Efficient Photocatalytic Reduction of CO₂ Catalyzed by the Metal–Organic Framework MFM-300(Ga)

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Photocatalytic reduction of CO₂ to carbon fuels is an important target but highly challenging to achieve. Here, we report the efficient photoconversion of CO₂ into formic acid over a Ga(III)-based metal–organic framework (MOF) material using triethanolamine as the sacrificial agent. Under light irradiation and at room temperature, photoreduction of CO₂ over MFM-300(Ga) yields formic acid with a selectivity of 100%, a high productivity of 502±18 μmol·gcat⁻¹·h⁻¹, and excellent catalytic stability. In situ electron paramagnetic resonance spectroscopy reveals that MFM-300(Ga) promotes the generation of CO₂⁻⁻ radical anions as a reaction intermediate driven by strong binding and activation of CO₂ molecules at the bridging –OH sites within the pore. This study represents the first example of a Ga(III)-based MOF catalyst for CO₂ reduction.

Introduction

The development of efficient photocatalysts to convert CO₂ into value-added chemicals has attracted much interest. In addition to TiO₂, various Ga-based semiconductors, such as GaN, GaP, Ga₂O₃, and ZnGa₂O₄, have been widely investigated as photocatalysts to drive this reaction. However, their wide optical bandgap (Eg) restricts the use of solar light mainly to the ultraviolet region, and, more importantly, their nonporous nature limits the mass transport of CO₂. This impedes charge transfer between catalyst and substrate and also leads to the undesirable recombination of photogenerated electrons and holes. A number of strategies have been exploited to improve the photocatalytic performance of Ga-based semiconductors. For example, doping of metals (e.g., Ge, Zn) or nonmetals (e.g., N, Si) can narrow the bandgap and improve the light-harvesting efficiency...
Fabrication of ultrathin nanosheets, nanowires, or porous structures can increase the surface area and CO₂ uptake. Meanwhile, the introduction of a cocatalyst, noble metal nanoparticles, or a second semiconductor to construct Z-scheme or heterojunction-type systems can promote electron transfer. However, the photocatalytic efficiency over state-of-the-art Ga-based semiconductors remains limited, and only gaseous products such as CH₄ and CO are produced. For example, a top-performing heterostructure of Au/Al₂O₃/p-GaN shows a photocatalytic productivity for CO of 230 μmol·g⁻¹·h⁻¹.

Metal–organic framework (MOF) materials incorporate active sites fixed uniformly in 3D space, thus preventing aggregation of catalytic centers and potentially enhancing charge separation. MOFs are therefore emerging as important photocatalysts for the reduction of CO₂, showing potential to overcome the barriers of conventional semiconductors. For example, the intrinsic microporosity and catalytically active sites confined in MOFs can form unique “microreactors” to promote the adsorption and activation of CO₂ via the formation of strong host-guest interactions. More importantly, the backbone of MOFs consisting of infinite metal-ligand linkages...

**Figure 1** Characterisation and crystal structure of MFM-300(Ga). (a) The UV-DRS spectrum of MFM-300(Ga) with Tauc plot (insert); (b) SEM image of MFM-300(Ga) with TEM image (insert); (c) high-resolution XPS spectrum of Ga 2p, and (d) ⁷¹Ga{¹H} D-HMQC 2D MAS NMR spectrum of MFM-300(Ga) and corresponding 1D direct excitation ⁷¹Ga (top) and ¹H (left) MAS NMR spectra, recorded at 20.0 T with a MAS frequency of 60 kHz; crystal structure of MFM-300 (Ga): (e) octahedral [GaO₄(OH)₂]; (f) ligand; (g and h) views of binding sites (bridging -OH groups) for adsorbed CO₂ molecules within MFM-300(Ga) studied by In situ synchrotron X-ray single-crystal diffraction. Host-guest hydrogen bonds and intermolecular dipole interactions are highlighted in cyan and yellow, respectively.

