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**Permalink**
https://escholarship.org/uc/item/53p8m0g2

**Journal**
ACS Catalysis, 5(9)

**ISSN**
2155-5435

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**Publication Date**
2015-09-04

**DOI**
10.1021/acscatal.5b01306

Peer reviewed
Directed Assembly of Cuprous Oxide Nanocatalyst for CO₂ Reduction Coupled to Heterobinuclear ZrOCo⁺ Light Absorber in Mesoporous Silica

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Supporting Information

ABSTRACT: Hierarchical assembly of an oxo-bridged binuclear ZrOCo⁺ light absorber unit coupled to a cuprous oxide nanocluster catalyst for CO₂ reduction on mesoporous silica support is demonstrated. The proper positioning of the Cu oxide cluster was achieved by photodeposition of a [Cu(NCCH₃)₄]²⁺ precursor by visible light excitation of the ZrOCo charge transfer chromophore, followed by mild calcination at 350 °C. Illumination of the CuO₂-ZrOCo unit so formed in the presence of a diethylamine electron donor resulted in the reduction of surface Cu centers to Cu⁰ as demonstrated by the characteristic infrared band of adsorbed _¹³CO probe molecules at 2056 cm⁻¹. For analogous CuO₂-TiOCo⁺ units, the oxidation state makeup of the surface Cu centers was dominated by Cu¹, and the Cu⁰, Cu², and Cu³ composition was found to depend on the wavelength of MMCT excitation. The observed strong dependence of the CO₂ photoreduction yield on the oxidation state of the surface Cu centers directly proves that CO₂ is reduced on the CuO₂ surface, thus establishing that the ZrOCo⁺ unit functions as light absorber, donating electrons to the CuO₂ catalyst on whose surface CO₂ is reduced.

KEYWORDS: photodeposition, carbon dioxide reduction, artificial photosynthesis, photocatalysis, copper oxide catalyst, heterobinuclear light absorber

1. INTRODUCTION

Efficient coupling of light absorber and multielectron catalysts for carbon dioxide reduction or water oxidation is a critical, and currently among the most challenging, task for developing viable artificial photosystems for renewable fuel generation. For visible light driven CO₂ reduction, typical examples of molecularly defined light absorber-catalyst assemblies are organo Ru or metallo-porphyrin complexes coupled via hydrocarbon linkage or amide bridge to a Re bipyridine tricarbonyl catalyst.¹⁻⁴ Exploring an alternative to organo-metallic systems because of the durability challenge of soft matter, we are pursuing an all-inorganic materials approach using oxo-bridged heterobinuclear units as molecularly defined light absorbers anchored on silica nanoparticle surfaces.⁵ Recent demonstration of a heterobinuclear ZrOCo⁺ light absorber coupled to an Ir oxide nanocluster catalyst on mesoporous silica support for the direct photoconversion of CO₂ by H₂O to CO and O₂ was made possible by a photodeposition method that allowed the coupling of the Co donor center to the IrO₂ catalyst.⁵ The construct affords remarkably efficient charge transfer from the Co center of the Zr³⁺OCo⁴⁺ → Zr⁵⁺OCo³⁻ excited charge-transfer unit to the IrO₂ cluster, thereby driving the multistep oxidation of H₂O to O₂. By analogy, this photodeposition method might offer a synthetic route for coupling a nanocluster catalyst for CO₂ reduction to the Zr acceptor center with the goal of photoreducing CO₂ beyond two-electron transfer products to four, six, or more highly reduced liquid products such as low alcohols.

Because of their robustness, catalysts in the form of inorganic particles are of special interest. Electrochemical CO₂ reduction at metallic Cu electrodes is known to produce a series of more deeply reduced C₁ (mainly methane or methanol) and C₂ (mainly C₂₂ hydrocarbon products).⁶⁻⁸ Rapidly growing research activity in this area has led to a series of reports regarding factors that influence product distribution or lowering of the (still high) overpotential, specifically surface morphology, nanostructure, oxidation/reduction pretreatment, and oxidation state of surface Cu centers.⁹⁻¹⁰ As a consequence, the activity and selectivity of CO₂ reduction have markedly improved over the past several years. Particularly promising and relevant to our approach are Cu oxide based particles as multielectron catalysts. Cuprous oxide clusters either deposited on photocatalytic particles or as stand-alone photocatalysts have been reported to afford reduction of CO₂ to formaldehyde and even...
methanol.\textsuperscript{17,18} While barely explored in light driven assemblies, such cuprous oxide nanoclusters hold promise for lowering overpotentials for CO\textsubscript{2} activation and extending the degree of multielectron reduction.

