108}$ .

#### **Supporting Figure S3**



**Figure S3** (a) Preparation process of  $Fe_2O_3$ @Ag-ZnO@C. (b) Preparation process of Ti-MOF/Ag/NiFeLDH. Cited with permission from reference <sup>5,6</sup>.



Figure S4 NH<sub>2</sub>-C@Cu<sub>2</sub>O Structure diagram. Cited with permission from reference <sup>7</sup>.

#### **Supporting Figure S5**



**Figure S5** (a) Diagram showing the isotherm of  $N_2$  absorption at 77 K for 2 wt% M@MIL-101 (M = Pt, Pd, Au, Rh) (b) Schematic diagram of the integration of Pt nanoparticles into MIL-101.Cited with permission from reference <sup>8</sup>.



**Figure S6** Proposed mechanism of the Cr(VI) photoreduction by CuPd@ZIF-8. Cited with permission from reference <sup>9</sup>.



**Figure S7** Photocatalytic mechanism of MO degradation by TiO<sub>2</sub>@Cd-MOF@ZnPp heterogeneous photocatalysts. Cited with permission from reference <sup>10</sup>.

The key variables influencing the improvement of the photocatalytic activity of the TiO<sub>2</sub>@Cd-MOF@ZnPp photocatalyst are the synergistic impact of Zheterojunction construction, improved light absorption, and efficient electron injection. The HOMO and LUMO values of Zn(II) porphyrin (ZnPp) are -5.07 and -2.83 eV, respectively. The ZnPb energy gap is 2.24 eV due to the difference between the HOMO and LUMO stages. The band gap value of the TiO<sub>2</sub>@Cd-MOF nanocomposite aerogel is also predicted to be 2.9 eV based on the Tauc diagram. The excited energy levels of ZnPp and the CB levels of TiO<sub>2</sub>@Cd-MOF overlap nicely because the energy gap of ZnPp (2.24 eV) is less than that of TiO<sub>2</sub>@Cd-MOF (2.9 eV). When exposed to visible light, the electrons in TiO<sub>2</sub>@Cd-MOF VB are stimulated to CB and induce the same number of holes in VB. In the meantime, a return origin is quickly produced by photogenerated electrons that are quickly injected into TiO2@Cd-MOF CB through the heterojunction structure as a result of visible light absorption on the surface of ZnPp. These electrons are taken up by O2 that has been deposited on the catalyst's surface, creating a highly reactive species  $(\bullet O_2^-)$  that may oxidize MO molecules. Additionally, photoinduced holes on the VB of TiO<sub>2</sub>@Cd-MOF are transferred to the VB of ZnPp to create oxidation sites. This causes an interaction with water to create (•OH), and the

last step results in the deterioration of MO. Charge separation is made possible by the potential difference between the matching energy levels of TiO<sub>2</sub>@Cd-MOF and ZnPp. Due to their heterogeneous structure, PTAC samples exhibit better photocatalytic efficiency than TAG and TAC samples.

The main reasons for the increased photocatalytic activity, as opposed to the loading of nanometallic particles, are the synergistic effect, enhanced light absorption, and effective electron injection due to the Z-type heterojunction structure created by the loading of TiO<sub>2</sub> and Zn(II) porphyrin (ZnPp). ZnPp has energy gaps of 2.24 eV between its HOMO and LUMO levels, which are -5.07 and -2.83 eV, respectively.

The band gap value of TiO<sub>2</sub> at Cd-MOF and ZnPp is around 2.9 eV, as seen by the Tauc figure. The energy gap of ZnPp (2.24 eV) is less than that of TiO<sub>2</sub>@Cd-MOF, therefore there is a good overlap between the excitation energy levels of ZnPp and the CB levels of that material (2.9 eV). When TiO<sub>2</sub>@Cd-MOF is exposed to visible light, the electrons in the VB are energised to travel to the CB and leave an equal number of holes behind. Photogenerated electrons swiftly enter the CB of TiO<sub>2</sub>@Cd-MOF through the heterojunction structure as they are created by the absorption of visible light on the ZnPp surface. These electrons are taken up by the O<sub>2</sub> adsorbed on the catalyst surface, which produces a highly reactive species that may oxidise MO molecules(•O<sup>2-</sup>). Additionally, photo-induced holes on the TiO<sub>2</sub>@Cd-MOF VB of ZnPp are transferred to the VB of TiO<sub>2</sub>@Cd-MOF to establish oxidation sites, which in turn cause a reaction with H<sub>2</sub>O to produce (•OH) and the last stage of MO degradation.



