Photocatalytic CO₂ reduction using visible light by metal-monocatecholato species in a metal–organic framework†

Yeob Lee, Sangjun Kim, Honghan Fei, Jeung Ku Kang* and Seth M. Cohen*

The conversion of CO₂ into hydrocarbons has attracted great attention owing to global warming caused, in part, by CO₂ from fossil fuel combustion.1,2 Inspired by photosynthesis, development of an artificial system that catalytically regenerates hydrocarbon fuels from CO₂, H₂O, and sunlight is one very intriguing approach.3–5 Artificial photosynthesis would consist of two reactions: water oxidation to extract electrons from water and CO₂ reduction to generate carbonaceous radicals using electrons generated from water oxidation. CO₂ requires a large driving force to be transformed to other compounds due to the high kinetic and thermodynamic stability of CO₂.6–8 Several photocatalytic systems for CO₂ reduction, including heterogeneous semiconductor systems and homogeneous transition metal-based complexes have been investigated but challenges remain. For example, many metal oxides are active under only UV light, functionalized organic linker (catbdc, 2,3-dihydroxyterephthalic acid, to produce UiO-66-CAT).19 Two different trivalent metal ions, Cr(m) and Ga(m), were then incorporated into the catbdc sites to afford unprecedented Cr- and Ga-monocatecholato species in a robust UiO-66. The catbdc organic linkers are responsible for visible light absorption and metalation by Cr(m) and Ga(m) facilitates electron transfer within the MOFs.

Herein, we report a new MOF photocatalysts that incorporate catalytic metal sites, using postsynthetic modification methods, for CO₂ reduction to formic acid in the presence of 1-benzyl-1,4-dihydronicotinamide (BNAH) and triethanolamine (TEOA). The material reduced CO₂ to HCOO⁻ in the presence of triethanolamine (TEOA) under visible-light irradiation.12 In addition, Li et al. developed a non-porous coordination polymer consisting of Y metal ions and Ir(ppy)₂(dcbpy) metalloligands; this material reduced CO₂ to HCOO⁻ under visible light irradiation.16 Despite these advances, the development of MOF photocatalysts for CO₂ reduction is still in its infancy.

Metal–organic frameworks (MOFs) are hybrid materials that consist of secondary building units (SBUs) and organic linkers. The rational design of MOFs with tunable properties through a selective combination of metal ions and organic ligands has produced materials useful for various applications. Photocatalytic applications of MOFs also have been studied.11–15 Lin and co-workers reported a MOF photocatalyst doped with Re(bpy)(CO)₃Cl complexes that reduced CO₂ to CO under UV light irradiation.11 This pioneering work for MOF photocatalysts showed poor efficiency due, in part, to a low doping of the Re catalyst into the MOF. Fu et al. synthesized visible-light sensitive NH₂-MIL-125(Ti) with an amine-functionalized organic linker. This material reduced CO₂ to HCOO⁻ in the presence of triethanolamine (TEOA) under visible-light irradiation.12

Metal–organic frameworks (MOFs) with isolated metal-monocatecholato groups have been synthesized via postsynthetic exchange (PSE) for CO₂ reduction photocatalyst under visible light irradiation in the presence of 1-benzyl-1,4-dihydronicotinamide and triethanolamine. The Cr-monocatecholato species are more efficient than the Ga-monocatecholato species.

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Herein, we report a new MOF photocatalysts that incorporate catalytic metal sites, using postsynthetic modification methods, for CO₂ reduction to formic acid in the presence of 1-benzyl-1,4-dihydronicotinamide (BNAH) and triethanolamine (TEOA). The Zr(iv)-based MOF (UiO-66, UiO = University of Oslo) was subjected to postsynthetic exchange (PSE)17–20 with a catechol-functionalized organic linker (catbdc, 2,3-dihydroxyterephthalic acid, to produce UiO-66-CAT).19 Two different trivalent metal ions, Cr(m) and Ga(m), were then incorporated into the catbdc sites to afford unprecedented Cr- and Ga-monocatecholato species in a robust UiO-66. The catbdc organic linkers are responsible for visible light absorption and metalation by Cr(m) and Ga(m) facilitates electron transfer within the MOFs.

