Selective CO₂ Reduction Catalyzed by Single Cobalt Sites on Carbon Nitride under Visible-Light Irradiation

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ABSTRACT: Framework nitrogen atoms of carbon nitride (C₃N₄) can coordinate with and activate metal sites for catalysis. In this study, C₃N₄ was employed to harvest visible light and activate Co²⁺ sites, without the use of additional ligands, in photochemical CO₂ reduction. Photocatalysts containing single Co²⁺ sites on C₃N₄ were prepared by a simple deposition method and demonstrated excellent activity and product selectivity toward CO formation. A turnover number of more than 200 was obtained for CO production using the synthesized photocatalyst under visible-light irradiation. Inactive cobalt oxides formed at relatively high cobalt loadings but did not alter product selectivity. Further studies with X-ray absorption spectroscopy confirmed the presence of single Co²⁺ sites on C₃N₄ and their important role in achieving selective CO₂ reduction.

The past few years witnessed increasing interest in hybrid photosynthetic systems that couple molecular catalysts with robust surfaces for solar fuel production. Light-absorbing semiconductors, electrode surfaces, and other solid-state materials have been employed as support for molecular CO₂-reduction catalysts. Among the light-absorbing semiconductors, some have wide bandgaps, and their activation requires the use of UV irradiation that accounts for less than 5% of the solar spectrum. Only a few semiconductors with relatively narrow bandgaps can harvest visible light for subsequent photoexcited electron transfer to the surface-bound molecular catalysts for CO₂ reduction. Metal–ligand complexes are often employed as molecular catalysts. These complexes usually render excellent reactivity and product selectivity, but their ligands may be expensive or difficult to synthesize in large scales. This present work employs graphitic carbon nitride (C₃N₄) to harvest visible light and activate single Co²⁺ sites, without the use of additional ligands, in selective CO₂ reduction (Figure 1a).

Recently, C₃N₄ has emerged as a semiconductor capable of mediating photocatalysis under visible-light irradiation. This polymeric material has been investigated in solar water splitting and CO₂ reduction. In photocatalytic CO₂ reduction, C₃N₄ has been studied as a photocatalyst alone, or coupled with catalysts including metal nanoparticles and metal–ligand complexes for enhanced solar fuel production. Theoretical studies by Gao and co-workers suggest that efficient visible-light CO₂ reduction can be achieved using single Pd and Pt atoms supported on C₃N₄. However, no experimental work has been reported regarding selective solar CO₂ reduction using single-metal-site catalysts in the absence of additional ligands.

In the present study, single Co²⁺ sites are prepared on C₃N₄ via a simple deposition method to achieve selective CO₂ reduction under visible-light irradiation. Activation of the single Co²⁺ sites on C₃N₄ is likely through Co–N coordination, as in a well-known molecular catalyst, [Co-(cyclam)Cl₂]Cl where cyclam is 1,4,8,11-tetraazacyclotetradecane (denoted “Co-cyclam”, structure shown in Figure 1b). This macrocyclic cobalt catalyst is often used with p-terphenyl as a photosensitizer in CO₂ reduction under UV irradiation. We also present spectroscopic evidence for the presence of single Co²⁺ sites and their essential role in photocatalysis.

The X-ray diffraction pattern of C₃N₄ prepared by pyrolysis of urea is shown in Figure 2a. Deposition of Co²⁺ sites on C₃N₄ was achieved by mixing CoCl₂ with C₃N₄ in acetonitrile, followed by microwave heating in the presence of triethylamine (TEA). In our study, TEA was employed to facilitate the deposition of Co²⁺ on C₃N₄. Cobalt loadings of the synthesized materials (denoted “Co²⁺@C₃N₄”) increased almost linearly with the amount of CoCl₂ used in synthesis (see Figure S1 in the Supporting Information). Approximately 200 was obtained for CO production using the synthesized photocatalyst under visible-light irradiation. Inactive cobalt oxides formed at relatively high cobalt loadings but did not alter product selectivity. Further studies with X-ray absorption spectroscopy confirmed the presence of single Co²⁺ sites on C₃N₄ and their important role in achieving selective CO₂ reduction.

Supporting Information

Figure 1. (a) Schematic of photocatalytic CO₂ reduction mediated by a single Co²⁺ site on C₃N₄; (b) molecular structure of a macrocyclic cobalt catalyst.

