Plasmon-Enhanced Photocatalytic CO₂ Conversion within Metal–Organic Frameworks under Visible Light

Kyung Min Choi,†,§,⊥ Dohyung Kim,‡,∥,¶ Bunyarat Rungratweevoranit,†,§,∥ Christopher A. Trickett,†,§ Jesika Trese Deniz Barmanbek,† Ahmad S. Alshammari,§ Peidong Yang,§,†,∥∥ and Omar M. Yaghi†,§,∥,¶

1Department of Chemistry, 2Department of Materials Science and Engineering, and 3Kavli Energy NanoSciences Institute, University of California, Berkeley, California 94720, United States
§Materials Sciences Division, 1Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
⊥Department of Chemical and Biological Engineering, Sookmyung Women’s University, Seoul 04310, Korea
#King Abdulaziz City for Science and Technology, Post Office Box 6086, Riyadh 11442, Saudi Arabia

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ABSTRACT: Materials development for artificial photosynthesis, in particular, CO₂ reduction, has been under extensive efforts, ranging from inorganic semiconductors to molecular complexes. In this report, we demonstrate a metal–organic framework (MOF)-coated nanoparticle photocatalyst with enhanced CO₂ reduction activity and stability, which stems from having two different functional units for activity enhancement and catalytic stability combined together as a single construct. Covalently attaching a CO₂-to-CO conversion photocatalyst Re(CO)₃(BPYDC)Cl, BPYDC = 2,2′-bipyridine-5,5′-dicarboxylate, to a zirconium MOF, UiO-67 (Re₃-MOF), prevents dimerization leading to deactivation. By systematically controlling its density in the framework (n = 0, 1, 2, 3, 5, 11, 16, and 24 complexes per unit cell), the highest photocatalytic activity was found for Re₃-MOF. Structural analysis of Re₃-MOFs suggests that a fine balance of proximity between photoactive centers is needed for cooperatively enhanced photocatalytic activity, where an optimum number of Re complexes per unit cell should reach the highest activity. Based on the structure–activity correlation of Re₃-MOFs, Re₃-MOF was coated onto Ag nanocubes (AgRe₃-MOF), which spatially confined photoactive Re centers to the intensified near-surface electric fields at the surface of Ag nanocubes, resulting in a 7-fold enhancement of CO₂-to-CO conversion under visible light with long-term stability maintained up to 48 h.

INTRODUCTION

Inorganic nanostructures and molecular complexes have been widely investigated as artificial photosynthetic catalysts.¹,² The challenge is to find catalysts for carbon dioxide reduction with good activity, selectivity, and durability, especially under visible light. In this context, metal–organic frameworks (MOFs) offer many advantages because of the flexibility with which they can be designed and their pore environment varied.³ Here, we demonstrate how tunable photocatalytic activity can be realized by quantitatively and precisely controlling the density of covalently attached photoactive centers within the MOF interior and how this prevents the dimerization of the molecular catalyst and its deactivation. Furthermore, for the first time, these MOF catalytic units can be spatially localized within the enhanced electromagnetic field surrounding plasmonic silver nanocubes to significantly increase their photocatalytic activity for carbon dioxide conversion under visible light.⁴ Specifically, we covalently attached Re(CO)₃(BPYDC)(Cl), BPYDC = 2,2′-bipyridine-5,5′-dicarboxylate [hereafter referred to as ReTC], within a zirconium MOF based on the UiO-67-type structure⁵ (hereafter, this Re-containing MOF is termed Re₃-MOF) and controlled its density in the pores in successive increments of n (n = 0, 1, 2, 3, 5, 11, 16, and 24 complexes per unit cell), finding the highest activity for n = 3 complexes. The effect of the molecular environment within MOFs for photocatalytic CO₂ reduction was studied, which provided further insights into the photocatalytic reaction pathway of the molecular Re complex. Placing this construct on silver nanocubes resulted in 7-fold enhancement of carbon dioxide photocatalytic conversion to carbon monoxide.

