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Unraveling the Intermediate Species of Co_3O_4 Hollow Spheres for CO_2 Photoreduction by In Situ X-ray Absorption Spectroscopy

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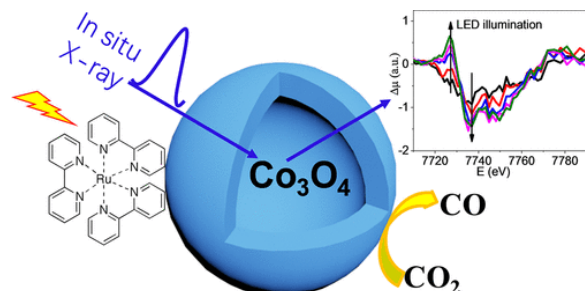
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Abstract



Nanostructured hollow materials have emerged as a promising class of materials for energy conversion and storage. In this work, we report a Co₃O₄ hollow sphere nanostructure that can serve as a CO₂ reduction catalyst to form CO with high selectivity upon visible-light illumination in the presence of a [Ru(bpy)₃]²⁺ molecular photosensitizer. Using in situ X-ray absorption spectroscopy, we not only showed that the Co center in the Co₃O₄ hollow sphere is the active site for CO₂ reduction but also identified a key intermediate species, that is, a reduced Co center, due to electron transfer from the [Ru(bpy)₃]²⁺ photosensitizer when the system can steadily generate CO.

1. Introduction

Efficient conversion of CO₂ to useful chemical fuels is a promising approach that may sustainably and simultaneously address future energy demand and global warming issues.(1–5) Among the various strategies that have been already developed, photocatalytic CO₂ reduction is perhaps the most attractive due to its simplicity and economy of the input energy source.(1,3,6–10) As the reduction of CO₂ is an uphill process with a high energy barrier, an appropriate photocatalyst is required in order for the reduction reaction to occur at a reasonable rate. As a result, diverse photocatalytic systems for CO₂ reduction have been developed in the past decades.(1–5) One class of these photocatalytic systems that have been intensively studied are the homogeneous photocatalysts based on molecular complexes. However, majority of these homogeneous molecular systems that demonstrate high catalytic efficiency with selectivity are the coordination complexes based on precious metals such as Ru, Re, and Ir,(6–11) where the high cost and scarcity of these metals largely prevent their long-term practicality. In addition, these molecular catalysts often suffer from poor photostability during prolonged irradiation as well as the inability for recyclability.(12–15) Due to these reasons, recent focus has geared toward exploring robust heterogeneous catalysts mainly based on semiconductors, evidenced by the large number of semiconductor systems evolved in the past decade.(16–21)

Among the various semiconductor photocatalysts that have been reported, nanostructured hollow materials are among the most promising photocatalysts for CO₂ reduction due to their inherent advantages over their solid structures.(22,23) For example, the hollow-structured photocatalysts, which typically have large specific surface area, can facilitate CO₂ adsorption and provide more active sites for the photocatalytic reaction on both the exterior and interior of the shells.(23) In addition, the hollow structure with the interior cavity may reduce the distance for charge transport and enhance the light absorption due to light scattering and reflection effects in the hollow voids.(24,25) However, the performance of these hollow structure systems for photocatalytic CO₂ reduction in terms of efficiency and selectivity is far from satisfactory.(26,27) Given the distinct benefits to employ hollow structure semiconductors as CO₂ reduction catalysts, such photocatalytic systems are especially ripe targets for further development. Progress in this endeavor will clearly require the fundamental understanding of the underlying mechanisms at the molecular level.

In this paper, we report a Co₃O₄ hollow sphere CO₂ reduction catalyst, which can effectively reduce CO₂ to form CO with high selectivity (88.6%) and activity (quantum efficiency of 0.228%) in the presence of the

[Ru(bpy)₃]²⁺ photosensitizer. Moreover, using in situ X-ray absorption spectroscopy under the standard catalytic conditions, we demonstrated that the Co center in the Co₃O₄ hollow sphere is the active catalytic site that is responsible for CO₂ reduction and identified a key intermediate species (i.e., reduced Co center) when the photocatalytic reaction reaches equilibrium.