In this work, we demonstrate photodeposition of 3 nm sized cuprous oxide nanoclusters (abbrev. Cu\textsubscript{0},O\textsubscript{y}) adjacent to binuclear units ZrOCo\textsuperscript{II} or TiOCo\textsuperscript{II} anchored on the silica pore surfaces of SBA-15. The oxidation state of surface Cu, determined by the infrared mode of adsorbed CO, can be controlled by reduction of the Cu\textsubscript{0} cluster upon metal-to-metal charge-transfer state (MMCT) of the binuclear light absorber. The observed strong dependence of the yield of CO\textsubscript{2} photoreduction on the oxidation state of surface Cu confirms that the heterobinuclear unit functions as a light absorber, donating electrons to the Cu\textsubscript{0},O\textsubscript{y} catalyst on whose surface catalytic CO\textsubscript{2} reduction takes place.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Reagents used were zirconocene dichloride ([ZrCp\textsubscript{2}Cl\textsubscript{2}] > 99%, Strem), titanocene dichloride ([TiCp\textsubscript{2}Cl\textsubscript{2}] > 97%, Aldrich), anhydrous cobalt chloride (>98%, Fluka), triethylamine (TEA, > 99%, Aldrich), diethylamine (DEA, > 99.5%, Aldrich), triethylamine (TEA, > 99%, Aldrich), dichloride ([TiCp\textsubscript{2}Cl\textsubscript{2}], > 97%, Aldrich), acetonitrile (>99.9%, Honeywell), \textsuperscript{13}C-carbon dioxide (99%, Cambridge Isotope lab, Inc.), \textsuperscript{13}C-carbon monoxide (99%, Aldrich), Pluronic P-123 (Aldrich), concentrated hydrochloric acid (37%, Aldrich), and tetrakis acetonitrile copper(I) hexafluorophosphate \textsuperscript{[Cu(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}}.

Solvents were dehydrated with 3 Å molecular sieves for acetonitrile, TEA, and DEA and 4 Å molecular sieves (Linde) for anhydrous methylene chloride for at least 72 h. Approximately 5 g of molecular sieves activated at 170 °C under a vacuum for 24 h were used per 100 mL of solvent. Acetonitrile, TEA, and DEA liquids were purged with nitrogen for 1 h and stored in a N\textsubscript{2} glovebox before use. Anhydrous cobalt chloride was heated at 120 °C under a vacuum for 16 h before use in order to obtain an air-free sample. DEA for CO\textsubscript{2} reduction experiments was placed in a Schlenk flask and frozen in liquid nitrogen, evacuated, and allowed to thaw. This process was repeated three times to completely degas DEA. \textsuperscript{[Cu(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} and \textsuperscript{[ZrCp\textsubscript{2}Cl\textsubscript{2}] and [TiCp\textsubscript{2}Cl\textsubscript{2}] were kept in a N\textsubscript{2} glovebox to avoid water contamination.

2.2. Synthesis of ZrOCo SBA-15 and TiOCo SBA-15. Mesoporous silica SBA-15 was synthesized according to the method used in previous reports.\textsuperscript{19,20} Both binuclear ZrOCo and TiOCo units were assembled in the pores of SBA-15 by reaction of the tetrahedral complex \textsuperscript{[Co\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}]} on the nanopore surface of Zr-SBA-15 and Ti-SBA-15, respectively.\textsuperscript{5,21,23} Briefly, Zr or Ti acceptor metal is first covalently attached to the silanol surface using a metallocene precursor (zirconocene dichloride or titanocene dichloride) in the presence of triethylamine, whose function is to partially deprotonate surface silanol groups.\textsuperscript{19–26} Stirring at room temperature in a dry N\textsubscript{2} box yields the as-synthesized tripodally anchored single metal with cyclopentadienyl ligand, which is readily removed by calcination in the air to yield the isolated tetrahedral Ti or Zr center. To yield the o xo-bridged binuclear unit, covalent anchoring of Co as a second metal was conducted with \textsuperscript{[Co\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}Cl\textsubscript{2}]} as a precursor and triethylamine in acetonitrile as reported previously.\textsuperscript{5,21,23} The reaction proceeds selectively due to the enhanced reactivity of the TiOH and ZrOH groups compared to the surrounding surface silanol groups, which are much more abundant, by virtue of the greater acidity of the TiOH and ZrOH groups.\textsuperscript{27} Following each grafting step (Zr (or Ti), Co), calcination was conducted to remove the remaining organic ligand at 550 °C for 12 h (Zr, Ti) and 350 °C for 5 h (Co), respectively. The detailed synthetic method and characterization of ZrOCo\textsuperscript{II} SBA-15 including comprehensive spectroscopic characterization by powder X-ray diffraction (PXRD), extended X-ray absorption fine structure (EXAFS), FT-IR, FT-Raman, optical spectroscopy, and ICP analysis were described in detail in our previous papers.\textsuperscript{5,21–23} Specifically, ICP analysis gave 1.0 ± 0.1 mol % Zr and 0.7 ± 0.1 mol % Co, which is within uncertainties close to the values obtained for the previously published ZrCo SBA-15 samples.\textsuperscript{23} Because the intensity of the MMCT absorption measured by DRS normalized to wafer thickness was also close to the MMCT intensity of the previously synthesized samples,\textsuperscript{23} we conclude that the ratio of binuclear ZrOCo units to isolated Zr or Co centers is the same within uncertainty as for the previous sample. In that case, curve fitting analysis of EXAFS measurements of the Zr and Co K-edge showed that the majority (at least 80%) of all Zr centers form a binuclear unit with Co, while all Co centers are bound to Zr.\textsuperscript{23}