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can facilitate efficient ligand-to-metal-charge-transfer (LMCT), thus prolonging the excitation lifetime by boosting the isolation and utilisation of photoinduced electrons.\textsuperscript{22} A number of MOF systems have been tested for photoreduction of CO$_2$,\textsuperscript{18,20} and Ti-based MOFs are particularly attractive.\textsuperscript{32,34} In contrast, to date, no Ga-based MOF has been shown to exhibit activity for CO$_2$ conversion, and we report here the first example for the efficient photoreduction of CO$_2$. Under light irradiation and at room temperature, MFM-300(Ga) catalyzes the conversion of CO$_2$ into formic acid with a 100% selectivity and an excellent productivity up to 502 ± 18 μmol·g$_{\text{cat}}^{-1}$·h$^{-1}$, significantly higher than conventional Ga-based semiconductors and among the best-behaving MOF-based photocatalysts for this reaction. Importantly, in situ electron paramagnetic resonance (EPR) spectroscopy confirms that the CO$_2$ radical anion (CO$_2$$^-$) is generated as an intermediate to the production of formic acid over MFM-300(Ga).

Results and Discussion

MFM-300(Ga), [Ga$_2$(OH)$_2$(L)] (H$_4$L = biphenyl-3,3’5,5’-tetracarboxylic acid) was chosen for the photoreduction of CO$_2$ due to its high stability, high adsorption, and strong binding of CO$_2$ molecules via the formation of hydrogen bonds to the bridging –OH groups in the pore.\textsuperscript{25} MFM-300(Ga) is comprised of chains of [GaO$_4$(OH)$_2$]$_\infty$ octahedra linked by cis-$\mu_2$-OH groups, and these chains are further bridged by tetracarboxylate ligands to form a ‘wine rack’ open framework. Desolvated MFM-300(Ga) shows a Brunauer-Emmett-Teller (BET) surface area of 1064 m$^2$·g$^{-1}$ and an uptake of CO$_2$ of 5.00 mmol·g$^{-1}$ at 298 K and 1 bar (see Supporting Information Figure S1). The purity of the bulk material has been confirmed by powder X-ray diffraction (PXRD) (see Supporting Information Figure S2) and thermogravimetric analysis (see Supporting Information Figure S3a). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that crystals of MFM-300(Ga) exhibit cuboid-shaped morphology with an average size of 15 μm (Figure 1b). High-resolution X-ray photoelectron spectroscopy (XPS) analysis of MFM-300(Ga) shows the peaks of Ga 2p$_{1/2}$, 2p$_{3/2}$, 3d$_{x^2-y^2}$, and 3d$_{3z^2-r^2}$ at 1145.5, 1186.6, 21.2, and 20.7 eV, respectively, consistent with the trivalent Ga(III) (Figure 1c, see Supporting Information Figure S4). Solid-state $^{13}$C and $^{71}$Ga NMR spectroscopy reveal a highly ordered structure consistent with a single repeating octahedral [GaO$_4$(OH)$_2$]$_2$ environment (see Supporting Information Figure S5).\textsuperscript{26} The high-field $^7$Ga($^1$H) 2D through-space (dipolar) heteronuclear correlation NMR spectrum of MFM-300(Ga) demonstrates this more extensively with strong correlations between the Ga environment and the hydroxyls (at $\delta$(1H) = 2.8 ppm) and a weaker interaction with the more distant aromatic proton between the carboxylates (at $\delta$(1H) = 9.0 ppm), with no other correlations observed (Figure 1d). Moreover, the ratio of the $^1$H NMR signal intensities of the aromatic protons to the hydroxy protons is ~3:1 (see Supporting Information Figure S5c), entirely consistent with the structural model shown in Figures 1e–1h. Solid-state UV-vis diffuse reflectance spectroscopy (UV-DRS) of MFM-300(Ga) shows an intensive and broad absorption band in the ultraviolet region, which is assigned to the $\pi$$\rightarrow$$\pi^*$ transition of the biphenyl ligand (Figure 1a).\textsuperscript{27} The Tauc plot yields an optical bandgap of 3.30 eV, lower than that of commercial Ga$_2$O$_3$ ($E_g$ = 4.56, 4.70, and 4.67 eV for $\alpha$-, $\beta$-, and $\gamma$-Ga$_2$O$_3$, respectively)\textsuperscript{28} and ZnGa$_2$O$_4$ ($E_g$ = 4.18 eV).\textsuperscript{9} The photocurrent response of MFM-300(Ga) confirms that the current density increases upon irradiation and decreases upon turning off the light (see Supporting Information Figure S6).

