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# In-situ self-assembly of Zirconium metal–organic<sup>DOI: 10.1039/C9TA14005K</sup> framework onto ultrathin carbon nitride for enhanced visible-light-driven conversion of CO<sub>2</sub> to CO

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#### Abstract

A series of Zr-porphyrinic metal organic frameworks (Zr-PMOFs)/ultrathin g-C<sub>3</sub>N<sub>4</sub> (UCN) heterostructure photocatalysts (ZPUCN), as stable and efficient catalysts for photoreduction CO<sub>2</sub>, are fabricated via a facile in situ hydrothermal self-assembly method. The interface interaction is formed by hollow Zr-PMOFs nanotubes being surrounded by 3D ultrathin g- $C_3N_4$  (UCN) and the covalent link due to the ultrathin and conjugated  $\pi$  structure of UCN, unsaturated metal atoms and organic ligands of Zr-PMOFs. The interaction provides a platform for UCN as a conductor to transfer e- or donor to transferring e- to Zr-O cluster active sites to catalyze CO<sub>2</sub>, substantially achieving the spatial separation of charge carries, suppressing the photogenerated electron-hole (e<sup>-</sup>-h<sup>+</sup>) pairs recombination rate. Benefitting from the cooperative effects of well-designed nanostructure and chemical grafting, in the absence of triethanolamine, cocatalysts and photosensitizers, the optimized ZPUCN hybrid not only exhibits a better CO evolution yield (5.05  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup>), which is 2.2 times and 3.2 times higher than that of pure Zr-PMOFs and UCN, but also display an excellent stability after 96 h photocatalysis. Mechanism information is also elucidated from selected characterizations.

Keywords: photocatalysis, CO<sub>2</sub> reduction, heterojunction, Porphyrin metal organic

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#### 1. Introduction

Greenhouse gases, carbon dioxide (CO<sub>2</sub>) levels have been increasing steadily over the past century with the combustion fossil fuels and activities expansion of humankind <sup>1-3</sup>. Along with the process of global industrialization, the global warming and the limited fossil fuels are unavoidable problems that people have to face. One promising and sustainable strategy to effectively and simultaneously solve these two environmental pollution and energy crisis problems is a chemical conversion CO<sub>2</sub> to valuable chemical fuels through photo catalytic CO<sub>2</sub> reduction by inexhaustible solar energy <sup>4</sup>. However, artificial photoreduction CO<sub>2</sub> is still challenging due to the grand kinetic and thermodynamic barrier of CO<sub>2</sub> and the sluggish reaction kinetics for producing solar fuels <sup>2</sup>. The development of highly effective photocatalysts is a key to boost the photoreduction process. Since the first investigation on TiO<sub>2</sub> for CO<sub>2</sub> photoreduction, lots of inorganic semiconductor photocatalysts have been explored and studied. Most reductive inorganic semiconductors including TiO<sub>2</sub> <sup>5</sup>, WO<sub>3</sub> <sup>6</sup>, ZnO <sup>7</sup>, Zn<sub>2</sub>GeO<sub>4</sub><sup>8</sup>, are UV-light-responsive ones, which restricts the utilization of solar energy for photocatalytic process.

Metal-organic frameworks (MOFs), as a new family of photocatalytic materials, has exhibited outstanding catalytic performance due to their porous framework structures, easy-manipulative functionalization, high designability and high surface area <sup>9</sup>. Extensive reports have studied that MOFs are excellent materials to photo-reduce CO<sub>2</sub>, such as UiO-based MOFs <sup>10</sup>, MIL-based MOFs <sup>11</sup> and PCN-based MOFs <sup>12, 13</sup>. Among them, Porphyrin metal organic frameworks (PMOFs), as a member of PCN-based MOFs, are a kind of porous coordination materials with (metallo) porphyrin-based linkers interconnected by metal ions or metal carboxylate cluster secondary building units. (metallo) porphyrin and their derivatives are well known for working on many biological functions, especially, light harvesting. Thus, some issues in photocatalytic process (e.g., light harvesting) could be solved by using (metallo) porphyrins as MOFs linkers <sup>14-16</sup>. However, the photocatalytic efficiency of pure