2.3. Photochemical Deposition of Cu\textsubscript{0},O\textsubscript{y}ZeOCo\textsubscript{II}SBA-15 and Cu\textsubscript{0},O\textsubscript{y}TiOCo\textsubscript{II}SBA-15. The precursor \textsuperscript{[Cu\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} for the assembly of copper oxide nanoclusters (abbrev. Cu\textsubscript{0},O\textsubscript{y}) was loaded into SBA-15 pores by adding 100 mg of as-synthesized ZrOCo\textsubscript{II}SBA-15 or TiOCo\textsubscript{II}SBA-15 to 1 mM (19 mg) of \textsuperscript{[Cu\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} dissolved in dichloromethane (50 mL); as-synthesized means that the final calcination step of the ZrOCo\textsuperscript{II} SBA-15 sample was omitted in order to utilize the remaining triethylamine as an electron donor for the Cu photodeposition reaction described below;\textsuperscript{5,21,23} some experiments were conducted with calcined ZrOCo\textsubscript{II} SBA-15 subsequently loaded again with triethylamine, which led to identical photodeposition results. The solution was stirred for 3 h at room temperature in a dark environment inside a N\textsubscript{2} glovebox. The powder was filtered, washed twice with 50 mL of dichloromethane, and dried in a vacuum for 8 h. The as-synthesized powder (5 mg) was pressed with a KBr press (13 mm diameter) under ≤1 ton of pressure for 5 s, which was exposed to air (10 h) for oxidizing the Cu complex to \textsuperscript{[Cu\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} and characterized by in situ FT-IR and UV-DRS. The wafer was subsequently evacuated for 1 h in a homemade stainless steel optical cell equipped with a quartz window. The wafer containing \textsuperscript{[Cu\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} was irradiated at room temperature for 30 min using the 355 nm emission (100 mW cm\textsuperscript{-2}) of a pulsed Nd:YAG laser at 10 Hz (Continuum model Surelite III) or the 458 nm emission (190 mW cm\textsuperscript{-2}) of an Ar ion laser (Coherent model Innova 90C) with the beam expanded to 1 in. diameter. The sample was subsequently calcined at 350 °C for 5 h under a flow of air, resulting in the formation of a greenish pellet containing ZrOCo\textsuperscript{II} or TiOCo\textsuperscript{II} groups and Cu oxide nanoclusters, termed Cu\textsubscript{0},O\textsubscript{y}ZeOCo\textsubscript{II}SBA-15 or Cu\textsubscript{0},O\textsubscript{y}TiOCo\textsubscript{II}SBA-15. Typical Cu\textsubscript{0},O\textsubscript{y} loading was estimated to be 3–4 wt % (Cu/Si ratio) based on ICP measurement, which was in agreement with the analysis of the Cu precursor that remained in solution. The photodeposition of \textsuperscript{[Cu\textsubscript{II}(NCCH\textsubscript{3})\textsubscript{4}]\textsubscript{PF\textsubscript{6}}} was monitored in situ by UV diffuse reflectance spectroscopy (UV-DRS, Shimadzu model UV-2450 spectrometer equipped with an integrating sphere model ISR-2200), in situ FT-IR spectroscopy (Bruker model IF66 V equipped with LN\textsubscript{2} cooled MCT detector Kolmar model KMPV8-1-J2 with an 8 μm band gap), and a UV-Raman spectroscopy system. The
Raman spectrometer was used with a continuous wave intracavity-doubled Ar ion laser (Spectra Physics) operating at 244 nm. Scattered light was collected and directed into a fully automated spectrometer (iHR550, Horiba) after passing through bandpass and edge filters. Spectra were recorded with an open electrode CCD detector (SynapseHoriba, 1024 × 256 pixels). Transmission electron microscopic imaging was conducted with a CM300 instrument, and EDX data were collected on a TitanX instrument of the National Center for Electron Microscopy.