Many studies involving the use of photoactive metal complexes,⁶ MOFs,⁷,⁸ and inorganic nanostructures⁹ for

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carbon dioxide reduction have been reported with varying levels of performance. The present catalysts’ unique performance is attributed to the precision and systematic variation applied in their design and the spatial resolution with which they can be interfaced with plasmonic nanostructures.

### EXPERIMENTAL SECTION

**Synthesis of ReI(CO)3(H2BPYDC)Cl, H2ReTC.** Re(CO)5Cl (0.360 g, 1.000 mmol) and H2BPYDC (0.240 g, 1.000 mmol) were added to methanol (100 mL). After the mixture was refluxed for 24 h under N2, the resultant precipitate was filtered and the solvent was evaporated under reduced pressure to give the product. 1H NMR (DMSO-d6): δ 9.35 (s, 2H), 9.01 (d, 2H), 8.79 (d, 2H).

**Synthesis of Reₙ-MOFs.** Different ratios of H₂ReTC and H₂BPDC (0, 5, 10, 20, 30, 50, 70, and 100 mol % of H₂ReTC, adding up to a total amount of 0.040 mmol of organic linker) were mixed with 10 mL of dimethylformamide (DMF) solution containing ZrCl₄ (9.320 mg, 0.040 mmol), and acetic acid (0.5 mL, 8.7 mmol) in a 20 mL vial, which was heated at 100 °C for 10 h. An orange precipitate was collected and washed three times with DMF using a centrifuge (9000 rpm for 10 min) and sonication and then sequentially immersed in anhydrous acetonitrile for three 24 h periods.

**Synthesis of Ag Nanocubes.** Silver nitrate (0.25 g) and copper(II) chloride (0.21 mg) were dissolved in 1,5-pentanediol (12.5 mL) in a 20 mL glass vial. In a separate vial, PVP (Mₜₐₜₐₜ = 55 000, 0.25 g) was dissolved in 1,5-pentanediol (12.5 mL). An oil bath, 1,5-pentanediol (20 mL) was heated for 10 min at 190 °C. Then the two precursor solutions were injected at different intervals: 500 μL of the silver nitrate solution every minute and 250 μL of the PVP solution every 30 s. The reaction was stopped once the solution turned opaque (~7 min).

**Synthesis of Ag⊂Reₙ-MOF.** Ag nanocubes were washed three times with DMF using a centrifuge (9000 rpm for 10 min) and concentrated to a 3 mg/mL Ag nanocube solution. A Re-MOF stock solution was prepared by dissolving H₂BPDC (9.110 mg, 0.037 mmol), H₂ReTC (1.320 mg, 0.002 mmol), ZrCl₄ (9.32 mg, 0.04 mmol), and acetic acid (0.500 mL, 8.700 mmol) in 10 mL of DMF. Then 2.1 mL of the Re-MOF stock solution and 2 mL of the Ag nanocube solution were combined with 1 mL of DMF containing 0.125 mL of acetic acid in a 20 mL vial with a magnetic stirrer and heated at 90 °C in an aluminum heating block with vigorous stirring. The thickness of the Re-MOF layer could be controlled with reaction time; Ag⊂Reₙ-MOF-16 nm and -33 nm were synthesized after 25 and 30 min, respectively. The precipitate was collected and washed three times with DMF using a centrifuge (9000 rpm for 10 min) and sonication and sequentially immersed in anhydrous acetonitrile for three 24 h periods.

**Photocatalytic Experiments.** The experiments were performed in a sealed batch-type custom cell. Samples were dispersed in acetonitrile (20 mL) with 1 mL of triethylamine added as a sacrificial electron donor. Initially, the cell was purged with CO₂ for 20 min and then sealed at 1 atm CO₂. A 300 W Xe lamp with visible band-pass filters was used so that the light contained regions in wavelengths...
between 400 and 700 nm. The amount of Re tricarbonyl complex in each sample was 0.5−8 μmol, depending on the degree of ReTC incorporation inside MOFs, while the nanocrystal number per volume was kept similar. The products were measured by injecting 1 mL of gas in the headspace to a gas chromatograph (SRI) after every 1 or 2 h run.