PMOFs is still unsatisfactory generally due to the fast combination of photoexeitee electron-hole (e<sup>-</sup>-h<sup>+</sup>) pair, which is related to the energy-level alignment flaws and asymmetry. Tremendous efforts have been devoted to boost the migration rate, such as doping <sup>17</sup>, tuning morphology <sup>18</sup>, coupling with other semiconductors <sup>1, 19</sup>. Among them, constructing a heterojunction is one of the most effective strategy to address e<sup>-</sup>-h<sup>+</sup> recombination in the recent years <sup>20</sup>. Especially, effective spatial separation of the charge carriers can be achieved when two semiconductors have suitable energy levels, consequently, suppressing the bulk and surface recombination<sup>21</sup>. For instance, Zheng synthesized 0D/2D carbon nitride quantum dots /porphyrin MOF for increasing photocatalytic CO<sub>2</sub> reduction, Ye et al. developed UiO-66/2D g-C<sub>3</sub>N<sub>4</sub> nanosheet heterostructures for  $CO_2$  photoreduction <sup>22</sup>. Xiong et al designed g- $C_3N_4$ nanotubes/ZIF-8 composite to enhance CO2 conversion efficiency <sup>23</sup>. However, examples of PMOFs-based heterojunction photocatalysts for CO2 reduction are insufficient. Graphitic carbon nitride  $(g-C_3N_4)$  have triggered great attentions in diverse field due to its nontoxicity, high stability and cheap <sup>24, 25</sup>. Notably, the suitable structure (bandgap Eg=2.7 eV, energy potential of the conduction band  $E_{CB}$  =-1.3 eV (versus NHE) makes it an important player in the field of photocatalysis (CO<sub>2</sub> photoreduction and hydrogen generation) <sup>23, 26</sup>. In addition, g-C<sub>3</sub>N<sub>4</sub> with pliable framework can effortlessly anchor or enclose on another materials, as a result, constructing the intimate contacted interface <sup>27</sup>. More importantly, as a metal free conjugated polymer semiconductor, the purely organic nature of  $g-C_3N_4$  plays a key strength to couple with MOFs.

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Herein, ultrathin 3D g-C<sub>3</sub>N<sub>4</sub> was implemented to decorate hollow Zr-PMOFs nanotubes to build a novel hybrid photocatalyst (ZPUCN-x, x is the actual mass of the addition of UCN) under mild reaction conditions to cooperatively convert CO<sub>2</sub> conversion. This work aims to make full use of the complementary features of Zr-PMOFs and g-C<sub>3</sub>N<sub>4</sub> to achieve the spatial separation of charge carries, suppressing the photogenerated electron-hole (e<sup>-</sup>-h<sup>+</sup>) pairs recombination rate. Benefitting from the cooperative effects of well-designed nanostructure and chemical grafting, the optimized ZPUCN heterojunctions boost charge transport and light-harvesting, and therefore presenting a high photocatalytic CO<sub>2</sub> reduction efficiency. 3D ultrathin g-C<sub>3</sub>N $_{\rm P}$ (UCN)/C9TA14005K exhibits superiority compared with the bulk g-C<sub>3</sub>N<sub>4</sub> (BCN) fabricated by melamine. Based on calculated energy band positions, the plausible enhanced mechanism for the Zr-PMOFs/UCN composite was also proposed in detail.

#### 2. Results and discussion

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#### 2.1. Structure and morphology

The XRD patterns of UCN, Zr-PMOFs and ZPUCN composites are shown in Fig. 1. The typical peak of UCN at 27.4 indexed to (002) plane is detected corresponding to the typical stacked graphite-like structure (JCPDS No. 87-1526). For comparison, the XRD pattern of bulk carbon nitride (BCN) was characterized. As shown in Figure 1a, there are two typical peaks around at 13.1° (100) and 27.6° (002) for BCN. The negative shift of (002) peak over UCN compared with that of the BCN is due to the loosely layered structure <sup>28</sup>. In addition, less prominent and broader typical peaks are relative to the smaller length of interlayer periodicity, meaning UCN possess a smaller interlayer periodicity and a larger layered spacing <sup>29</sup>. SEM was carried to further make the contrast of the pure BCN and UCN (Figure S3a and S3b). Unlike the tightly stacked bulk BCN, UCN exhibits an ultrathin and loose stacked nanoflakes, which enhances the specific surface area, and provides abundant active sites for anchoring other materials and surface redox reactions. The consistent XRD pattern of Zr-PMOFs with those reported previously <sup>12</sup> indicates Zr-PMOFs has been successfully synthesized. For the ZPUCN-x composites, the in situ grafting of Zr-PMOFs on UCN has no obvious effect on the crystal structure. The characteristic peaks of Zr-PMOFs are remained for all ZPUCN hybrids, except for slight differences on the peak intensity, indicating that more UCN has been introduced into the ZPUCN-x composites. The unique peaks of UCN were not found obviously due to the relatively low peak intensity or/and low content.