2.4. Photochemical Reduction of CuO2−xZrOCoOxSBA-15 and CuO2−xTiOCoOxSBA-15. The calcined wafer was placed in a home-built stainless infrared vacuum cell equipped with CaF2 windows and mounted in the FT-IR spectrometer. After 3 h of evacuation at room temperature, 0.5 Torr of diethylamine was admitted to the infrared cell. For photoreduction of the Cu oxide nanocluster after calcination, the wafer was reloaded with DEA and irradiated at room temperature using the 355 nm light, laser photolysis (355 nm, 100 mW cm−2) for 3 h or 458 nm emission (190 mW cm−2) for 5 h with the beam expanded to the size of the wafer (1 cm diameter).

2.5. Photochemical CO2 Reduction. The reduced (or nonreduced) CuO2−xZrOCoOxSBA-15 and CuO2−xTiOCoOxSBA-15 wafer (5 mg) was placed in a home-built stainless infrared vacuum cell (volume 3.7 cm3) equipped with CaF2 windows and mounted in the FT-IR spectrometer for in situ monitoring of photocatalysis. After evacuation for 3 h at room temperature, diethylamine (0.5 Torr) and 13CO2 (760 Torr) gas were admitted to the infrared cell. After a 30 min dark period to confirm that no spectral changes occurred in the absence of light, laser photolysis (355 nm, 100 mW cm−2) was conducted at room temperature over a period of 5 h and infrared spectra recorded at regular intervals. The spectral resolution was 0.25 cm−1. To identify the origin of any carbon containing product, all experiments were carried out using isotopically labeled 13CO2. Gas phase 12CO and 13CO can readily be differentiated by the characteristic ro-vibrational bands in the 2200−2000 cm−1 region.

3. RESULTS

3.1. Photodeposition of CuO2−x Coupled to Binuclear Light Absorber Unit. Our approach for assembling a Cu oxide nanocluster coupled to the Zr center of the ZrOCo unit is based on recent precedents for the coupling Ti or Ir precursors to other metal centers anchored on a silica nanopore surface through redox reactions. For example, we have shown that a TiIII precursor undergoes spontaneous redox coupling with CrVI centers anchored on mesoporous silica surfaces to form TiO3CrV units. Similarly, the dark redox reaction of an IrIII precursor with anchored CrVI centers was found to form CrOIrIV units. Subsequent calcination at mild temperature gave an IrO2 nanocluster coupled to the Cr center. Reaction of an IrIII precursor with the TiO3CrV unit mentioned above followed by calcination yielded a TiOIrIV group coupled to an IrO2 catalyst. By analogy, Ir oxide clusters coupled to Co centers of ZrOCo units were made by a photoinduced version of this chemistry, namely excitation of ZrOCo centers to generated transient CoIII that couples with an IrIII precursor, followed by calcination to obtain an Ir oxide nanocluster coupled to Co3. Building on these precedents, we proposed here that assembly of a Cu oxide nanocluster coupled to the Zr center of a ZrOCo unit should be feasible by generating transient ZrIII upon photoexcitation of ZrO3CoV in the presence a reducible CuII precursor, followed by mild calcination. Figure 1 shows the optical spectra of ZrO2−xZrOCoOxSBA-15 after loading of [CuI(NCCH3)4]+ (trace 1, black) and after exposing to air for 1 h (trace 2, red) and 10 h (trace 3, blue). Inset: Difference spectrum trace (3−1). The sample wafer (5 mg, loaded with 0.8 mg [CuI(NCCH3)4]PF6) was held in a vacuum.

Figure 1. UV−vis DRS of ZrOCoOxSBA-15 after loading of [CuI(NCCH3)4]+ (trace 1, black) under a N2 atmosphere and after exposing the sample to air for 1 h (trace 2, red) and 10 h (trace 3, blue). Inset: Difference spectrum trace (3−1). The sample wafer (5 mg, loaded with 0.8 mg [CuI(NCCH3)4]PF6) was held in a vacuum.

CoOxSBA-15 after loading of the [CuI(NCCH3)4]+ complex (trace 1, black). In order to oxidize the CuI complex to CuII, the sample was exposed to air for 1 h (trace 2, red) and a total of 10 h (trace 3, blue). As we reported previously, loading of the [CuI(NCCH3)4]+ complex into mesoporous silica and evacuation of the sample at room temperature results in CuI centers in the silica nanopores that remain coordinated with acetonitrile ligands. Growth of the very broad CuII d−d band (2E →2T2 transition) with a maximum close to 800 nm is observed, indicating a distorted octahedral coordination of the CuII center.30−33 The difference spectrum (Figure 1 inset) shows the emerging CuII band most clearly, although the profile is perturbed by the ligand field bands of CoII. The oxidation of the Cu center is further confirmed by comparison of the in situ FT-IR spectra in the ν(C≡N) region of the CH3CN ligands attached to anchored CuIII (2331 and 2302 cm−1)19 and CuII, which are red-shifted to 2322 and 2296 cm−1, as shown in Figure 2.