**Characterization.** Powder X-ray diffraction patterns (PXRD) were recorded using a Bruker D8 Advance diffractometer (Göbel mirror monochromated Cu Kα radiation, λ = 1.54056 Å). Gas adsorption analysis was performed on a Quantachrome Quadrasorb-SI automatic volumetric gas adsorption analyzer. A liquid nitrogen bath (77 K) and ultrahigh purity grade N2 and He (99.999%, Praxair) were used for the measurements. Samples were prepared and measured after being evacuated at 100 °C for 12 h. For transmission electron microscopy (TEM) observation, samples were first dispersed in an organic solvent by sonication and dropped onto a TEM grid. TEM was carried out at 200 kV using a JEOL JEM-2100. The amount of Re complexes in Re_n-MOFs was analyzed by an ICP−AES spectroscope (Optima 7000 DV, PerkinElmer). Samples (10 mg) were digested using a mixture of nitric acid (0.5 mL), hydrochloric acid (1.5 mL), and hydrofluoric acid (30 μL) and then diluted with 2 vol % of nitric acid solution (10 mL) before measurement. For NMR, 10 mg of dried sample was digested and dissolved by sonication in a mixture of DMSO-d_6 (1 mL), hydrofluoric acid (20 μL), and D_2O (20 μL). The digested solution was used directly for 1H NMR. Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy of neat samples was performed on a Bruker ALPHA platinum ATR-FTIR spectrometer equipped with a single reflection diamond ATR module. Liquid samples were measured by placing a sample droplet on the sample stage covered with a cap for preventing solvent evaporation.

![Figure 2. Characterization and photocatalytic activity of Re_n-MOFs.](image)

**RESULTS AND DISCUSSION**

**Structural Analysis and Photocatalytic Activity of Re_n-MOFs.**

**Structural Analysis of Re_3-MOF.** The structural determination of Re_3-MOF was carried out by single-crystal X-ray diffraction (Figure 1). Single crystals of Re_3-MOF were prepared by dissolving the protonated form of H_2ReTC (20 mol %), H_2BPDC (80 mol %, BPDC = 4,4′-biphenyldicarboxylate), and ZrOCl_2·8H_2O in a solution mixture of DEF/formic acid in a 20 mL screw-capped vial and heating at 140 °C for 12 h [Figure S1 in Supporting Information (SI)]. The analysis of single-crystal X-ray diffraction data reveals that Re_3-MOF crystallizes in the cubic Fm3m space group with a unit cell parameter a = 26.7213(8) Å (Table S1 and Figure S2). Each Zr secondary building unit, Zr_6O_4(OH)_4(−CO_2)_12, is coordinated to a total of 12 linkers (ReTC and BPDC), resulting in a three-dimensional fcu network. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis performed on these crystals gave a molar ratio of 0.12 mol of Re to 1 mol Zr. This corresponds to 3 ReTCs per unit cell (i.e., Re_3-MOF), as confirmed by the X-ray structure of single-crystalline
ZrO2(OH)2[Re(CO)3(Cl)-BPYDC]0.72(BPDC)3.28, where covalently bound ReTCs are found in octahedral cavities of face-centered cubic arrangement. Moreover, chloride occupies the axial position and was refined from the Fourier difference map, indicating fac-arrangement of the ReTC in Re−MOF, which is an identical geometry compared to that of the mononuclear Re complex in solution10 (Figure S2 in SI). The IR spectrum of Re3-MOF was measured in powder form, resulting in the identical geometry compared to that of the mononuclear Re complex in solution10 (Figure S2 in SI). The IR spectrum of Re3-MOF was measured in powder form, and ν(CO) bands were observed at 2222, 2120, and 1890 cm⁻¹ (Figure S3 in SI), consistent with the fac-isomer of molecular ReTC.10 The UV–vis spectrum, measured as a powder mixed with KBr, has a metal-to-ligand charge transfer (MLCT) absorption band at 400 nm, indicative of the fac-isomer of ReTC10 (Figure S4 in SI). The amount of ReTC in the MOF and its molecular configuration were further confirmed from H NMR of a HF-digested solution of Re2-MOF (Figure S5 in SI).