2. Methods

2.1. Synthesis of Co-Glycolate and Co₃O₄

0.0582 g of Co(NO₃)₂, 6 mL of isopropanol, 6 mL of ethylene glycol, and 0.2 mL of DI water were mixed in a 30 mL Teflon-lined autoclave under 1 h of magnetic stirring to give a good mixture. The Teflon-lined autoclave was then heated in an oven at 185 °C and maintained at that temperature for 12 h. After that, the obtained purple powders were collected, washed several times with absolute ethanol, and dried at 60 °C for 12 h. The Co₃O₄ hollow spheres were obtained by annealing Co-glycolate at 300 °C for 2 h in air with a ramp rating of 5 °C/min.

2.2. Photocatalytic CO₂ Reduction

[Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) was synthesized following the published literature procedure.⁽²⁸⁾ CO₂ photoreduction was performed in 11 mL glass vials with rubber septa. Each sample was made up to a volume of 4 mL, including a certain amount of Co₃O₄ hollow spheres, 1 mg of [Ru(bpy)₃]²⁺, 0.2 mL of TEOA (triethanolamine), and CH₃CN and H₂O with different volume ratios. The mixture was purged with CO₂ for 15 min before irradiation by 450 nm LEDs at the optimized power (19 mW). The mixture was kept under stirring during the photocatalytic reaction. The amount of CO generated was quantified using a gas chromatograph by analyzing 200 μL of the headspace.

2.3. Characterization

Scanning electron microscopy (SEM) was performed with a JEOL JSM-6510LV operating in the secondary electron mode. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100 operating at 200 KV. Powder XRD data were collected by using a Rigaku Miniflex II XRD diffractometer with Cu Kα radiation. Steady-state and in situ X-ray absorption (XAS) spectra were measured at the beamline 12BM-B at the Advanced Photon Source in Argonne National Laboratory. The conditions for the in situ XAS experiment were 0.5 mg of Co₃O₄, 0.15 mL of TEOA, 0.75 mg of [Ru(bpy)₃]²⁺, 0.57 mL of H₂O, and 2.28 mL of acetonitrile. The amount of CO generated was quantified using an Agilent 490 micro gas chromatograph (5 Å molecular sieve column). GC-MS (Agilent Technologies 6850-5973 with an HP-PLOT Molesieve column) was used for the ¹³C-label experiment.

3. Results and Discussion

The Co₃O₄ hollow spheres were synthesized by annealing the Co-glycolate sphere at 300 °C in air for 2 h. The Co-glycolate sphere was prepared according to the established synthetic protocols.⁽²⁹⁾ The X-ray diffraction (XRD) patterns of annealed samples (Figure 1a) agree well with the standard diffraction data of pure Co₃O₄ (JCPDS card No. 43-1003), indicating the formation of Co₃O₄. The SEM image of Co₃O₄ (Figure 1b) shows sphere-like morphology, which resembles that of Co-glycolate spheres (Figure S1). The low-magnification transmission electron microscopy (TEM) image of Co₃O₄ spheres (Figure 1c) confirmed the hollow structure. The magnified TEM image (Figure 1d) indicates the crystallized phase of the Co₃O₄ hollow spheres which are comprised of small nanocrystals.

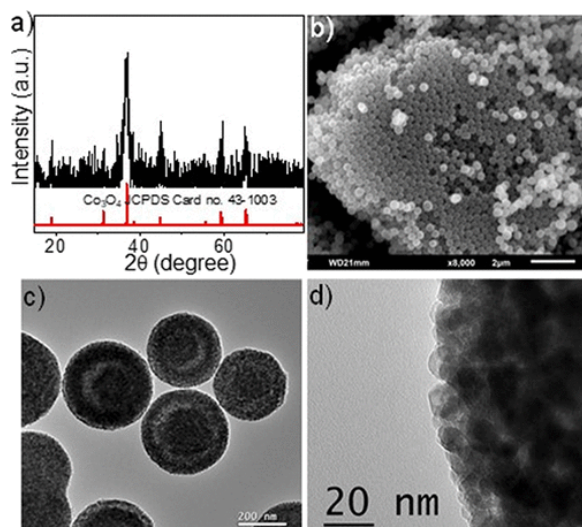


Figure 1. (a) XRD patterns, (b) SEM image, (c) low-magnification TEM, and (d) the magnified TEM images of Co_3O_4 hollow spheres.