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45% of CoCl₂ used in synthesis was successfully deposited on C₃N₄. Cobalt loadings in this work varied between 0.004 and 0.430 μmol Co²⁺ per 1 mg C₃N₄. When the microwave synthesis was carried out in the absence of TEA, however, the highest cobalt loading obtained was 0.016 μmol/mg even when a large excess of CoCl₂ was used in synthesis (Figure S1).

The optical spectrum of bare C₃N₄ features significant photoresponse in the visible region (400−800 nm, Figure 2b), similar to that of C-doped C₃N₄ reported in the literature (Figure S2). Deposition of Co²⁺ on C₃N₄ resulted in a negligible change in its optical spectrum. The infrared spectra of the Co²⁺@C₃N₄ samples are almost identical to that of bare C₃N₄ (Figure 2c). In addition, no morphological changes were observed upon deposition of Co²⁺ (Figure S3a−d). The presence of Co²⁺ sites in the Co²⁺@C₃N₄ samples is seen in their X-ray photoelectron spectra, as indicated by a peak at 781 eV associated with the Co 2p₃/₂ transition (Figure 2d).

Microscopic mapping revealed uniform distribution of cobalt on C₃N₄ (Figure S3f).

The Co²⁺@C₃N₄ samples were tested for photocatalytic CO₂ reduction in acetonitrile containing triethanolamine as a sacrificial electron donor. A halogen lamp was used to provide photons with wavelength greater than 350 nm (see lamp output spectrum in Figure S4). Under the experimental conditions employed in this study, CO and H₂ were detected as major products in CO₂ reduction using the Co²⁺@C₃N₄ samples. Negligible CO production was observed using bare C₃N₄ (Figure S5).

The effect of cobalt loading on the photocatalytic activity of Co²⁺@C₃N₄ was further examined under the same experimental conditions. Significant CO production was observed even at cobalt loadings lower than 0.010 μmol/mg (Figure 3a).

The amount of CO generated in CO₂ reduction increased linearly with cobalt loading until it reached 0.128 μmol/mg. Further increase in cobalt content resulted in a slight decrease in the amount of CO produced. Quantum yields up to 0.40% were obtained for CO production using the synthesized materials (Tables S1 and S2).

The effect of cobalt loading was also investigated by comparing turnover numbers (TONs), which were calculated based on the amount of product and the amount of cobalt present in the reaction suspension. Figure 3b shows TON for CO and H₂ production as a function of reaction time (Figure 3c). The TONs for CO decreased drastically as the cobalt loading was increased (Figure 3c), suggesting the existence of single-site catalysis at low cobalt loadings. At relatively high loadings, a significant portion of cobalt likely exists in the form of inactive cobalt oxides. An interesting observation in CO₂ reduction using Co²⁺@C₃N₄ is that product selectivity appeared to be independent of the cobalt loading, as can be seen from Figure 3d. Therefore, the inactive cobalt component in Co²⁺@C₃N₄ did not promote undesired competing reactions, including H₂ production.

The Co²⁺@C₃N₄ samples demonstrated excellent activity under visible-light irradiation (λ > 420 nm, see Figure S4). A TON greater than 200 was obtained after CO₂ reduction after 24 h using a Co²⁺@C₃N₄ sample (Figure S6). Isotopic studies clearly showed that CO was produced as a result of CO₂ reduction (Figure S6, inset). The Co²⁺@C₃N₄ samples also demonstrated reasonable stability, as indicated by significant CO production using recycled Co²⁺@C₃N₄ samples in photocatalysis (Figure S7).
changes were observed for the Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} samples before and after photocatalysis (Figures S8 and S9).

The unique structure of C\textsubscript{3}N\textsubscript{4} (Figure 1a) allows it to serve as a "ligand", in which framework N atoms coordinate with and activate metal sites for catalysis. This concept of catalysis at single metal sites was previously explored electrocatalytically using metal-doped C\textsubscript{3}N\textsubscript{4}\textsuperscript{n+1} and metal/N-doped carbon-based electrodes.\textsuperscript{37–54} Similar efforts were reported in photocatalytic water oxidation\textsuperscript{37,56} and \textsubscript{2}H\textsubscript{2} evolution\textsuperscript{37,58} using single Co sites on C\textsubscript{3}N\textsubscript{4}. However, visible-light CO\textsubscript{2} reduction using single metal sites on C\textsubscript{3}N\textsubscript{4} has not been previously observed in the absence of additional coordinating ligand. Our study is the first example demonstrating the use of single Co\textsuperscript{2+} sites on C\textsubscript{3}N\textsubscript{4} for selective CO\textsubscript{2} reduction under visible-light irradiation.