![Figure 2](https://doi.org/10.31635/ccschem.022.202201931)

| Figure 2 | Photocatalytic CO$_2$ reduction over MFM-300(Ga). (a) Different reaction time; (b) recycling tests. Reaction conditions: MFM-300(Ga) (10 mg), TEOA/CH$_3$CN (3 mL/15 mL, saturated with CO$_2$), 25 ºC, 350–780 nm, light irradiation for 4 h.
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The photocatalytic activity of MFM-300(Ga) toward the reduction of CO$_2$ has been studied in CO$_2$-saturated CH$_3$CN-containing triethanolamine (TEOA) as the sacrificial agent under irradiation at 350–780 nm for 1–12 h. The gaseous products were analysed by gas chromatography and the liquid product by $^1$H NMR spectroscopy. The photocatalytic efficiency was measured as the moles of product obtained per gram of catalyst per hour (mol·g$_{\text{cat}}^{-1}$·h$^{-1}$) to afford a direct comparison with reported catalysts. Formic acid was the only product detected in the liquid phase, and no carbon-containing gaseous products were detected. The photocatalytic performance as a function of reaction time over MFM-300(Ga) indicates that a high productivity of 502 ± 18 μmol·g$_{\text{cat}}^{-1}$·h$^{-1}$ for formic acid was achieved at 4 h (Figures 2a, see Supporting Information Figure S7). More importantly, the photocatalytic activity and the crystallinity of MFM-300(Ga) were retained over three cycles of reaction (Figure 2b). The photocatalytic efficiency of MFM-300(Ga) is higher than the majority of reported MOFs (Table 1) for converting CO$_2$ into formic acid, such as amino-functionalised MIL-125(Ti), UiO-66(Zr), and MIL-101(Fe), and is only lower than two cases. One is the mixed metal and mixed ligand systems of NH$_2$-UiO-66(Zr/Ti) and (NH$_2$)$_2$-UiO-66(Zr/Ti), which are prepared via post-synthetic modifications to introduce Ti(IV) sites into the framework. The other is a recent report describing a π-conjugated naphthoporphyrin system constructed with Zr metal clusters, which demonstrates the highest value (6630 μmol·g$_{\text{cat}}^{-1}$·h$^{-1}$) reported in the literature. A comparison of state-of-the-art studies of thermal hydrogenation of CO$_2$ into formic acid over MOF-based catalysts is given in Supporting Information Table S1.

To gain further insights into this reaction, a series of control experiments were conducted (Table 2). No carbon-containing product was detected from reactions in the absence of (1) MFM-300(Ga), (2) CO$_2$ (where N$_2$ is used instead), or (3) light. These results confirm that the carbon source of formic acid is CO$_2$ and that the reaction proceeds via photocatalytic routes driven by the MOF catalyst. Replacement of TEOA with triethylamine (TEA) gives a low productivity of 64 μmol·g$_{\text{cat}}^{-1}$·h$^{-1}$ for formic acid, which is consistent with recent reports on the important role of TEOA in binding and assisting the transport of CO$_2$ in CH$_3$CN. A range of different organic solvents have been tested, and CH$_3$CN demonstrates the highest activity due to the optimal efficiency of mass transfer and the enhanced binding of CO$_2$ by TEOA in CH$_3$CN (see Supporting Information Figure S8). Interestingly, no product was observed when using Ga$_2$O$_3$ (~50 mesh, $E_g = 4.57$), GaN ($E_g = 3.04$), or a powdered mixture of Ga(NO$_3$)$_3$ and H$_2$L as the photocatalyst (see Supporting Information Figure S9). This indicates that the

Table 1: Comparison of the Photocatalytic Efficiency of MFM-300(Ga) and a Selection of MOFs Reported for this Reaction in the Literature