In addition to their bulk structure, the local structure of Co_3O_4 nanospheres at the Co center was evaluated using steady-state X-ray absorption spectroscopy (XAS). Figure 2a shows the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra (inset) of Co_3O_4 hollow spheres (powder sample) at the Co K-edge. The edge energy and the pre-edge feature, consistent with literature results,^(30,31) indicate the presence of both $T_d \text{Co}^{2+}$ and $O_h \text{Co}^{3+}$, which is expected for the spinel structure of Co_3O_4 . These results were further supported by the Fourier-transformed EXAFS spectrum in R-space. As shown in Figure 2b, the Fourier-transformed EXAFS spectrum of Co_3O_4 is featured with three peaks, which can be assigned to the convolution of two Co–O bond distances resulting from $T_d \text{Co}^{2+}$ and $O_h \text{Co}^{3+}$ coordination, Co–Co connected by the di- μ -oxo bridge, and Co–Co connected by the mono- μ -oxo bridge. The quantitative analysis of these data using the FEFF model results in a Co–O distance of 1.93 Å and coordination number of 5.33, which is an averaged value from two different Co coordinations, the four Co–Co distances of 2.86 Å connected by the di- μ -oxo bridge, and eight Co–Co distances of 3.36 Å connected by the mono- μ -oxo bridge (Table S1). These results are consistent with previous reports and further confirm the formation of Co_3O_4 via annealing treatment of the Co-glycolate sphere.^(30–32)

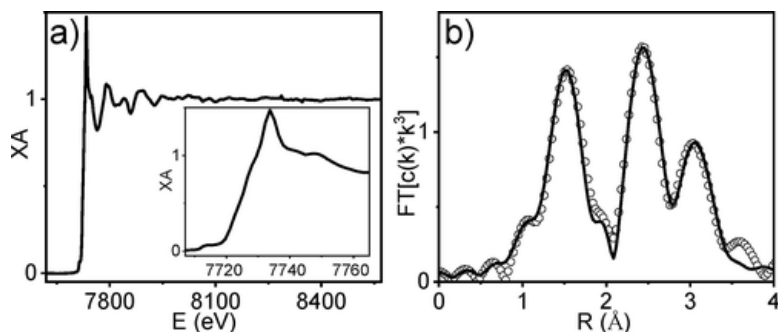


Figure 2. (a) X-ray absorption spectrum of Co_3O_4 hollow spheres (solid sample) at the Co K-edge. The inset shows the XANES spectrum. (b) Fourier-transformed EXAFS spectrum of Co_3O_4 hollow spheres at R-space. The open circles and solid lines are experimental and fitted results, respectively.

The catalytic performance of the prepared Co_3O_4 hollow spheres for CO_2 photoreduction was evaluated in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) as the photosensitizer and TEOA (triethanolamine) as the sacrificial donor under 450 nm LED irradiation. The control experiments that either omit $[\text{Ru}(\text{bpy})_3]^{2+}$, TEOA, or