PSE has become a facile and efficient strategy to functionalize MOFs under mild conditions (Fig. 1). UiO-66 was prepared solvothermally in DMF containing 1:1 molar ratio mixture of ZrCl₄ and H₂bdc with acetic acid as a modulator at 120 °C. UiO-66 was then exposed to DMF/H₂O solution containing 2 equiv. catbdc at 85 °C to achieve PSE into UiO-66.19 This gave a UiO-66 derivative that contained ~34% catbdc and ~66% bdc ligand. The metalation of the catechol functionality in UiO-66-CAT was conducted using aqueous K₂CrO₄ under acidic conditions (pH = 3). After incubation...
at room temperature (1 h) the pale yellow UiO-66-CAT changed to a dark brown color. Similarly, an aqueous solution of Ga(NO$_3$)$_3$($\text{H}_2\text{O}$)$_x$ was used to achieve metalation with Ga(III). After metalation, the MOFs were isolated by centrifugation, washed extensively with deionized water and MeOH, and dried under vacuum.

The MOFs formed as nanocrystallites ~150 nm on an edge, with an octahedral morphology. The crystallinity of the MOFs did not change upon PSE or metalation as evidenced by the PXRD patterns as shown in Fig. 2a. Scanning electron microscopy (SEM) images showed that the morphology and crystal size of UiO-66-CrCAT and UiO-66-GaCAT were also unchanged from the parent UiO-66 material (Fig. S1 and S2, ESI†). The characteristic M(III) signals were detected using energy dispersive X-ray spectroscopy (Fig. S1, ESI†).

The UV-visible spectroscopy of the MOFs was altered upon PSE and metalation as illustrated in Fig. 2b. The diffuse reflectance of samples was measured and the reflectance values were subjected to the Kubelka-Munk function (1 − $R^2$/2R) to quantify the light absorption ability of samples. H$_2$bdc derivatives with electron donating functionality such as NH$_2$, OH, and SH are known to increase the HOMO level of H$_2$bdc. Thus, UiO-66-CAT is expected to absorb some visible light as a result of the catechol groups. A color change to dark brown was observed upon metalation with Cr(III). As expected, Cr(III) binding to catechol results in the generation of ligand-to-metal charge transfer (LMCT). A similar color change was not observed upon metalation with Ga(III), as expected for this closed-shell ion.

X-ray photoelectron spectroscopy (XPS) of UiO-66-CrCAT and UiO-66-GaCAT was carried out to determine the oxidation states of Cr and Ga. The 2p orbital information was obtained and each spectrum exhibits two peak contributions. Chromium oxide (Cr$_2$O$_3$) and gallium oxide (Ga$_2$O$_3$) were selected as references for both UiO-66-M(III)CATs. UiO-66-CrCAT shows two peaks at 586.10 eV and 576.58 eV corresponding to 2p$_{3/2}$ and 2p$_{1/2}$ binding energies, respectively. These values vary with energy levels in Cr$_2$O$_3$ (586.13 eV and 576.33 eV). This indicates that the Cr(III) in K$_2$CrO$_4$ was reduced to Cr(III) upon metalation, as previously observed. The XPS for UiO-66-GaCAT also consists of two peaks at 1144.79 eV and 1117.89 eV corresponding to 2p$_{3/2}$ and 2p$_{1/2}$ energy levels, respectively. These values match well to binding energies in Ga$_2$O$_3$ (1144.67 eV and 1117.79 eV). Therefore, XPS of UiO-66-CrCAT and UiO-66-GaCAT confirm the trivalent oxidation state of Cr and Ga in these MOFs.