Figure 2. FT-IR spectra of ZrOCoOxSBA-15 upon loading of [CuI(NCCH3)4]+ (trace 1, black) and after exposing to air for 10 h (trace 2, red). The sample (5 mg wafer loaded with 0.8 mg [CuI(NCCH3)4]PF6) was held under a vacuum.

Illumination of the ZrO3CoV → ZrIIIOCOIII MMCT absorption of this CuII loaded ZrOCo SBA-15 material at 355 nm (100 mW cm−2) resulted in the photodeposition of the Cu centers under reduction to CuI. As can be seen from UV−vis DRS traces in Figure 3a recorded before (trace 1, black) and after 1 h illumination (trace 2, red), the CuII d−d absorption around 800 nm and the CuI charge transfer transition decrease under a concurrent rise of the 3d5→ 3d4s4 absorption of CuI.
as manifested by an absorbance increase around 550 nm and shorter wavelengths. In these experiments, preloaded trimethylamine was used as an electron donor. The spectral changes indicate electron transfer from Zr centers to Cu, resulting in the reduction of CuII to CuI. No absorbance loss at 800 nm and hence no reduction of CuII was observed when the photodeposition process was attempted with single metal (Zr or Co) SBA-15 or with bare SBA-15 (Figure S1). Hence, the results demonstrate that the reduction of CuII is driven by light absorbed by the ZrOCoII chromophore, which extends from the UV into the visible spectral region with an onset around 550 nm. Photoconversion of CuII to CuI was also achieved when exciting the TiOCo MMCT absorption at 458 nm (190 mW cm$^{-2}$) in the presence of anchored CuII, as shown in Figure 3b. Growth of infrared bands of free, physisorbed acetonitrile at 2942, 2265, 1443, 1400, and 1375 cm$^{-1}$ in the experiments with ZrOCo and TiOCo (Figure S2a and b, respectively) signals detachment of CH$_3$CN ligands from Cu centers during the photodeposition process, although some residual CH$_3$CN remains coordinated as indicated by the bands at 2318 and 2292 cm$^{-1}$.

The CuII$\rightarrow$CuI oxidation state conversion upon photodeposition was further confirmed by UV−Raman spectroscopy. The broad absorption band of the symmetric CuOCo mode with a maximum at 484 cm$^{-1}$ observed for ZrOCoII SBA-15 after loading and air oxidation of the Cu precursor complex (Figure S3a, trace 1, black) agrees exactly with the UV−Raman spectrum of a powder of CuO shown in Figure S3b, trace 3, black. Illumination of the ZrOCoI$^2$ SBA-15 sample at 355 nm for 1 h results in a red shift of the band by about 5 cm$^{-1}$ (Figure S3a, trace 2, red). The shift is close to the one measured for CuO powder shown in Figures S3b, trace 4 (red), consistent with the reduction of a substantial fraction of CuII centers to CuI.

Following the photodeposition process, mild calcination at 350 °C for 5 h under air flow resulted in the formation of Cu$_2$O clusters as shown by the analysis of high angle annular dark field (HAADF) images recorded in the scanning transmission electron microscopy (STEM) mode and energy dispersive X-ray (EDX) measurements. The results are presented in Figure 4 for ZrOCoI$^2$SBA-15 and Figure S4 for TiOCoII$^2$SBA-15. FT-IR spectra confirmed that no acetonitrile or triethylamine donor remained in the SBA-15 after calcination. The small bright spots (example marked by dotted circle) are copper oxide nanoclusters based on EDX spot analysis of five different bright spots. The EDX signal for dark areas of the mesoporous channels between the bright spots in the HAADF image of Figure 4 (Figure S4) was close to the noise level, which confirmed the assignment of the bright spots to Cu containing clusters. Histogram analysis using a digital micrograph (Gatan Microscopy Suite) program revealed an average Cu$_x$O$_y$ cluster size of 3.0 ± 0.4 nm (Figure S5).

Figure 3. (a) UV−vis DRS of ZrOCoII$^2$SBA-15 loaded with [CuI(NCCH$_3$)$_4$]$^+$ after air oxidation for conversion to CuII (trace 1, black), followed by 1 h of photodeposition at 355 nm (100 mW cm$^{-2}$; trace 2, red). Inset: Difference spectrum (2 − 1). Sample wafer was 5 mg; [CuI(NCCH$_3$)$_4$PF$_6$] loading, 0.8 mg. (b) Same experiment with TiOCoII$^2$ SBA-15 showing the spectrum before (trace 1, black) and after (trace 2, red) photodeposition at 458 nm irradiation for 1 h (190 mW cm$^{-2}$). Samples were held under a vacuum.