Co₃O₄ hollow spheres or replace TEOA with TEA (triethylamine) yield a negligible amount of CO, suggesting that these species play critical roles in the CO₂ photoreduction reaction. Previous studies have shown that the amount of water contained in the reaction system has a significant effect on both the activity and selectivity of the catalysts.⁽³³⁾ We thus evaluated the catalytic performance and selectivity of Co₃O₄ hollow spheres for CO₂ reactions by varying the amount of water in the solution. It is interesting to note that, without water in the solution (pure acetonitrile), H₂ is the only product (Figure 3a), which suggests that water may not serve as the proton source. This is similar to our previous findings where the system can generate H₂ without water as TEOA can provide protons.⁽³⁴⁾ Once 0.4 mL of water (14% of the total volume of solvent) was added to the system, more than 1 μmol of CO was detected, which results in 72% selectivity for CO formation, suggesting that water is essential for CO₂ reduction to form CO. The enhanced performance for CO₂ reduction upon addition of water might be due to promotion of the reaction kinetics due to a reduced thermodynamic barrier in the presence of water⁽³⁵⁾ or due to the fact that the addition of water may induce photolabilization of the bipyridine ligand from [Ru(bpy)₃]²⁺ to form a catalytically active species.^(36,37) If the water content was further increased to 20%, the yield of CO remains similar, but the selectivity for CO formation increases to 90.5%. Further addition of water results in a gradual decrease of the produced CO and H₂ amounts until neither CO nor H₂ was produced when the solvent is pure water. These results suggest that both water and acetonitrile are essential for CO production, but the presence of a large amount of water can inhibit the formation of CO and H₂. One possible reason for the reduced production of CO with water concentration may result from the poor affinity of water to CO₂ molecules.⁽³³⁾ According to these results, the solvent containing 20% water was used for the following catalytic reactions. Catalytic experiments were also carried out by varying the concentrations of Co₃O₄ hollow spheres. As shown in Figure 3b, the amounts of both CO and H₂ decrease with increasing concentration of the Co₃O₄ hollow spheres, which results in a significant drop of activity in terms of the amount of CO/g of catalyst, while the selectivity remains similar. As a result, 0.1 mg of Co₃O₄ hollow spheres was used in the catalytic system for the following experiment.

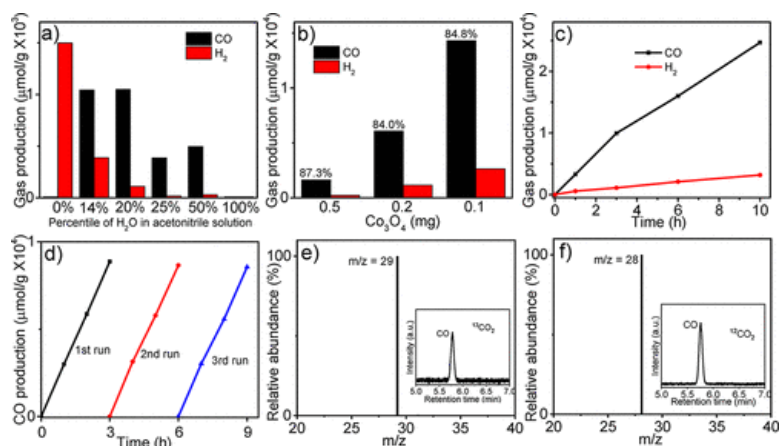


Figure 3. (a) Dependence of CO and H₂ production (μmol/g Co₃O₄) on the amount of H₂O. The reactions were conducted in 1 mg of Co₃O₄, 1 mg of [Ru(bpy)₃]²⁺, and 0.2 mL of TEOA. The gas products were collected after 17 h of illumination. (b) The dependence of CO and H₂ production (μmol/g Co₃O₄) on the amount of catalyst. The reactions were run for 3 h with 1 mg of [Ru(bpy)₃]²⁺, 0.2 mL of TEOA, 0.76 mL of H₂O, and 3.04 mL of acetonitrile. (c) Time profiles of CO and H₂ production catalyzed by Co₃O₄ under the optimized conditions (0.1 mg Co₃O₄, 1 mg [Ru(bpy)₃]²⁺, 0.2 mL TEOA, 0.76 mL H₂O, and 3.04 mL acetonitrile). (d) Recycling of Co₃O₄ catalyst after multiple 3 h experiments. Mass spectroscopic analyses of the carbon source of the generated CO obtained from the photocatalytic CO₂ reduction reaction under (e) ¹²CO₂ and (f) ¹³CO₂ (inset: corresponding gas chromatography of CO). All the photocatalytic reactions were performed under 450 nm (19 mW) light illumination.

