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Photochemical Nitrogen Conversion to Ammonia in Ambient Conditions with FeMoS-Chalcogels

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S *Supporting Information*

ABSTRACT: In nature, nitrogen fixation is one of the most important life processes and occurs primarily in microbial organisms containing enzymes called nitrogenases. These complex proteins contain two distinct subunits with different active sites, with the primary N_2 binding site being a FeMoS core cluster that can be reduced by other nearby iron–sulfur clusters. Although nitrogen reduction to ammonia in biology does not require the absorption of light, there is considerable interest in developing catalyst materials that could drive the formation of ammonia from nitrogen photochemically. Here, we report that chalcogels containing FeMoS inorganic clusters are capable of photochemically reducing N_2 to NH_3 under white light irradiation, in aqueous media, under ambient pressure and room temperature. The chalcogels are composed of $[Mo_2Fe_6S_8(SPh)_3]^{3+}$ and $[Sn_2S_6]^{4-}$ clusters in solution and have strong optical absorption, high surface area, and good aqueous stability. Our results demonstrate that light-driven nitrogen conversion to ammonia by MoFe sulfides is a viable process with implications in solar energy utilization and our understanding of primordial processes on earth.
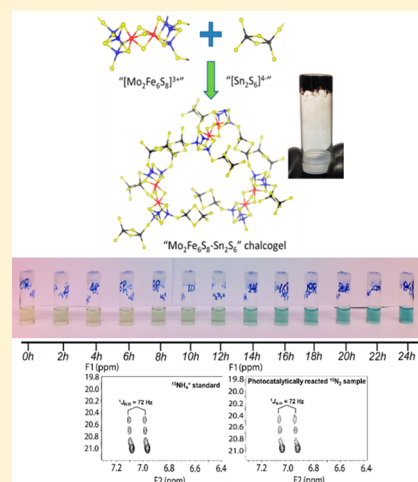
INTRODUCTION

Biological nitrogen reduction, catalyzed by the enzyme nitrogenase,[1] is postulated to occur with concurrent proton reduction to form H_2, as suggested by the equation:[1a,2]

$$N_2 + 8H^+ + 8e^- + 16ATP$$
$$\rightarrow 2NH_3 + H_2 + 16ADP + 16P_i \qquad (1)$$
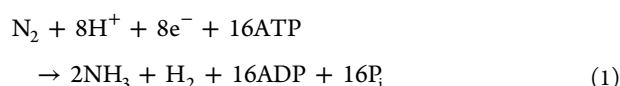
Unlike photosynthetic processes, biological nitrogen fixation is an aphotic process; it does not require the absorption of light to proceed. Light-driven biomimetic catalysis is an attractive proposition, however, as it can take full advantage of the abundant solar energy. This concept is demonstrated successfully in the formation of hydrogen and oxygen via photochemical water splitting, known as artificial photosynthesis.[3] Industrially, the reaction of N_2 with H_2 to form NH_3 is accomplished using high temperatures (300−400 °C) and pressures (∼250 atm) with an iron catalyst, that is, the Haber–Bosch process. Such a process is highly energy demanding, as the N_2 must react with the solid surface, and consumes more than 1% of the world's energy supply.