Figure 1. XRD patterns of (a) Zr-PMOFs and ZPUCN-x, (b) UCN and BCN.

#### 2.2. Photocatalytic activity

Photocatalytic CO<sub>2</sub> reduction studies was implemented in a customized glass system without any cocatalysts or electron donors under visible light. CO was detected as the only gas product as shown in Figure 2a. Bare BCN or UCN is not active to reduce  $CO_2$  under this system, the CO evolution rates are only 0.30 µmol h<sup>-1</sup> g<sup>-1</sup> and 1.59 µmol  $h^{-1}$  g<sup>-1</sup> respectively. Besides, there are traces of CH<sub>4</sub> (0.19 µmol  $h^{-1}$  g<sup>-1</sup>) in UCN (Figure S4). The Zr-PMOFs showed moderate  $CO_2$  reduction with CO evolving rates of 2.32 umol h<sup>-1</sup> g<sup>-1</sup>. However, the ZPUCN-x heterojunctions photocatalysts show enhanced CO<sub>2</sub> photoreduction performance. Strikingly, ZPUCN-3 manifested higher CO<sub>2</sub>-to-CO conversion rate of 5.05 µmol h<sup>-1</sup> g<sup>-1</sup> even in the absence of any sacrificial agent, cocatalyst and photosensitizer, which is about 3.2 times and 2.2 times higher than that of pure UCN and Zr-PMOFs. Meanwhile, ZPUCN-3 hybrids also present durable photoreduction CO<sub>2</sub> performance during consecutive photoreaction for 96 h (Figure S4), providing an accumulated CO yield of ca.  $4.89 \times 10^2$  µmol g<sup>-1</sup>. The remarkable CO<sub>2</sub> reduction performance of ZPUCN-x should be related to the unique heterostructures for accelerating the separation and transfer of photoinduced carriers. To exclude the possibility that carbon source of CO is from acetonitrile or ZPUCN-x photocatalyst, a blank experiment was carried out in the presence of N2 instead of CO2 under the same other conditions, no CO product was detected, demonstrating that C species of CO originates from CO<sub>2</sub>. The potential products generated in the liquid phase was detected by another gas chromatography equipped by headspace sample injector and GC-MS.

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However, no HCHO, CH<sub>3</sub>OH and HCOOH were detected in the obtained diquid 9/C9TA14005KGenerally, the products of the photoreduction of CO<sub>2</sub> are HCOOH, CO, HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub>, the reduction potentials are -0.67 V, -0.52 V, -0.49 V, -0.40 V and -0.25 V, respectively <sup>30</sup>. However, only CO is detected in the present work, indicating good photocatalytic selectivity, which may be due to the following reasons. (i) The photoreduction of CO<sub>2</sub> tends to undergo proton-coupled electron transfer. But the amount of H<sub>2</sub>O is too low to favor hydrogenation reaction under this experimental condition. (ii) the reduction of CO<sub>2</sub> to CO needs 2 protons, while 4, 6 and 8 electrons are required to reduce it to HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub>. (iii) Reduction potentials for the formation of CO is moderate. In addition, the cyclic stability of CO evolution on ZPUCN-3.0 hybrid structures was test. As shown in Figure S5, the CO yield has no obvious decline after five photoreduction cycles. Furthermore, Figure S6 displays that no obvious changes in the crystal structure could be observed in XRD patterns of fresh and used ZPUCN-3.0.



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**Figure 2.** (a) CO<sub>2</sub> photoreduction activities of different samples. (b) Time-yield plots of products.