The full time CO and H₂ generation profiles were measured under the catalytic conditions including 0.1 mg of Co₃O₄ hollow spheres, 1 mg of [Ru(bpy)₃]²⁺, 0.2 mL of TEOA, 0.76 mL of H₂O, and 3.04 mL of acetonitrile. As shown in Figure 3c, under these conditions, the amounts of CO and H₂ increase steadily with irradiation time, which can last for at least 10 h, reaching an activity of 24,700 μmol/g Co₃O₄ hollow spheres (photon-to-CO efficiency of 0.228%) and 88.6% selectivity for CO production. To evaluate the duration of the Co₃O₄ catalytic system, the recycling experiments were explored by collecting Co₃O₄ after each 3 h of illumination via centrifugation and dispersal in a fresh catalysis solution. As shown in Figure 3d, the system can be recycled for at least three cycles. To validate whether CO originated from CO₂, we carried out the ¹³C-labeled isotropic experiment using ¹³CO₂ gas under the same catalytic conditions. As shown in Figure 3e, when ¹³CO₂ was used as the reactant, ¹³CO (*m/z* = 29) was detected as the product by gas chromatography mass spectrometry, which is distinct from the product of ¹²CO (*m/z* = 28) when ¹²CO₂ was used (Figure 3f). Furthermore, no other liquid products such as formate or formic acid were detected using NMR and FT-IR (Figure S2). These results confirm that the produced CO originates from photoreduction of CO₂ molecules, not from the decomposition effect of any organics in the system, and that CO is the only product from CO₂ reduction.

To gain mechanistic insight, we measured the in situ XAS spectra of the Co₃O₄ catalytic system under the standard catalytic conditions. The in situ XAS spectra at the Co K-edge were collected at beamline 12-BM at Advanced Photon Source, Argonne National Laboratory. Figure 4a shows the in situ XANES spectra of Co₃O₄ collected at the Co K-edge during the CO₂ photoreduction. These spectra were featured by a prominent absorption in the region of 7720–7730 eV and a small pre-edge feature at ~7715 eV, which can be attributed to the dipole-allowed Co 1s–4p transition and dipole-forbidden but quadrupole-allowed 1s–3d transition. Upon the turn-on of LED lamp, notable changes were observed at the XANES spectra, which can be more clearly seen in the difference XANES spectra (Figure 4b) obtained by subtracting the XANES spectrum before LED illumination from that during LED illumination. Immediately following the illumination (20 min spectrum), we observed a broad negative feature in 7720–7770 eV, suggesting the decrease in the spectral intensity of the in situ XAS spectra. Initially, we had thought that this broad negative feature might be an intermediate species at the early stage of the CO₂ reduction reaction. However, further in situ XAS experiments under different conditions (e.g., excluding LED illumination, [Ru(bpy)₃]²⁺, CO₂, or TEOA) showed that this broad negative signal was always present once XAS measurements initiated (Figure S3), suggesting that this negative feature is not related to the light-driven CO₂ reduction reaction. While the origin of this spectral feature remains uncertain to us, one possible reason could be that the sample concentration or structure changes slightly due to X-ray illumination. After that, the edge feature gradually grows toward the positive signal (7727 eV), while the multiscattering region (7735 eV) grows further to negative with an isosbestic point (7731.8 eV) between them (Figure 4b and inset), suggesting that these two processes are associated with each other. At about 100 min after the light irradiation, the XANES spectra stop changing and the positive feature at edge energy is fully developed. These results suggest that the photocatalytic system likely reaches an equilibrium and the intermediate species under equilibrium is featured by a reduced Co center, which results from the reduction of the Co center due to electron transfer from [Ru(bpy)₃]²⁺.