The active sites of all nitrogenases are observed to have an inorganic metal/sulfur cluster, in most cases consisting of a central iron–molybdenum–sulfur cluster, the so-called FeMoS cofactor.[4] Many inorganic molecular analogues of the nitrogenase FeMoS cluster active site have been successfully synthesized,[5] and a great deal of them do show effective catalytic ability in transformations related to nitrogenase activity, such as the reduction of hydrazine to ammonia.[5c,d] Recent work on nitrogenase itself using light sensitizer molecules has shown that the enzyme can be driven by light to carry out some transformations such as HCN to CH_4 and NH_3; however, no N_2 conversion was observed.[5e−g] However, ammonia production from nitrogen has been highly sought in molecular analogues of the nitrogenase active site (i.e., synthetic clusters bearing Mo−Fe linkages), and some reports of molecular analogues have been shown to produce ammonia from N_2 under strongly reducing conditions created by chemical of electrochemical means.[6] Conversely, photochemical ammonia production has been previously demonstrated using ultraviolet light in systems such as semiconductor thin films (e.g., titania,[7] diamond,[8] and fullerenes[9]). Molecular complexes of molybdenum, iron, or titanium, due to their high instability in air, have to be handled under carefully controlled inert atmosphere, with nitrogen fixation reactions observed to be occurring at extremely low temperatures, as for example, −78 °C for $[\{tris(phosphine)borane\}Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$,[6e] and −30 °C for $[(C_5Me_4SiMe_3)_3Ti_3(\mu\text{-}H)_7]$.[6a] Conversely, fullerenes are reported to catalyze nitrogen fixation at higher temperatures of 60 °C.[9] To the best of our knowledge, we present here the first solid-state nitrogenase analogue containing Fe/Mo/S capable of visible light-driven ammonia

production from nitrogen at room temperature and ambient pressure.

Here, we report that biomimetic chalcogels[10] are capable of photochemical reduction of nitrogen to ammonia with light. The chalcogels are composed of double-cubane $Mo_2Fe_6S_8$ cluster units linked by Sn_2S_6 ligands, forming a random, amorphous network with strong optical absorption. Like nitrogenase enzymes, our chalcogels are stable in aqueous environments, and can thus be thought of as solid-state analogues.

Inorganic molecular analogues of the FeMoS cofactor have already been known in the literature for some time,[5a,b] but they are not functional analogues as they are not known to bind and convert nitrogen. With suitable terminal ligands, the FeMoS clusters, reported by Holm and co-workers,[11] can be cross-linked with $[Sn_2S_6]^{2-}$ anions to form a polymeric and porous chalcogenide framework, as illustrated in Figure 1. The reaction

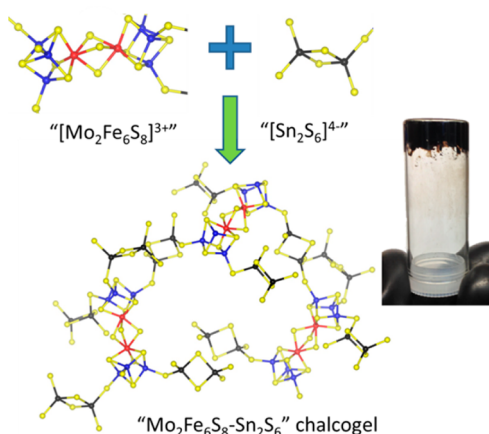**Figure 1. Chalcogel synthesis.** Schematic representation of $Mo_2Fe_6S_8-Sn_2S_6$ biomimetic chalcogel (FeMoS-chalcogel), building block scheme (Mo, blue; Fe, red; S, yellow; Sn, black), and a complete chalcogel shown at right.

proceeds from the metathesis displacement of the terminal Cl^- ligands in the $[Mo_2Fe_6S_8(SPh)_3Cl_6]^{3-}$ cluster (**2**) by the terminal sulfides of $[Sn_2S_6]^{4-}$.[12] For the preparation of FeMoS-chalcogels for the purposes of nitrogen-fixation, we used a mixture of *N*-methylformamide/*N,N'*-dimethylformamide for gel formation (see Methods in the Supporting Information for details). Upon standing at room temperature for 15−20 days, solutions of this mixture form a black gel, referred to here as FeMoS-chalcogel.

Electron microscopy reveals the spongy, porous nature of the FeMoS-chalcogels, always appearing as an amorphous solid, as determined from TEM-SAED and SEM experiments (Figure 2A,B). Energy dispersive spectroscopy (EDS) was used to determine the elemental composition of the chalcogels (see the Supporting Information). Nitrogen adsorption/desorption measurements (Figure 2C) on the dried chalcogels (aerogels) indicate a Type IV porosity (average surface area of 118 m^2/g).[13] We note that once the $[Mo_2Fe_6S_8(SPh)_3Cl_6]^{3-}$ cluster is integrated into the FeMoS-chalcogels, it becomes stable against hydrolysis contrary to the hydrolytically unstable precursor.