The SEM images of pure UCN reveals the 3D ultrathin structure composed by the cross-linked wrinkling or rolling nanoscale crystal layers (Figure 3a, b). Uniform Zr-PMOFs prisms are prepared by a solvothermal reaction. Figure 3c shows the average diameter and length of the Zr-PMOFs prisms are about 200 nm and 400 nm, respectively. The magnified image presents the Zr-PMOFs are composed of well-organized assembled ultrathin nanosheets (Figure 3d). By visualizing the morphology



**Figure 3.** Typical SEM images of (a, b) UCN, (c, d) Zr-PMOFs and (e, f) ZPUCN-3 composites.

of the ZPUCN-3 composites (Figure 3e, f), Zr-PMOFs prisms are surrounded by hierarchical UCN. No freestanding Zr-PMOFs prisms are observed, which indicates that the growth of Zr-PMOFs prisms are exactly confined to the surface of UCN, resulting in the formation of heterostructure interface. For comparison, the Zr-PMOFs/BCN (ZPBCN) composite was prepared in a similar way expect that UCN was used instead BCN shown in Figure S7. By contrast the SEM images, Zr-PMOFs are evenly dispersed and are preferred to enclose on the surface of UCN because of the loose lamellar structure, resulting to strong interaction between Zr-PMOFs and UCN.

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Overall, the SEM information verifies the formation of heterojunctions and suggests ap/C9TA14005K

interfacial interaction between Zr-PMOFs and UCN. To further prove to the observation interaction, XPS was measured as shown in Figure 4. The main elements are C1s and N1s for pure UCN, and C1s, N1s, O1s, Zr3d for Zr-PMOFs (Figure 4a). The XPS survey spectrum of ZPUCN-3.0 shows all of the above elements. With respect to Zr 3d of Zr-PMOFs (Figure 4b), two characterized peaks at 184.75 eV and 182.43 eV were corresponded to Zr 3d3/2 and Zr 3d5/2, respectively, verifying the presence of Zr4+ ions. By contrast, the Zr 3d binding energy of ZPUCN-3.0 had a negative shift to 184.45 eV and 182.14 eV, indicating the existence of interaction between UCN and Zr-PMOFs.



**Figure 4.** (a) XPS survey spectra of UCN, Zr-PMOFs and ZPUCN-3.0, (b) High resolution XPS spectra of Zr 3d of Zr-PMOFs and ZPUCN-3.0.

#### 2.3. Optical and electronical properties

The UV-vis diffuse reflectance spectroscopy (DRS) was carried out to obtain the optical information <sup>31</sup>. To great extent. the electronic structure of  $g-C_3N_4$  could be tuned by the design of nanostructure. Accordingly, the adsorption edge of UCN has a significant red shift from ~450nm (BCN) to ~650 nm, which mainly is due to nanoscale effects <sup>32</sup>. Furthermore, compared with BCN, the longer tail absorption from 550 nm to 800 nm is observed for UCN, which should be resulted from the abundant defects in UCN. Zr-PMOFs can efficiently harvest visible light due to the H<sub>2</sub>TCPP ligand as a visible light absorption unit shown in Figure 5. After UCN incorporation, a slight reduction in the light harvesting capacity is observed for ZPUCN-x versus Zr-PMOFs,

which should be related to the surface coating of UCN. However, importantly, itt is //C9TA14005K verified ultrathin porous layer could be integrated on Zr-PMOFs without weaken light absorption ability by in-situ synthesis.



Figure 5. UV-vis diffuse reflectance for as-synthesized pure BCN, UCN, Zr-PMOFs and ZPUCN-x.

Generally, the separation efficiency of photogenerated charge is a critical factor affecting photocatalytic activities. Photoelectrochemical measurements were carried out to further study the interface separation and migration properties of photoinduced charge carriers. As shown in Figure 6a, the ZPUCN-x heterojunctions show enhanced photocurrent intensity to different extent compared with pure UCN and Zr-PMOFs during switching on visible light. The high photocurrent response of ZPUCN-x heterojunctions should be owing to the lower recombination rate of the photoinduced  $e^{-}h^{+}$  pairs in the hybrid structures. Electrochemical impedance spectroscopy (EIS) is also an efficient way to characterize the interfacial charge transfer, in which there is a strong negative correlation between the radius of EIS curve and the charge transfer rate. As presented in Figure 6b, the EIS Nyquist plots of the ZPUCN-x composites show smaller radius than that of pure UCN and Zr-PMOFs. A smaller resistance leads to a better conductivity and was favorable for the transmission of photogenerated electron. Note that, the smallest radius from ZPUCN-3.0 hybrids is in accord with the result of the photocurrent test and CO<sub>2</sub> photoreduction performance. The current-time curve of ZPUCN-3.0 composites is exhibited in Figure S8 under continuous light illumination. The current density of ZPUCN-3.0 can remain unchanged after 3600s, suggesting a

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well photoelectrochemical stability of ZPUCN-3 in accord with the results of  $CO_2$  photoreduction.