**Figure S8** (A) Mechanism of photocatalytic degradation of MB by PDA@MOF photocatalyst under LED visible light irradiation. (B) Schematic diagram of water splitting by PDA@MOF. (C) IPCE (%) results compared with Ag/AgCl electrodes under or without light. (D) corresponding ABPE (%) results under or without light. (E) PL spectra of PDA@MOF, photocurrent reaction of PDA@MOF nanostructures with and without  $H_2O_2$ . Cited with permission from reference <sup>11</sup>.



**Figure S9** Mechanism of the photocatalytic reduction of Cr(VI) and degradation of BPA by MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub>. Cited with permission from reference <sup>12</sup>.

Feiping Zhao et al.<sup>12</sup> created a MIL-101(Fe)/g-  $C_3N_4$  heterojunction on the surface of g- $C_3N_4$  to synthsise a MIL-101(Fe)/g-  $C_3N_4$  photocatalyst. When the heterojunction was used as a bifunctional photocatalyst for the simultaneous reduction of Cr(VI) and degradation of bisphenol A (BPA) under visible light, the photocatalytic performance was significantly improved. The greater activity is due to the improved light absorption and effective charge carrier separation made possible by the formation of direct Z-type heterojunctions between MIL-101 (Fe) and g- $C_3N_4$  with the appropriate band alignment. The use of electron spin resonance and radical trapping demonstrated that light-generated electrons were responsible for oxygen-induced Cr(VI) reduction and BPA degradation.

Higher  $O_2$  concentrations are essential for the photocatalytic degradation of BPA on MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub>. As was already mentioned, the ESR and  $O_2$  concentration tests demonstrate that a typical oxygen-induced radical route includes photocatalytic oxidation of water contaminants. Other reduction processes, such as the reduction of Cr, can employ the concurrently created electrons (VI). The presence of OH<sup>-</sup>, on the other hand, indicates that the photocatalytic heterojunctions system successfully produces hole h<sup>+</sup>. Both aqueous contaminants can be treated simultaneously by separating electron-hole pairs using visible light-induced stimulation. Charge transfer at the interface stage might happen via a straight Z-scheme method or a dual transfer mechanism. ESR studies show that the CB of g-C<sub>3</sub>N<sub>4</sub> and the VB of MIL-101(Fe) both contain photogenerated electrons and holes.

The typical dual transfer method is not used for the charge transfer. However, a direct Z-scheme mechanism best explains the improved photocatalytic reduction of Cr(VI) in MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub>. Figure S9 depicts the band structure diagram and charge transport roadmap of the MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub> heterojunction based on ESR

measurements and band alignment. As a result of their respective band alignments, MIL-101(Fe) and g-C<sub>3</sub>N<sub>4</sub> form a direct Z-scheme heterojunction. Photogenerated electrons in the CB of MIL-101(Fe) and photogenerated holes in the VB of g-C<sub>3</sub>N<sub>4</sub> combine again in such a system, but photogenerated electrons in the CB of g-C<sub>3</sub>N<sub>4</sub> with strong reduction capabilities are ready to reduce Cr(VI) to Cr(III), whereas photogenerated holes in the VB of MIL-101(Fe) with strong oxidizing abilities can promote the oxidation of water pollutants. Each semiconductor's charge recombination is significantly reduced by the aforementioned direct Z-type process, producing exceptional photocatalytic performance. As a result, the photocatalytic activity of MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub> heterojunctions for simultaneous Cr(VI) reduction and BPA oxidation is enhanced due to the excellent separation of photo-induced e<sup>-</sup> and h<sup>+</sup> couples.



**Figure S10** 3D framework of In-MOF along the c (a) and b (b) axes. (c and d) Cited with permission from reference <sup>13</sup>.



**Figure S11** Schematic diagram of the process of loading MOC-16 into ZIF-8. Cited with permission from reference <sup>14</sup>.