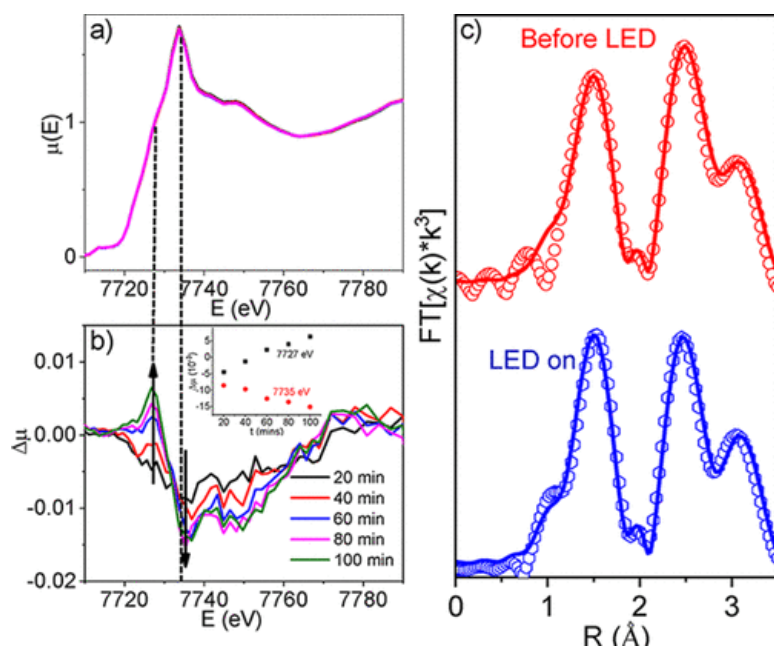


Figure 4. (a) In situ XANES spectra of Co_3O_4 hollow spheres at Co K-edge collected under catalytic conditions (in solution). (b) The difference XANES spectrum of Co_3O_4 hollow spheres obtained by subtracting the XANES spectrum collected before LED illumination from that collected during catalysis. The inset plots the intensities of the positive feature at 7727 eV and negative feature at 7735 eV as a function of time, which illustrates the evolution of these two features during catalysis. (c) The EXAFS spectrum at R-space collected before LED illumination (top panel) and when the system reaches equilibrium during catalysis (bottom panel). The open circles and solid lines are experimental and fitted results, respectively.

To gain more insight into the intermediate species at equilibrium, we collected the EXAFS spectrum within the time region when the XANES spectra stop changing (~ 4 h after light illumination). However, little changes were observed in the EXAFS spectrum at equilibrium compared to the spectrum collected before catalysis (Figure 4c), which is expected due to the small number of surface Co atoms in the hollow spheres. This is further confirmed by quantitative analysis of these EXAFS spectra where the coordination numbers remain the same with slight reduction in the Co–ligand bond distance due to LED illumination (Table S1 and Figure S4). These results together suggest that the intermediate species at equilibrium undergoes net reduction at the Co center without a change in the nature of the structure during catalysis.

4. Conclusions

In summary, we report a Co_3O_4 hollow sphere that can efficiently catalyze CO_2 to form CO in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer and TEOA as the sacrificial donor under 450 nm LED illumination. Under the optimized conditions, this system can achieve an external quantum efficiency of 0.228% with 88.6% selectivity. More importantly, using in situ X-ray absorption spectroscopy, we identified a key intermediate species that is responsible for CO_2 reduction, that is, the reduced Co center, due to electron transfer from $[\text{Ru}(\text{bpy})_3]^{2+}$ to the Co_3O_4 hollow sphere. These results not only demonstrated the great potential of Co_3O_4 hollow spheres as photocatalysts for CO_2 reduction but also provided unprecedented new insight on the catalytic mechanism of these hollow materials.

Supporting Information

The Supporting Information is available free of charge at <https://0-pubs-acsc-org.libus.csd.mu.edu/doi/10.1021/acs.jpcc.0c00101>.

- SEM image of Co-glycolate; the fitting parameters of XAS data; difference spectra of in situ XAS measurements under different conditions; EXAFS spectra in k-space (PDF)

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Notes

The authors declare no competing financial interest.

Acknowledgments

This work was supported by National Science Foundation (DMR-1654140) and ACS-PRF (57503-DNI6). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-AC02-06CH11357.

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