The clusters in the chalcogels were characterized by a variety of means.[12] The stability of the FeMoS cluster in the chalcogel matrix is confirmed with thiol extrusion studies. The FeMoS-chalcogels are observed to be stable in practically all solvents,
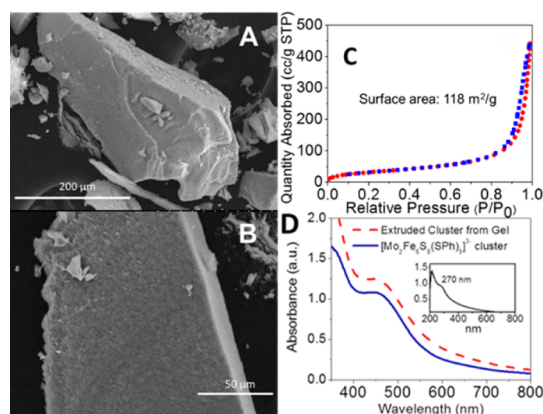
Figure 2. Chalcogel structural characterization. (A) Scanning electron micrographs of a representative FeMoS–Sn_2S_6 chalcogel. (B) High-resolution scanning electron micrograph of the aerogel surface showing sponge-like morphology. (C) Nitrogen adsorption/desorption isotherm obtained at 77 K of FeMoS–Sn_2S_6 chalcogels synthesized in NMF/DMF solvent mixture. (D) UV−vis spectra of DMF solutions of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ and extruded FeMoS cluster from chalcogel with excess benzenethiol. Inset shows the UV−vis spectra of a colloidal suspension of FeMoS–Sn_2S_6 chalcogel in water.

including water, without any dissolution. However, in the presence of a large excess of benzenethiol in solution, the gel dissolves rapidly as the $\{Mo_2Fe_6S_8(SPh)_3\}$ cluster is extruded from the gel by benzenethiol, yielding the $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ anion in solution, showing characteristic spectral features (Figure 2D).[5c,12] A semiquantitative estimation of the $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ anion (ε_M at 449 nm = 37 000) concentration in solution gave a value of 0.51 mM for 1.0 mM of gel used (see the Supporting Information for details). The UV−vis spectra of an aqueous colloidal suspension of the gel, prepared by sonication of the gel in water for ∼2 min, also show a broad characteristic absorption in the visible spectrum peaking at 270 nm (Figure 2D, inset).

The FeMoS cluster in the chalcogel matrix is a strong chromophore. The ability of the FeMoS-chalcogel to be photoexcited to sufficiently high energy capable of interacting with N_2 was confirmed by nanosecond transient absorption (nsTA) experiments. Experiments were performed on the chalcogel sonicated in *o*-dichlorobenzene and spun-cast onto a glass slide, yielding a thin film. After photoexcitation at 416 nm, both ground-state bleach and excited-state features are observed (Figure 3A). The ground-state bleach, monitored at 520 nm, is found to have a lifetime of around 200 ns (Figure 3B). The excited state that arises at 660 nm decays with a lifetime similar to that of the bleach.