| MOF-Based Materials | Chemical Formula | CO$_2$ Uptake /mmol kg$^{-1}$ (atm) | Sacrificial Agent | Solvents | Photocatalytic Efficiency /μmol·g$_{\text{cat}}^{-1}$·h$^{-1}$ | References |
|---------------------|------------------|----------------------------------|-----------------|---------|-----------------------------|------------|
| TNP-MOF            | Zn$_6$(OH)$_2$(TMP)$_3$ | 1.69 (273 K) | TEOA | CH$_3$CN | 6630 | This work |
| NH$_2$-MIL-101(Fe)  | NH$_2$-MIL-88(Fe) | 1.52 (273 K) | TEOA and BNAH | CH$_3$CN | 1052 | 23 |
| NH$_2$-MIL-101(F)   | NH$_2$-MIL-88(F) | 1.48 (273 K) | TEOA | CH$_3$CN | 782 | 31 |
| Co-MOF             | Fe$_3$(OH)$_3$(BDC-NH$_2$)$_3$ | 0.60 (273 K) | TEOA | CH$_3$CN | 502 | 31 |
| NH$_2$-MIL-101(Fe)  | Fe$_3$(OH)$_3$(BDC)$_3$ | 0.64 (273 K) | TEOA | CH$_3$CN | 456 | 24 |
| NH$_2$-MIL-53(Fe)   | Ni$_2$(OH)$_2$(BDC-NH$_2$)$_3$ | 0.66 (273 K) | TEOA | CH$_3$CN | 445 | 24 |
| Ni$_2$(OH)$_2$(BDC)$_3$ | Ni$_2$(OH)$_2$(BDC-NH$_2$)$_3$ | 0.66 (273 K) | TEOA | CH$_3$CN | 148 | 24 |
| Fe$_3$(OH)$_3$(BDC-NH$_2$)$_3$ | Fe$_3$(OH)$_3$(BDC)$_3$ | 0.66 (273 K) | TEOA | CH$_3$CN | 116 | 24 |
| Fe$_3$(OH)$_3$(BDC-NH$_2$)$_3$ | Fe$_3$(OH)$_3$(BDC)$_3$ | 0.66 (273 K) | TEOA | CH$_3$CN | 74 | 24 |

(Continues)
| MOF-Based Materials | Chemical Formula | CO₂ Uptake /mmol g⁻¹ (1 atm) | Chemical Agent | Solvents | Photocatalytic Efficiency (μmol·gcat⁻¹·h⁻¹) | References |
|---------------------|------------------|-------------------------------|----------------|----------|---------------------------------------------|------------|
| AD-MOF-2            | [Co₂(HAD)₂(AD)₂ (IA)₂]·DMF | 1.86 (298 K)                  | TIPA           | CH₃CN   | 443                                         | 32         |
| AD-MOF-1            | [Co₂(HAD)₂ (AD)₂-(BA)]·DMF·2H₂O | 2.33 (298 K)                  | TIPA           | CH₃CN/H₂O | 179                                         |            |
| Fe₃⁺Fe₂⁺-NH₂         | [(Fe₂⁻Tı)(Fe₂(µ₃-O)(BDC-NH₂)₃)·4NO₃ | 1.38 (298 K)                  | TIPA           | CH₃CN/H₂O | 396                                         | 33         |
| Fe₃⁺Fe₂⁺             | [(Fe₂⁻Tı)(Fe₂(µ₃-O)(BDC)₃)·4NO₃ | 1.23 (298 K)                  | (1)            |          | 309                                         |            |
| PCN-138             | [Zr₆(µ₃-O)₄(µ₅-OH)₄][TCP][TBTB]₈/₃ | 2.82 (273 K)                  | TIPA           | H₂O      | 168                                         | 34         |
|                     |                  | 1.82 (298 K)                  |                |          |                                              |            |
| Ir-CP               | [Y(Ir(ppy)₂(dbcbpy)₂][OH] | -                             | TEOA           | CH₃CN   | 158                                         | 35         |
| Eu-Ru(Phen)₃       | [Eu₂(µ₂-H₂O)(H₂O)₃(L)₃]·(NO₃)₂·(2-FBA)·(H₂O)₂ | -                             | TEOA           | CH₃CN   | 94                                          | 36         |
| Cd/Ru-MOF-1         | {Cd₃[Ru-L]₂·2(Me₂NH₂)·solvent}n | -                             | TEOA           | CH₃CN   | 67                                          | 37         |
| Cd/Ru-MOF-2         | {Cd[Ru-L]₃·3(H₂O)}n | 72                            |                |          |                                              |            |
| PCN-222(Zr)         | Zr₆(µ₅-OH)₆(OH)₆(TCPP)₂ | 2.59 (273 K)                  | TEOA           | CH₃CN   | 60                                          | 38         |
|                     |                  | 1.56 (298 K)                  |                |          |                                              |            |
| NNU-28(Zr)          | [Zr₄O₄(OH)₆(L)₆]·6DMF | 2.83 (273 K)                  | TEOA           | CH₃CN   | 53                                          | 39         |
|                     |                  | 1.49 (298 K)                  |                |          |                                              |            |
| PCN-136             | Zr₆(µ₃-O)₄(µ₅-OH)₆(OH)₆(HCHC) | 2.72 (273 K)                  | TIPA           | CH₃CN/H₂O | 44                                          | 40         |
| Zr-SDC-NH₂          | [Zr₄O₄(OH)₆(L)₆]·8DMF | 3.74 (273 K)                  | TEOA           | CH₃CN   | 41                                          | 41         |
|                     |                  | 1.57 (298 K)                  |                |          |                                              |            |
| NNU-31-Zn           | Fe₂⁺Zn(µ₃-O)(TCA)₂(H₂O)₃ | 1.65 (298 K)                  | -              | H₂O      | 26                                          | 42         |
| NH₂-MIL-125(Ti)     | TiO₆O₆(OH)₄(BDC-NH₂)₆ | 5.90 (273 K)                  | TEOA           | CH₃CN   | 16                                          | 23         |
| MIL-125(Ti)         | TiO₆O₆(OH)₄(BDC)₆ | 4.40 (273 K)                  | TEOA           | CH₃CN   | 4                                           |            |
| NH₂-UO-66-(Zr/Ti)   | (Zr/Ti)₆O₆O₆(OH)₆(BDC-NH₂)₆ | 3.79 (273 K)                  | TEOA           | CH₃CN   | 12                                          | 43         |
| NH₂-UO-66(Zr)       | ZrO₆O₆(OH)₄(BDC-NH₂)₆ | 3.04 (273 K)                  | TEOA           | CH₃CN   | 7                                           |            |
| NH₂-UO-66(Zr)       | ZrO₆O₆(OH)₄(BDC-NH₂)₆ | 3.04 (273 K)                  | TEOA           | CH₃CN   | 26                                          | 44         |
| Uio-66(Zr)          | Zr₂O₆(OH)₄(BDC)₆ | 2.37 (273 K)                  | TEOA           | CH₃CN   | 0                                           |            |