These M(III)-monocatecholato functionalized MOFs were investigated for their photocatalytic CO$_2$ reduction activity. The MOFs were introduced into a mixed solution of 4 : 1 (v/v) MeCN and TEOA, which contained BNAH (0.1 M). In this photocatalytic reaction, BNAH serves as a reductant for CO$_2$ to produce carbonaceous radicals and TEOA acts as a sacrificial base to capture protons from BNAH. The product solutions were found to consist of water, ethyl acetate, MeCN, and HCOOH. The photocatalytic activity of each UiO-66-M(III)CAT is shown in Fig. 3a. Turnover numbers were calculated from the amount of HCOOH produced versus the number of M(III)-catecholato sites in each MOF. Turnover numbers were calculated as 11.22 ± 0.37 for UiO-66-CrCAT and 6.14 ± 0.22 for UiO-66-GaCAT, respectively. UiO-66-CrCAT and UiO-66-GaCAT produced 51.73 ± 2.64 μmoles and 28.78 ± 2.52 μmoles of HCOOH from CO$_2$ photocatalysis, respectively (6 h of visible light irradiation). These numbers indicate that each Cr-catecholato species catalyzed the conversion of ~11 CO$_2$ molecules, while each Ga-catecholato species catalyzed the conversion of ~6 CO$_2$ molecules over the 6 h reaction time. UiO-66-CrCAT proved to be a more efficient catalyst than UiO-66-GaCAT under these reaction conditions. Both UiO-66-M(III)CATs produced negligible amount of H$_2$ and CO that can be
generated from photocatalysis of CO₂ in the presence of TEOA and BNAH. This indicates that metalated catecholato species are suitably selective for CO₂ reduction to formate.

Both MOFs were tested over three catalytic cycles to investigate the stability and reusability of the MOF photocatalysts. Samples were recovered by centrifugation, washed with copious amounts of MeOH, and activated under vacuum after each cycle. The numbers of M(III)-catecholato sites were also redetermined for each cycle to obtain accurate turnover numbers. The catalytic activities of both MOFs were relatively unchanged over the three cycles (Fig. 3a and Fig. S4, ESI†). However, a small amount of M(III) ions leached from the MOFs based on an decreasing M(III)/Zr(IV) ratio as determined by ICP-MS (Table S1, ESI†) after each reaction. The photocatalysis results in Fig. 3a were reproducible based on findings from three independent samples (Fig. S5, ESI†). Quantum yields for both UiO-66-M(III)CAT MOFs were obtained under monochromatic light irradiation using a band-pass optical filter (450 nm). UiO-66-CrCAT showed a higher quantum yield value (1.83 ± 0.16%) when compared to UiO-66-GaCAT (1.17 ± 0.11%). The Fe(III) metalated UiO-66-CAT was also prepared following a previous report. Under identical photocatalytic conditions, UiO-66-FeCAT (Fe : Zr = 0.27, ~80% of catbdc metalated) produced little HCOOH (147 μmoles, Table S2, ESI†). The redox potential for Fe(III) is not suitable (0.77 V vs. SHE) for CO₂ reduction (unlike Cr(III) and Ga(III)), and hence this MOF derivative is not a suitable photocatalyst.

The use of UiO-66-CAT prior to metalation as a photocatalyst did not produce HCOOH as measured by GC-MS (and ¹³C NMR, see below). This rules out the catbdc ligand alone or the Zr₆ SBU clusters as the catalytic sites for reduction. UiO-66-CAT is not suited to accept photo-generated electrons from the catbdc ligand because the redox potential of Zr₆ SBU is higher than the LUMO of bdc linkers. The control reactions with UiO-66-CAT and UiO-66-GaCAT showed a higher quantum yield value (1.47 ± 0.16%) when compared to UiO-66-GaCAT (1.17 ± 0.11%). The Fe(III) metalated UiO-66-CAT was also prepared following a previous report. Under identical photocatalytic conditions, UiO-66-FeCAT (Fe : Zr = 0.27, ~80% of catbdc metalated) produced little HCOOH (147 μmoles, Table S2, ESI†). The redox potential for Fe(III) is not suitable (0.77 V vs. SHE) for CO₂ reduction (unlike Cr(III) and Ga(III)), and hence this MOF derivative is not a suitable photocatalyst.