Figure 4. (a) High angle annular dark field (HAADF) images of Cu$_2$O−ZrOCoII SBA-15 and (b) EDX spectra of Cu bright spot and dark mesopore section of image a. Au signals are due to the use of a gold grid.

3.2. Photochemical Reduction of Cu$_2$O$_x$ Clusters. The electronic structure (oxidation state) of the Cu centers at the Cu oxide nanocluster surface is critical for the reduction activity and possibly the selectivity of the CO$_2$ multielectron catalyst. X-ray photoelectron (XPS) and X-ray Absorption Near Edge Structure (XANES) spectroscopy are typically the preferred methods for determining oxidation states of metal containing catalysts, with XPS exhibiting surface sensitivity. However, these methods do not allow selective probing of the oxidation state of metal centers in the top surface layer of the cluster directly exposed to the reactants. Here, infrared spectroscopy of adsorbed CO molecules provides the desired surface selectivity.
To unambiguously identify gas adsorbed carbon monoxide molecules, isotopically labeled $^{13}$CO was used for these experiments.

As shown in Figure 5, spectra of adsorbed carbon monoxide are drastically different for Cu oxide nanoclusters of Cu$_x$O$_y$-ZrOCo SBA-15 after calcination (Figure 5a) and following photoreduction at 355 nm (100 mW cm$^{-2}$) for 3 h. The SBA-15 wafer was 5 mg with 3.4 wt % Cu loading.

ZrOCo SBA-15 after calcination (Figure 5a) and following photoreduction at 355 nm (100 mW cm$^{-2}$) for 3 h using DEA (0.1 Torr) as an electron donor (Figure 5b). For the calcined clusters, the adsorbed $^{13}$CO profile observed upon loading of 100 Torr gas is, as expected, dominated by Cu$^{II}$ surface sites (2086, 2095, and 2107 cm$^{-1}$). A weak shoulder at 2066 cm$^{-1}$, most clearly seen in Figure 5a at 10 Torr loading, indicates the presence of Cu$^{I}$ centers on the clusters’ surface as well as some isolated Cu$^{I}$ centers on the silica nanopore surface by a shoulder at 2130 cm$^{-1}$. In light of the several-fold larger extinction coefficient of the infrared band of CO adsorbed on Cu$^{I}$ compared to Cu$^{II}$, the spectrum before photoreduction confirms the dominance of Cu$^{II}$ on the nanocluster surface. After 355 nm illumination, fully reduced Cu$^{0}$ is the only detectable surface site as shown by the characteristic CO band at 2056 cm$^{-1}$ (Figures 5b and 7a), indicating efficient photoreduction of the cluster by the ZrOCo charge-transfer chromophore.

Photochemical reduction of the Cu$_x$O$_y$ clusters coupled to TiOCo units was conducted at two wavelengths, 355 and 458 nm, in order to explore the photon energy dependence of the process. According to Figures 6a and 7a, the occupancy of CO adsorbed on the various Cu sites of Cu$_x$O$_y$-TiOCo SBA-15 after calcination very closely resembles that of Cu$_x$O$_y$-ZrOCo SBA-15 samples. By contrast, the photoreduced catalyst prepared by illumination of the TiOCo unit shows very different Cu oxidation state distributions. For 355 nm irradiation (100 mW cm$^{-2}$, 3 h, DEA as electron donor), a broad band with a maximum at 2066 cm$^{-1}$ observed upon 100 Torr $^{13}$CO loading indicates that Cu$^{I}$ centers dominate the surface layer of the catalyst. At lower loadings of 1 and 10 Torr, the adsorbed $^{13}$CO band profile is clearly asymmetric with a sizable component on...
the low frequency side. According to spectral deconvolution shown in Figure S6, at 1 Torr loading (Figure 56a), CuII and Cu0 centers are the dominant adsorption sites on the CuO2 cluster surface, taking into account that the extinction coefficient of CO on Cu0 is larger than that for CuII or Cu0. An increase of the loading to 10 Torr results in continued adsorption on CuII and Cu0 sites, while no further adsorption is observed for the CuII sites, presumably because the latter are already saturated at 1 Torr loading. An increase of the carbon monoxide pressure to 100 Torr results in exclusive additional adsorption on surface CuI sites (Figure S6c). Therefore, the dominant Cu sites on the cluster surface are CuI, with significantly smaller reservoirs of CuII and Cu0 centers. On the other hand, when conducting the photoreduction of CuO2-TiOCo SBA-15 at longer wavelengths (458 nm, 190 mW cm−2, 5 h), CuI are the only surface sites observed at all CO loading levels, as shown in Figure 7b. We conclude that comparison with the 355 nm result reveals a significant wavelength dependence of the photoreduction process, with the more reduced Cu0 surface centers only formed at the higher photon energy.