Notes: TEOA, triethanolamine; BNAH, 1-benzyl-1,4-dihydronicotinamide; H₂L, biphenyl-3,3′,5,5′-tetracarboxylic acid; H₂BDC, benzene-1,4-dicarboxylic acid; HAD, adenine; BA, butanedioic acid; IA, isobutyric acid; DMF, N,N-dimethylformamide; Tri, 1,2,4-triazole; DMAc, N,N-dimethylacetamide; TIPA, trispropanolamine; H₂TCP, tetrakis(4-carboxyphenyl)porphyrin; TBTB, 4,4′,4″-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzene; ppy, 2-phenylpyridine; dbcbpy, 2,2′-bipyridine-4,4′-dicarboxylate; H₄L₂, 2-amino-[1,1′:4,1″-terphenyl]-3,3′,5,5″-tetracarboxylic acid; H₃L₁, Ru(phen)₃-derived tricarboxylate acid metallogand; 2-FBA, 2-fluorobenzoate; L₁=5,5″-dbcbpy=2,2′-bipyridine-5,5″-dicarboxylate; L₂=(4,4′-dbcbpy)₂(bpy), bpy=2,2′-bipyridine; H₂L₁, 4,4′-anthracene-9,10-diylbis(ε-thyne-2,1-diyl) dibenzoic acid; HCHC, hexakis(4-carboxyphenyl)hexabenzocoronene; H₂L₂, 2,2-diamino-4,4′-stilbene dicarboxylic acid; TCA, 4,4′,4″-tricarboxytriphenylamine.
Table 2 | Summary of Reaction Conditions of Comparison Experiments