The nature of single Co\textsuperscript{2+} sites and their role in photocatalysis using Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} was further investigated with X-ray absorption spectroscopy using two samples with cobalt loadings of 0.016 \textmu mol/mg (denoted “low-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4}”) and 0.430 \textmu mol/mg (denoted “high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4}”). For this study, a control sample was prepared by depositing CoCl\textsubscript{2} on SiO\textsubscript{2}, in the presence of TEA (denoted “CoO/SiO\textsubscript{2}”). The oxidation state of cobalt in Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} (Figure S11). The oxidation state of cobalt in both Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} samples remained at \textit{2}\textsubscript{+}, consistent with similar Co-doped C\textsubscript{3}N\textsubscript{4} materials reported in the literature.\textsuperscript{55,59} In prior studies by others\textsuperscript{57,60} and one of the coauthors,\textsuperscript{61} a shoulder feature along the rising edge around 7715 eV was observed in the XANES of Co-porphyrins having the four-coordinate square-planar structure. This shoulder feature is not present in the XANES of our samples, indicating Co\textsuperscript{2+} is not in the same plane as the flat framework of N atoms in C\textsubscript{3}N\textsubscript{4}.

The XANES spectral shape for low-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} is different from those of CoO and Co\textsubscript{3}O\textsubscript{4}, likely due to the coordination of Co\textsuperscript{2+} with N atoms in the C\textsubscript{3}N\textsubscript{4} framework. In contrast, the XANES spectral shapes of high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} and CoO\textsubscript{2}/SiO\textsubscript{2} are similar to that of CoO, consistent with the presence of CoO in both samples (Figure 4). The presence of cobalt oxide in Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} at relatively high cobalt loadings was confirmed with X-ray photoelectron spectroscopy (Figure S12).

The extended X-ray absorption fine structure (EXAFS) spectra of these samples are shown in Figure 5. The k-range from 2 to 11 Å\textsuperscript{-1} and k\textsuperscript{2} weighting were used in all Fourier transforms. Similar to Co-cyclam, the spectra of both high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} and low-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} have a peak around 1.55 Å (uncorrected for the photoelectron phase shift), which indicates coordination of Co\textsuperscript{2+} with N atoms in these samples. A peak at around 2.7 Å corresponding to Co–O bond in CoO structure is present in the EXAFS spectra of high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} and CoO\textsubscript{2}/SiO\textsubscript{2} with the former having lower intensity. This comparison indicates that (1) the cobalt oxide species in high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} has a similar structure to that in CoO/SiO\textsubscript{2}; and (2) the cobalt oxide species in high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} has a lower coordination number at Co and/or higher disorder than that in CoO/SiO\textsubscript{2}, possibly because the size of cobalt oxides in high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} is smaller than in CoO/SiO\textsubscript{2}, despite significantly higher cobalt loading in high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} than in CoO/SiO\textsubscript{2}.

The spectra shown in Figure 5 demonstrate that in cobalt species in low-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4}, no Co–O–Co contribution can be detected, consistent with the conclusion obtained from the XANES data (Figure 4). Therefore, cobalt species in this sample exist as isolated, single sites with a coordination environment similar to that of Co-cyclam. In comparison, the high-Co\textsuperscript{2+}@C\textsubscript{3}N\textsubscript{4} sample contains cobalt oxides, which are inactive in photocatalytic CO\textsubscript{2} reduction under the experimental conditions employed in this study (Figure 1a).

In summary, we have successfully prepared single Co\textsuperscript{2+} sites on C\textsubscript{3}N\textsubscript{4} for use in selective CO\textsubscript{2} reduction under visible-light irradiation. Photocatalysis and spectroscopic studies clearly demonstrated the formation of single Co\textsuperscript{2+} sites and their important role in achieving selective CO\textsubscript{2} reduction. Our work contributes to the field of solar fuels by providing a rare example of CO\textsubscript{2}-reduction photocatalysts featuring single catalytic sites based on earth-abundant transition metals.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10380.
Experimental details on materials, catalyst synthesis, materials characterization, X-ray absorption spectroscopy, photocatalytic testing; estimated quantum yields; and supporting figures (PDF)

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Notes
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