**ReTC Density Varied in Ren-MOFs.** To examine how the amount of ReTC in MOFs affects the structural environment within the MOF interior for CO₂ catalytic turnover, the ReTC density was varied in the range from Re0-MOF (ReTC free MOF) to Re24-MOF (ReTC at maximal loading). This was done by adding increasing amounts of H₂ReTC to the total amount of organic linkers during MOF synthesis, which resulted in Ren-MOFs (n = 0, 1, 2, 3, 5, 11, 16, and 24) identified from ICP-AES (Figure 2a). All samples were synthesized as monocrystalline nanoparticles (Figures S6–S8 in SI) as this may facilitate diffusion of substrates and products to and from the active Re catalytic centers. Representative scanning electron microscopy (SEM) images (Figure 2b,c and Figure S7 in SI) of Ren-MOFs show great size uniformity (ca. 300 nm) and identical octahedral geometry of particles regardless of the amount of ReTC incorporated. The crystallinity of Ren-MOFs was examined by PXRD (Figure 2d and Figure S8 in SI), which gave sharp diffraction lines matching those of the simulated pattern obtained from experimental single-crystal X-ray diffraction data of Re₃-MOF. This clearly indicates preservation of the single-crystalline Re₃-MOF structure upon introduction of different density of ReTC in Ren-MOFs. The permanent porosity of all Ren-MOF samples was confirmed by measurement of their N₂ sorption isotherms (Figure S9 in SI). UV–vis spectroscopy for all Ren-MOFs showed that the MLCT absorption band intensities increase as more ReTCs are incorporated into the framework, further confirming the varied density of the photoactive units in Ren-MOFs (Figure S10 in SI).

**Photocatalytic CO₂ Conversion for Ren-MOFs.** All Ren-MOFs used for photocatalytic CO₂ conversion were dispersed in an acetonitrile/triethylamine mixture (MeCN/TEA = 20:1) saturated with CO₂, where TEA served as a sacrificial electron donor. Measurements were conducted under visible light (300 W Xe lamp, visible band-pass = 400–700 nm) to utilize the visible light absorption feature of ReTC. We note this is in contrast to previous work where it relied on the intense absorption at the UV region (300–350 nm) associated with π−π* energy transition of the bipyrinedine linker. The products were analyzed and quantified using gas chromatography and normalized to the number of ReTC in Ren-MOFs to get the turnover number (TON). Photocatalytic CO₂-to-CO conversion behavior of Ren-MOFs is shown in Figure 2e, reaching peak activity with Re₅-MOF. In the absence of CO₂ (under Ar atmosphere) or with no ReTC, there was no CO generation observed. The performance of Ren-MOFs was stable at least up to 4 h (Figure S11 in SI) compared to the molecular counterpart, which deactivates within the first hour (Figure S12 in SI). The enhanced stability of Ren-MOFs is from the covalent attachment of Re centers in ReTC, which prevents the prevailing deactivation pathway of dimerization commonly observed with photoactive molecular complexes (Figures S13 and S14 in SI). IR spectra of Ren-MOF before and after the reaction (Figure S15 in SI) show that Ren-MOFs preserve the molecular configuration of fac-ReTC after photocatalysis, while, in comparison, the ν(CO) bands for molecular H₂ReTC are shifted because of dimerization. This clearly indicates the inability of ReTC to dimerize due to its covalent bonding to the MOF in Ren-MOFs.