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in the organic linkers was markedly decreased upon metalation, suggesting that charges were transferred to other sites in the MOFs. The decreases in emission intensity were different for UiO-66-CrCAT and UiO-66-GaCAT, suggesting that the metalted catbdc centers are the acceptors. This indicates that LMCT occurred between the catechol units and metal elements, as expected. In particular, UiO-66-CrCAT quenched ~80% of the photo-generated charges in catbdc and this value is close to the ratio of Cr-bound catechol ligands in UiO-66-CrCAT. This increased electron transfer ability may explain the greater photocatalytic efficiency of UiO-66-CrCAT over UiO-66-GaCAT. The charge accepting ability of these trivalent ions are expected to be quite different due to differences in their outer shelf electronic configurations (Cr(III) [Ar]3d3 versus Ga(III) [Ar]3d10). More energy is needed to accept electrons for Ga-species because the redox potential of Ga(III)/Ga(II) is higher than Cr(III)/Cr(II). This is consistent with the ~2 x higher turnover number demonstrated by UiO-66-CrCAT when compared to UiO-66-GaCAT. Moreover, lifetimes of solid-state fluorescence, obtained by time-correlated single photon counting (TCSPC), confirmed that charge transfer between catbdc ligand and metals occurred through a LMCT mechanism (Fig. 4b, see details in ESI†). This result also suggests that UiO-66-CrCAT holds charges longer than UiO-66-GaCAT for possible electron transfer to CO2.

The catalytic ability with respect to turnover frequency (TOF, h\(^{-1}\)) of the UiO-66-M(III)CAT MOFs were compared to other catalytic systems (Tables S4–S6, ESI†). The turnover frequency of UiO-66-CrCAT (1.87 h\(^{-1}\)) and UiO-66-GaCAT (1.02 h\(^{-1}\)) were substantially greater than many reported heterogeneous systems that produce formate or formic acid as the photoproduct (Table S4, ESI†). In contrast, the TOF of these MOFs was lower than that of many homogenous systems reported (Table S5, ESI†); however, the MOFs have the advantage of being both recyclable and not requiring an exogenous photosensitizer, which are both shortcomings of the homogenous systems reported. Therefore, the MOF catalysts reported here balance the advantages of existing heterogeneous and homogenous photoreduction catalysts. In addition, the UiO-66-M(III)CAT MOFs showed good photocatalytic ability when compared to other MOF-based CO2 reduction photocatalytic systems studied to date (Table S6, ESI†). When compared to other MOFs that do not use an added exogenous photosensitizer, TOF values for the UiO-66-M(III)CAT MOFs are noticeably better than previously studied MOFs that generate formate from CO2.

New MOF CO2 reduction photocatalysts were prepared from isolated monocatecholato metal sites that were active under visible light irradiation. The catbdc substituted UiO-66-CAT generated electron–hole pairs under visible light without light sensitizers. Both UiO-66-M(III)CAT-derivatives reduced CO2 to HCOOH with the aid of BNAH and TEOA. The Cr-derivative showed better efficiency than Ga due to its open shell electronic structure. Further optimization of these systems may produce materials with the advantages of heterogeneous systems, but with activities comparable to homogenous reduction catalysts.

These experiments were supported by a grant from the Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-08ER46519 (Y. L., H. F., S. M. C.). Additional support for XPS, PL, and TCSPC studies were provided to S. K. and J. K. K. by the Korea Center for Artificial Photosynthesis (2009-093381).

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