**Figure 6.** (a) Transient photocurrent response, (b) the EIS Nyquist plots of the BCN, UCN, Zr-PMOFs and ZPUCN-x.

In addition, the photoluminescence (PL) emission spectra was measured to further investigate the lifetime of photogenerated charge carriers. As shown in Figure 7, the photoluminescence of ZPUCN-3.0 quenched obviously compared with Zr-PMOFs, indicating that the photoinduced charge recombination rate occurring in the hybrids has been greatly inhibited <sup>29, 33</sup>. The efficient charge migration should be ascribed to the benefits of ZPUCN-3.0 heterojunction structure, since two-step excitation and charge separation processes occur in the coupled system, in which the photogenerated e<sup>-</sup> and h<sup>+</sup> migrate to two materials in opposite directions and achieve e<sup>-</sup>-h<sup>+</sup> spatial separation <sup>34</sup>. Hence, ZPUCN-3.0 enable provide long-lifetime e<sup>-</sup> for the CO<sub>2</sub> photoreduction with a higher performance than that of pure Zr-PMOFs. This result also shows good agreement with the photoelectrochemical measurements discussed above.



View Article Online Figure 7. Photoluminescence spectra of Zr-PMOFs and ZPUCN-3.

A potential CO<sub>2</sub> photocatalytic mechanism for the ZPUCN-x system was proposed in Figure 8. The CO<sub>2</sub> photoreduction test as the base of the mechanism information the photogenerated charge transfer between the interfacial phase mainly follow the typical heterojunction mechanism under visible light irradiation. Benefiting from the ultrathin and conjugated  $\pi$  structure of UCN, unsaturated metal atoms and organic ligands of Zr-PMOFs can be covalently linked to organic g-C<sub>3</sub>N<sub>4</sub>, leading an interfacial interaction. The interfacial interaction provides a platform for UCN as a conductor to transfer e<sup>-</sup> from ligands, or transferring e<sup>-</sup> to Zr-O cluster active sites to catalyze CO<sub>2</sub>. Since the Zr-PMOFs are capable of the high CO<sub>2</sub> uptake, subsequently, the enriched electrons would interact with the enrichment of CO<sub>2</sub> on Zr-PMOFs, facilitating the photocatalytic efficiency. Moreover, more negative CB of UCN compared with Zr-PMOFs (Figure S9) drives the transportation of e<sup>-</sup>. As a result, the electron re-localization suppressed the recombination rates of photoexcited charge carriers in both UCN and Zr-PMOFs, which is in accordance with photo-electrochemistry and PL results. In addition, as e<sup>-</sup> donators, the photoinduced e<sup>-</sup> generated on the UCN would also react with CO<sub>2</sub> directly.



**Figure 8.** Schematic illustration for the enhanced CO<sub>2</sub> photoreduction performance of the coupled of UCN and Zr-PMOFs under visible light irradiation. **Conclusions** 

It is demonstrated that a series of ZPUCN-x hybrid structure were synthesizes by a facile in-situ solvothermal method, in which the Zr-PMOFs nanotubes are surrounded by 3D ultrathin g-C<sub>3</sub>N<sub>4</sub>. Benefiting from the ultrathin and conjugated  $\pi$  structure 100/C9TA14005K

UCN, unsaturated metal atoms and organic ligands of Zr-PMOFs can be covalently linked to organic g-C<sub>3</sub>N<sub>4</sub>. The interfacial interaction provides a platform for UCN transferring e- to Zr-O cluster or as a conductor to transfer e<sup>-</sup>, thus the separation and migration efficiency of photoexcited charge carriers on ZPUCN-x hybridization are facilitated. In addition, mention that in the absence of triethanolamine, cocatalysts and photosensitizers, the optimized ZPUCN-3.0 composites exhibit a CO<sub>2</sub> to CO rate of  $5.05 \,\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ , which is roughly 3.2 times and 2.2 times higher than that of the pure UCN and Zr-PMOFs. Of importance is to note that the photocatalytic activity of ZPUCN-3.0 composites has negligible decrease after 96 h photocatalysis, possessing great prospect for implementing highly efficient solar fuel conversion.

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