While infrared bands of adsorbed CO afford assessment of the oxidation states of Cu centers at the surface, UV−vis spectra confirm photoreduction across the bulk of the Cu oxide cluster by decrease of the 800 nm Cu2+ (d−d) and the 350 nm charge-transfer band33 under concurrent growth of the visible CuO absorption with the onset at 630 nm (Figure S6).34

3.3. Photochemical Reduction of CO2. To demonstrate carbon dioxide reduction at the CuO2 cluster driven by the photoexcited ZrOCoII MMCT chromophore, and to investigate the influence of the surface oxidation state of the copper oxide on the photocatalysis, CO2 reduction at CuO2-ZrOCoII units in SBA-15 was conducted using samples that were, or were not, photoreduced prior to CO2 photocatalysis. As shown in Figure 8, trace 1, for the case of CuO2-ZrOCoII SBA-15 samples that were not subject to photoreduction after calcination, a broad absorption at 1624 cm−1 upon loading of 760 Torr 13CO2 and 0.5 Torr DEA indicates formation of the familiar carboxylate type structure of weakly adsorbed carbon dioxide on metal oxide surfaces.44−46 By contrast, loading of CuO2-ZrOCoII SBA-15 material with 13CO2 that was first photoreduced gave an additional infrared band at 1656 cm−1, as shown in Figure 8, trace 2. The corresponding band in the case of 12CO2 loading was at 1682 cm−1 (inset of Figure 8). We attribute the new band to carbon dioxide molecules adsorbed on Cu0 surface sites featuring a carboxylate structure, consistent with infrared spectra of CO2 adsorbed on metallic Cu surfaces.47

Illumination at 355 nm (100 mW cm−2) resulted in consumption of the adsorbed carbon dioxide species for the CuO2-ZrOCoII SBA-15 sample that was subject to prior photoreduction. Figure 9 shows the depletion of the 1682 cm−1 12CO2 species during the first few minutes of photolysis (the experiment with 13CO2 is shown here because there is less overlap with the residual H2O band at 1635 cm−1 than in the case of 13CO2). In prolonged photolysis experiments in the presence of 760 Torr CO2, the adsorbed 1682 cm−1 species is continually replenished, which results in a steady state concentration of the surface species. Illumination at 355 nm (100 mW cm−2) of a sample that was subject to prior photoreduction resulted in the formation of carbon monoxide as indicated by the absorbance growth of the ro-vibrational bands of gas phase 13CO in the region 2075 to 2050 cm−1 over a period of 5 h (Figure 10a). The growth kinetics of the 13CO product shown in trace 1 (red) of Figure 10b is close to linear with time, with 59.2 nmol CO produced over the 5 h photolysis period. To minimize the systematic error of intensity measurements caused by the smaller natural line width of CO ro-vibrational bands (0.01 cm−1) compared to the resolution of the spectrometer (0.25 cm−1), integrated intensities were used. The growth is about 3 times faster than an otherwise identical CO2 reduction experiment with a CuO2-ZrOCoII SBA-15 sample that was not subject to prior photoreduction treatment (Figure 10b, trace 2 (black)). The rate of CO2 reduction upon continued photocatalysis using this sample will eventually approach that of the prereduced CuO2-ZrOCo as surface Cu centers are gradually reduced to the Cu0 state. For illumination at 458 nm (190 mW cm−2) of the CuO2-TiOCoII unit that was photoreduced prior to 13CO2 reduction, 13CO production was 10 times lower than for clusters driven by the ZrOCoII chromophore (Figure 10b, trace 3 (blue)). No CO2 photoreduction was observed under identical illumination conditions for CuO2-ZrOCoII SBA-15 samples which have no ZrOCo units (Figure 10b, trace 4 (green)), demonstrating that direct light absorption by the cuprous oxide...
cluster does not contribute to the observed photocatalysis on a time scale under which the Cu\textsubscript{x}O\textsubscript{y}-ZrOCo\textsuperscript{II} system readily shows CO production. In addition to gas phase carbon monoxide, adsorbed \textsuperscript{13}CO with a maximum at 2056 cm\textsuperscript{-1} was also formed, as can be seen in Figure 11. Hence, the photoproduct adsorbed primarily on the Cu\textsuperscript{0} site, which is the main surface site of prereduced Cu\textsubscript{x}O\textsubscript{y}. The spectra were recorded at a lower resolution of 1 cm\textsuperscript{-1} in order to show more clearly the contribution of the broad bands of adsorbed \textsuperscript{13}CO. For clarity, minor contributions of \textsuperscript{12}CO generated by concurrent photodecomposition of the electron donor DEA were removed by spectral subtraction, shown in Figure S9.