**Figure S12** Diagram of mechanism of photocatalytic hydrogen production from water splitting by EY-sensitized S-g-C<sub>3</sub>N<sub>4</sub>/CoS. Cited with permission from reference <sup>15</sup>.



**Figure S13** (a) EIS response of  $TiO_2$ ,  $MoS_2$  and  $MoS_2@TiO_2$  (b) Mechanism of H<sub>2</sub> production by photocatalytic water splitting under visible light (c) Photodegradation plots of Fl monitored by UV-Vis absorption spectra (d) Photodegradation plots of Fl monitored by UV-Vis absorption spectra for system containing  $MoS_2@TiO_2$  (5.0 mg), Fl (5.0 mg), TEOA (7.5% v/v). Cited with permission from reference <sup>16</sup>.

Bing Ma et al.<sup>16</sup> synthesized a  $MoS_2@TiO_2$  nanobridge using hydrothermal method at the expense of MOF precursor. When the optimal ratio of  $MoS_2$  was 14.6 wt%, the obtained materials showed outstanding photocatalytic activity in water splitting. With fluorescein acting as the photosensitizer and visible light irradiation, the hydrogen generation rate reached 10046 µmol/g·h. The creation of a high number of active sites on the surface as a result of the uniform dispersion and strong binding of  $MoS_2$  and TiO<sub>2</sub> was primarily responsible for the increased catalytic performance.

Ma later presented the evolution mechanism of MOF-driven  $MoS_2@TiO_2$ photocatalytic hydrogen. It's likely that visible light first excites the ground state of FI to create an excited state of FI\*, which is subsequently reduced and quenched by the electron donor (TEOA) or oxidised by the acceptor in the photocatalytic process (MoS<sub>2</sub> at TiO<sub>2</sub>). TEOA and MoS<sub>2</sub>@TiO<sub>2</sub> were present while measuring the luminous emission of Fl. The apparent rate constant (kq) of MoS<sub>2</sub> at TiO<sub>2</sub> oxidation quenching is calculated by linearly fitting the Stern-Volmer diagram and is  $6.23 \times 10^6$  M<sup>-1</sup>s<sup>-1</sup>. The kq generated by reducing quenching TEOA is  $5.43 \times 10^8$  M<sup>-1</sup>s<sup>-1</sup>, which is over two orders of magnitude larger than that generated by oxidation quenching. According to these findings, there is a considerably larger probability of a reductively quenched route for TEOA in systems with Fl/MoS<sub>2</sub>@TiO<sub>2</sub>/TEOA than there is in systems with MoS<sub>2</sub>@TiO<sub>2</sub>, which allows electrons to go from TEOA to Fl\* and subsequently create that the excited state lifetime is 11.53 ns in the presence of MoS<sub>2</sub> at TiO<sub>2</sub> and decays to 10.23 ns before falling to 4.01 ns, provide additional evidence for the aforementioned mechanism.

What's more, electrons can go from Fl<sup>-</sup> to the TiO<sub>2</sub> conduction band in  $MoS_2@TiO_2$  because Fl<sup>-</sup> has a greater negative oxidation potential. In order to stimulate H<sub>2</sub> evolution, the doped MoS<sub>2</sub> can function as an electron sink, absorbing electrons from TiO<sub>2</sub>. The TiO<sub>2</sub> emission peak is visible in the PL emission spectrum at 365 nm, and emission strength steadily drops when MoS<sub>2</sub> load is increased, suggesting that MoS<sub>2</sub> may absorb electrons from the TiO<sub>2</sub> conduction band. MoS<sub>2</sub> and TiO<sub>2</sub> are closely in touch and evenly distributed inside the mixed catalyst, which is particularly advantageous for electron transport and subsequent hydrogen synthesis. Additionally, MoS<sub>2</sub> can offer active sites to promote the evolution of hydrogen because of its quantum sealing effect. EIS measurements studied at the catalyst's conductivity in further detail. According to Figure S13(a), the doped MoS<sub>2</sub>@TiO<sub>2</sub> nano mixture exhibits a lower impedance when compared to ordinary TiO<sub>2</sub> and MoS<sub>2</sub>.

## References

1. Fang, H. *et al.* Ppb-level H<sub>2</sub>S gas sensor based on CuNi-MOFs derivatives for meat freshness detection at low temperature environment. *Sens. Actuators B Chem.* **368**, 132225 (2022).