**Effect of the Molecular Environment within MOFs for Photocatalytic CO₂ Reduction.** IR Spectroscopy of Ren-MOFs and Molecular H₂ReTC. The photocatalytic trend observed for Ren-MOFs should be closely related to the configuration of ReTC and its surrounding environment. The vibrational stretching modes of ReTC carbonyl ligands in Ren-MOFs were probed by IR spectroscopy and compared with those of the molecular H₂ReTC (Figure 3). In the cases of Re₂⁻,

![Figure 3. IR spectra of Ren-MOFs and H₂ReTC.](image-url)
work is most reasonable to expect. Beyond this point, the likelihood of ReTCs occupying adjacent linkers and hence overlapping increases. Indeed, if the linkers can rotate 180° into adjacent octahedral cavities, beyond 4 per unit cell, there will unavoidably be some ReTCs clashing from this rotation (Figure S17a in SI). The IR spectra are consistent with the unit cell structure considerations where Re5-MOF is just beyond the limit of ReTC being undisturbed. Therefore, the excessive occupation of ReTCs in Reₙ-MOFs appears to cause a change in their vibrational state, which may not be favorable for reducing CO₂ and decreases activity for Reₙ-MOFs with n greater than 4. Another aspect to note is the accessible pore volume of Reₙ-MOFs: N₂ uptake on a volumetric scale (Figure S9 in SI) is lower for frameworks with more than 4 ReTC per unit cell. This indicates that substrate and product diffusion may also be limited within Reₙ-MOFs with n greater than 4, further resulting in the observed lowering of activity.

Reₙ-MOFs with n Less than 4. However, we see an increase in activity in the lower regime of ReTC incorporation, from Re₁ to Re₃. Though a unimolecular pathway has been reported to exist for molecular ReTC, the observed rise in photocatalytic activity with more ReTC units within Reₙ-MOF (n < 4) implies that the bimolecular reaction pathway (bridging or outer-sphere electron transfer) is the source of the higher turnover, which is expected for a reaction involving 2 electrons (Figures S17b and 18 in SI). Therefore, a fine balance of proximity between photoactive centers is needed for such cooperatively enhanced activity. Furthermore, reduced activity compared to the molecular ReTC in solution (Figures S11 and S12 in SI) indicates that restricting the free motion of the molecular complex may limit its activity though it is protected from rapid deactivation. The present study of Reₙ-MOFs not only elucidates the effect of the molecular environment within MOFs for photocatalytic CO₂ reduction but also provides further insights into the photocatalytic reaction pathway of molecular ReTC.

Plasmon-Enhanced Photocatalytic Activity of Reₙ-MOFs. Synthesis and Characterization of Reₙ-MOFs Coated on Plasmonic Ag Nanocubes. Coupling Reₙ-MOF to a plasmonic Ag nanoparticle was performed to demonstrate an effective strategy in creating a bifunctional catalyst with enhanced activity and long-term stability. The optimal Re₃-MOF structure with the highest turnover was coated on Ag nanocubes (AgCRe₃-MOF). Once irradiated with light, the Ag nanocubes generate intensified near-surface electric fields at their surface plasmon resonance frequency that can be orders of magnitude higher in intensity than the incident electromagnetic field. Therefore, it is expected that Re₃-MOF coating on the
Ag nanocubes can spatially localize photoactive Re centers to the intensified electric fields with enhanced photocatalytic activity. More recently, there have been some examples of combining metal nanoparticles with MOFs capable of catalysis that led to enhancement in their performance. Ag nanocubes prepared by the polyol process were used in the synthesis procedure of Re$_2$-MOF to give Ag-Re$_2$-MOF. Figure 4a shows a TEM image of Ag-Re$_2$-MOF. The dark area in the core is the Ag nanocube (98 nm in size), and the brighter outer part is the Re$_2$-MOF with a thickness of 33 nm. The magnified image of the outer part (Figure 4b) shows lattice fringes from the crystalline Re$_2$-MOF layer. ICP-AES analysis revealed that the Re$_2$-MOF layer contains the expected three ReTCs per unit cell. The crystallinity of Ag-Re$_2$-MOF was examined by PXRD (Figure S19 in SI). The resulting diffraction lines of Ag-Re$_2$-MOF match those of Ag and Re$_2$-MOF, indicating the preservation of the Ag metallic phase and the formation of the Re$_2$-MOF structure on the surface of Ag. The permanent porosity of Ag-Re$_2$-MOF was confirmed by N$_2$ sorption (Figure S20 in SI). IR spectroscopy showed that ν(CO) bands were consistent with those of molecular H$_2$ReTC and Re$_3$-MOF (Figure S21 in SI). From the UV–vis spectrum (Figure 4c), the Ag nanocube exhibits a strong quadrupolar localized surface plasmon resonance (LSPR) scattering peak ($\lambda_{\text{max}} \sim 480$ nm), which overlaps with the absorption range of ReTC (400 nm < $\lambda$ < 500 nm) in the visible region. Furthermore, the Ag-Re$_2$-MOF structure retains the characteristic LSPR features of the Ag core after being coated with the Re$_2$-MOF. Therefore, it is expected that the intensified near-field created at the surface of Ag nanocubes can be absorbed by ReTCs incorporated into the Re$_2$-MOF layer for photocatalytic enhancement.