4. DISCUSSION

The observation of photoreduction of surface Cu centers from oxidation state Cu\textsuperscript{II} to Cu\textsuperscript{0} or Cu\textsuperscript{I} upon excitation of the Zr\textsuperscript{IV}OCo\textsuperscript{II} \rightarrow Zr\textsuperscript{III}OCO\textsuperscript{III} MMCT transition demonstrates the functional Cu\textsubscript{x}O\textsubscript{y}-ZrOCo unit in which the transiently reduced Zr acceptor transfers electrons to the nanocluster catalyst. Hence, the photodeposition method introduced in this work provides the proper coupling of the acceptor metal center with the catalyst cluster. While the precise atomic structure of the coupled Zr acceptor center and Cu oxide cluster is not revealed by the current vibrational and optical spectroscopy measurements, the observed strong dependence of the CO\textsubscript{2} photoreduction yield on the oxidation state of the surface Cu centers directly proves that CO\textsubscript{2} is reduced on the Cu\textsubscript{x}O\textsubscript{y} surface. As expected, no CO\textsubscript{2} reduction is observed at Cu\textsubscript{x}O\textsubscript{y} clusters if the ZrOCo chromophore is absent. Furthermore, the CO\textsubscript{2} reduction yields depend strongly on the chemical identity of the acceptor (Zr versus Ti) and the photolysis wavelength used for MMCT excitation. Hence, these photochemical observations establish that the heterobinuclear unit functions as a light absorber, donating electrons to the Cu\textsubscript{x}O\textsubscript{y} catalyst on whose surface CO\textsubscript{2} is reduced.

Among the studies of metallic Cu nanoparticles and Cu oxide nanoclusters for photo or electrocatalytic reduction of CO\textsubscript{2} reported in the literature,\textsuperscript{6,7,8} the work reported here constitutes one of just a few examples in which the oxidation state of...
surface Cu centers is spectroscopically defined and the relationship to catalytic activity or selectivity investigated. Using Cu L-edge XANES and Auger spectroscopy, Le et al. identified Cu(I) centers as active sites for electrochemical reduction of CO2 to methanol.\textsuperscript{12} Li and Kanan established that Cu(I) and Cu(II) at the surface of an electrocatalyst prepared by two step oxidation/reduction of Cu foil, which were identified by XPS, showed better selectivity to CO and HCOOH than in the absence of the pretreatment.\textsuperscript{9} The coexistence of Cu(I) and metallic Cu was also found beneficial for the selective electrocatalytic reduction of CO2 by Garcia-Esparza et al. using the surface sensitive XPS technique to probe the Cu oxidation state.\textsuperscript{46} Hence, our finding that reduced Cu centers on the CuO/TiO2 nanocluster introduced here points to the selective electrocatalytic reduction of CO2 by Garcia-Esparza et al. Further studies indicate that the size and morphology of the CuO catalyst nanoparticles on TiO2 influence product selectivity, in addition to the specific reaction conditions. For example, CuO functionalized TiO2 particles at very light loading (0.04 wt % Cu) illuminated at lower photon energy gave methane as a major product instead.\textsuperscript{52} CuO crystalline particles as stand-alone visible light absorbing catalysts have been found to exhibit facet selectivity in aqueous media with respect to competing hydrogen generation.\textsuperscript{53} CuO nanoparticles on TiO2, on the other hand, play a different mechanistic role in photodriven CO2 reduction, namely as a p-type semiconductor component forming a p–n heterojunction in the CuO/TiO2 particle.\textsuperscript{54,55} Detailed knowledge of the electronic structure provided by spectroscopy is essential for guiding the preparation of Cu based nanoparticle catalysts for CO2 reduction.

5. CONCLUSIONS

The all-inorganic system for the CO2 reduction half reaction consisting of a heterobinuclear light absorber coupled to a cuprous oxide nanocluster introduced here points to the general utility of metal-to-metal charge-transfer excitation as a method for achieving proper hierarchical arrangement of the photocatalytic assembly. The ability to manipulate the oxidation state of surface Cu centers, with Cu(I) giving the highest photo reduction rates provides direct evidence for the cuprous oxide cluster acting as multielectron catalyst driven by the ZrOCo charge transfer unit. Successful coupling of the binuclear unit with the catalyst nanocluster is further manifested by the strong dependence of the CO2 reduction rate on the nature of the acceptor center (Zr versus Ti) and the photolysis excitation wavelength used. Time-resolved FT-IR experiments are currently in progress for elucidating the detailed mechanism for CO2 reduction on the cuprous oxide catalyst surface. Detection and structural identification of intermediates is expected to provide insights for steering the catalysis to deeper reduction products beyond CO.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01306.

Spectroscopic and electron microscopic data for materials characterization (UV–vis, FT-IR, UV–Raman, HAADF, EDX), and additional photochemical data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical, Geological and Biosciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors acknowledge the support of the National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, which is supported by the U.S. Department of Energy.

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