2. Lee, M. *et al.* Pilot-Scale Testing of UV-A Light Treatment for Mitigation of NH<sub>3</sub>,H<sub>2</sub>S, GHGs, VOCs, Odor, and O<sub>3</sub> Inside the Poultry Barn. *Front. Chem.* **8**, (2020).

3. Subudhi, S. & Parida, K. Zr-based MOF: An enhanced photocatalytic application towards H<sub>2</sub> evolution by consequence of functional group and LSPR effect. *Mater. Today Proc.* **35**, 198–202 (2021).

4. Brongersma, M. L., Halas, N. J. & Nordlander, P. Plasmon-induced hot carrier science and technology. *Nat. Nanotechnol.* **10**, 25–34 (2015).

5. Constructing Fe-MOF-Derived Z-Scheme Photocatalysts with Enhanced Charge Transport: Nanointerface and Carbon Sheath Synergistic Effect | ACS Applied Materials & Interfaces. https://pubs.acs.org/doi/abs/10.1021/acsami.0c06601.

6. Liu, S., Jiang, X., Waterhouse, G. I. N., Zhang, Z.-M. & Yu, L. Construction of Z scheme Titanium-MOF/plasmonic silver nanoparticle/NiFe layered double hydroxide photocatalysts with enhanced dye and antibiotic degradation activity under visible light. *Sep. Purif. Technol.* **278**, 119525 (2021).

7. Zhu, Q. *et al.* CO<sub>2</sub> reduction to formic acid via NH<sub>2</sub>-C@Cu<sub>2</sub>O photocatalyst in situ derived from amino modified Cu-MOF. *J. CO2 Util.* **54**, 101781 (2021).

8. Yadav, M. & Xu, Q. Catalytic chromium reduction using formic acid and metal nanoparticles immobilized in a metal–organic framework. *Chem. Commun.* **49**, 3327 3329 (2013).

 Zhang, Y. & Park, S.-J. Stabilization of dispersed CuPd bimetallic alloy nanoparticles on ZIF-8 for photoreduction of Cr(VI) in aqueous solution. *Chem. Eng. J.* 369, 353–362 (2019).

10. Ramasubbu, V. *et al.* Zn(II) porphyrin sensitized (TiO<sub>2</sub>@Cd-MOF) nanocomposite

aerogel as novel photocatalyst for the effective degradation of methyl orange (MO) dye. *Opt. Mater.* 112558 (2022) doi:10.1016/j.optmat.2022.112558.

11. Celebi, N., Aydin, M. Y., Soysal, F., Yıldız, N. & Salimi, K. Core/Shell
PDA@UiO-66 Metal–Organic Framework Nanoparticles for Efficient Visible-Light
Photodegradation of Organic Dyes. *ACS Appl. Nano Mater.* 3, 11543–11554 (2020).
12. MIL-101(Fe)/g-C<sub>3</sub>N<sub>4</sub> for enhanced visible-light-driven photocatalysis toward
simultaneous reduction of Cr(VI) and oxidation of bisphenol A in aqueous media

ScienceDirect.https://www.sciencedirect.com/science/article/pii/S0926337320304483.

13. Lu, C. *et al.* Indium-Based Metal–Organic Framework for Efficient Photocatalytic Hydrogen Evolution. *Inorg. Chem.* **61**, 2587–2594 (2022).

14. Luo, Y.-C. et al. Heterogenization of Photochemical Molecular Devices:

Embedding a Metal–Organic Cage into a ZIF-8-Derived Matrix To Promote Proton and Electron Transfer. *J. Am. Chem. Soc.* **141**, 13057–13065 (2019).

15. Fan, Z., Guo, X., Jin, Z., Li, X. & Li, Y. Bridging Effect of S–C Bond for Boosting Electron Transfer over Cubic Hollow CoS/g-C3N4 Heterojunction toward

Photocatalytic Hydrogen Production. Langmuir 38, 3244-3256 (2022).

16. MOF-Derived Flower-like MoS<sub>2</sub>@TiO<sub>2</sub> Nanohybrids with Enhanced Activity for

Hydrogen Evolution | ACS Applied Materials & Interfaces.

https://pubs.acs.org/doi/10.1021/acsami.6b08740.