**Photocatalytic Activity and Stability of Ag-Re$_2$-MOFs.** Photocatalytic CO$_2$-to-CO conversion activity of Ag-Re$_2$-MOF was performed under conditions identical to those expressed above (Figure 4d). As expected, Ag-Re$_2$-MOF exhibits 5-fold enhancement of activity over Re$_2$-MOF under visible light. Since the intensity of the near-field from LSPR decays exponentially with the distance from the surface of the nanoparticle, ReTCs in a thinner MOF layer will be under the influence of a stronger electric field on average, leading to superior turnover. A thinner Re$_2$-MOF layer (16 nm) was coated on Ag nanocubes by controlling the synthetic conditions (Figure S22 in SI), and this structure provided 7-fold enhancement of photocatalytic activity (Figure 4d). When there was no ReTC in the MOF layer (i.e., Ag-Re$_2$-MOF) (Figure S23 in SI), there was no activity observed, ruling out the possibility of Ag being responsible for CO production. Additionally, when Re$_2$-MOF was coated on Cu nanoparticles of similar size (~100 nm, Figure S24 in SI), activity enhancement was not observed (Figure 4d) as the Cu nanoparticles do not have LSPR characteristics that match the absorption features of ReTC (Figure S25 in SI).

The Ag nanocube coated with Re-MOF should exhibit not only enhanced photocatalytic activity but long-term stability as well from having ReTCs covalently bound within the MOF. The stability of the Ag-Re$_2$-MOF structure was tested by measuring its activity up to 48 h under visible light (Figure 4e). Compared to molecular H$_2$ReTC, which rapidly deactivates within the first hour possibly from dimerization as previously reported, Ag-Re$_2$-MOF shows stable photocatalytic performance throughout the entire period, and its cumulative TON exceeds that of H$_2$ReTC after 24 h. The stability of the structure was confirmed with TEM and IR spectroscopy following the long-term measurement (Figures S26 and S27 in SI). The CO produced from Ag-Re$_2$-MOF almost doubled from that of H$_2$ReTC after 48 h, demonstrating the combined effects gained from this bifunctional catalyst construct.

**SUMMARY**

We show how covalently attached photoactive centers within MOF interior can be spatially localized and subjected to the enhanced electromagnetic field surrounding plasmonic silver nanocubes to significantly increase their photocatalytic activity. We covalently attached Re$_x$(CO)$_y$(BPYDC)Cl, BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate, into a zirconium MOF, UIO-67, and controlled its density in the pores in increments (0, 1, 2, 3, 5, 11, 16, and 24 complexes per unit cell), which led to observing the highest activity for three complexes. This activity trend resulted from the molecular environment within MOFs that varied with ReTC density. Placing the optimal Re$_2$-MOF structure with the highest turnover on silver nanocubes resulted in 7-fold enhancement of photocatalytic activity under visible light.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11027.

Materials and methods, structural analysis of single-crystalline Re$_2$-MOF, and additional characterization of Re$_2$-MOF and Ag-Re$_2$-MOF (PDF)

X-ray data for Re$_3$-MOF (CIF)

**AUTHOR INFORMATION**

Corresponding Authors

*pyang@berkeley.edu
*yaghi@berkeley.edu

Author Contributions

*K.M.C. and D.K. contributed equally.

Notes

The authors declare no competing financial interest.

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