| Entry | Catalyst | Light (nm) | Gas | HCOOH |
|-------|----------|------------|-----|-------|
| 1     | MFM-300(Ga) | 350–780 | TEOA | CO₂ | 502 |
| 2     | n.a. | 350–780 | TEOA | CO₂ | n.a. |
| 3     | MFM-300(Ga) | 350–780 | TEOA | N₂ | n.a. |
| 4     | MFM-300(Ga) | 350–780 | n.a. | CO₂ | n.a. |
| 5     | MFM-300(Ga) | n.a. | TEOA | CO₂ | n.a. |
| 6     | MFM-300(Ga) | 350–780 | TEOA | CO₂ | 64 |
| 7     | Ga(NO₃)₂·9H₂O and H₄L | 350–780 | TEOA | CO₂ | n.a. |
| 8     | Ga₂O₃ | 350–780 | TEOA | CO₂ | n.a. |
| 9     | GaN | 350–780 | TEOA | CO₂ | n.a. |
| 10    | GaP | 350–780 | TEOA | CO₂ | n.a. |
| 11    | MIL-53(Ga) | 350–780 | TEOA | CO₂ | n.a. |
| 12    | MIL-68(Ga) | 350–780 | TEOA | CO₂ | n.a. |

Reaction conditions: MFM-300(Ga) (10 mg), TEOA/CH₃CN (3 mL/15 mL, saturated with CO₂), 25 °C, 350–780 nm, light irradiation for 4 h. For entry 6, 3 mL TEA was added to replace TEOA. For entry 7, a powdered mixture of Ga(NO₃)₂·9H₂O (0.04 mmol, 16.7 mg) and H₄L (0.02 mmol, 6.6 mg) were used (H₄L, biphenyl-3,3',5,5'-tetracarboxylic acid). For entry 8–12, the catalysts used were 10 mg in each reaction.

The catalystic cycle for this reaction is proposed (Figure 3b). Upon light irradiation, MFM-300(Ga) is activated, and the electrons in the VB (2.2 V) are promoted to the CB (1.09 V), and the photoinduced holes at the VB are readily filled up by the electron sacrificial agent TEOA. Surprisingly, the photoinduced electrons with a reductive potential of −1.09 V versus NHE (see Supporting Information Table S3). This indicates that the CO₂ radical anion (CO₂−) is the direct intermediate to form formic acid. No radical was captured for the reaction conducted under dark conditions. Significantly, to the best of our knowledge, this is the first time that a direct intermediate radical has been detected in the photoreduction of CO₂ over a MOF-based catalyst.
simultaneously at a redox potential of $-0.61$ V versus NHE

$$E^0_{\text{redox}} = -1.90 \text{ V vs. NHE} \quad (1)$$

$$E^0_{\text{redox}} = -0.61 \text{ V vs. NHE} \quad (2)$$

## Conclusion

The porosity and design flexibility of MOFs, coupled with their intrinsic semiconductor and photoelectrical properties, make them promising candidates as efficient photocatalysts. We report the first example of a Ga-MOF-based semiconductor that can promote the photoreduction of CO$_2$ to formic acid with a selectivity of 100% and a high productivity of $502 \pm 18 \mu$mol·g$_{\text{cat}}^{-1}$·h$^{-1}$ under light irradiation and at room temperature using TEOA as an electron sacrificial agent. MFM-300(Ga) shows excellent catalytic stability over three cycles of reactions with full retention of the productivity of formic acid. In situ EPR spectroscopic analysis confirms the generation of the CO$_2$$^{2-}$ radical anion as the reaction intermediate promoted by the strong host–guest interactions between the bridging $\mu_2$-OH groups of MFM-300(Ga) and the adsorbed CO$_2$ molecules. Compared with other reported Ga-MOFs in literature, the presence of strong binding sites and efficient LMCT plays an important role in boosting the photocatalytic activity toward CO$_2$ reduction, which sheds light on the design of future MOF-based photocatalysts with improved activity.

## Supporting Information

Supporting Information is available and includes detailed experimental procedures and characterization data.

## Conflict of Interest

There is no conflict of interest to report.

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**Figure 3**

(a) In situ X-band EPR spectra of photocatalytic reactions over MFM-300(Ga) using DMPO as spin trap, (black) before and (red) after light irradiation, with simulated (blue) spectrum showing a major component, DMPO-CO$_2$$^{2-}$ (green, simulation), and a minor component, DMPO-O$_x$ (cyan, simulation) under photocatalytic conditions over MFM-300(Ga). (b) The proposed mechanism of the photocatalytic reduction of CO$_2$ over MFM-300(Ga).
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