To better understand these initial results, nsTA was then used to probe the interaction of nitrogen with a colloidal species of the chalcogel in solution. These samples were prepared in the presence of pyridinium chloride and sodium ascorbate, to create conditions identical to those of the catalytic studies (see Methods in the Supporting Information for details). Sonication of this aqueous mixture of the chalcogel for a few minutes yielded a fine colloidal suspension of the gel in water. Photoexcitation of this sample in the absence of nitrogen yields a broad ground-state bleach, which decays with a lifetime longer than the instrument window of 4.5 μs (Figure 3C). After the sample was bubbled with nitrogen for 1 h, the ground-state bleach was found to decay biexponentially with a new 100−200 ns decay component in addition to a similarly
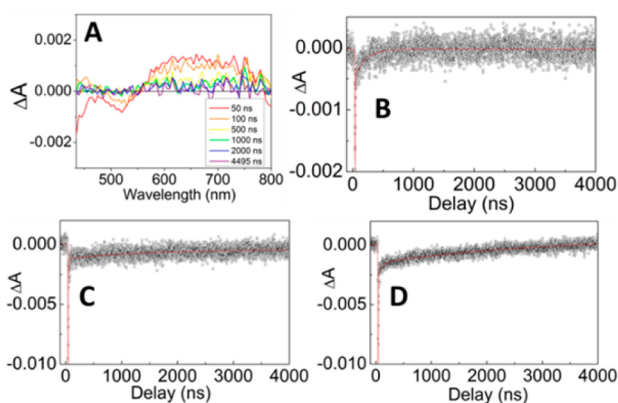
Figure 3. Chalcogel electronic characterization. (A) Nanosecond transient absorption (nsTA) spectra of chalcogel film. (B) nsTA kinetics of chalcogel film at 520 nm. (C) nsTA kinetics of suspension in the absence of nitrogen at 435 nm. (D) nsTA kinetics of chalcogel colloid in the presence of nitrogen at 435 nm, showing the emergence of a new kinetic component.

long decay component as the nitrogen-free sample (Figure 3D). The observed results are consistent with a portion of the FeMoS-chalcogel being quenched by interaction with nitrogen, presumably heralding one of the first steps in the catalytic activity.

The chalcogels have very strong optical absorption in the ultraviolet to visible region of the spectrum, as seen by UV−vis studies of the gel in water (Figure 2D, inset). Because of the distinct role FeMoS clusters play in nitrogenase enzymes, we explored the ability of the FeMoS chalcogels to produce ammonia from nitrogen photochemically. We thus performed nitrogen fixation with our biomimetic chalcogels using ultraviolet to visible-light. Slices of the chalcogels were placed in aqueous solutions containing pyridinium hydrochloride (proton source) and sodium ascorbate (electron donor). Nitrogen was continually flowed through the solution at a rate of 8−10 mL/min, which was illuminated with a 150 W xenon lamp, with the light intensity at the sample being 100 mW/cm². The reactions were monitored for typical periods of 32 or 48 h, and at regular intervals of 2 and 4 h, respectively, aliquots were drawn from the reaction solutions. To have maximum exposure of the chalcogel to the light source as well as the reactants, the mixture was kept under constant stirring. The aliquots were then assayed for $[NH_4]^+$ ions in solution by use of the direct method of ion chromatography,[14] as well as the indirect chemical indophenol method.[15] Ion chromatography analysis require no sample preparation. $[NH_4]^+$ determination was performed with a cation exchange column equipped with an electrolytically regenerated suppressor and using 20 mM methanesulfonic acid as the eluent, with a flow rate of 1 mL/min. Na⁺ ions were observed to elute first with a retention time (R_t) of ∼8.2 min, followed by $[NH_4]^+$ ions with a R_t of ∼10.6 min. The amount of ammonium obtained could be estimated very accurately with a calibration curve, obtained from concentrations in the range from 2 μM to 2 mM (see Methods in the Supporting Information). The indophenol method is a different approach based on the reaction of phenol and ammonia in basic conditions and in the presence of hypochlorite as the oxidizing agent and iron nitroprusside as a catalyst. Each test requires 24 h to complete. Its advantage is that it produces a distinct blue color due to formation of the indophenol dye (λ_{max} = 630 nm, FW: 199 g/mol) acting as a

unique visual indicator and allowing spectroscopic identification of NH₃ in solution. However, because this method employs a complex chemical reaction toolkit, it is susceptible to interference from many sources and requires elaborate handling of the reaction products that can introduce losses and errors.[16] It is time-consuming, cumbersome, subject to interference, and thus inadequate for an accurate quantification of the amount of ammonia for our aliquots.

Ammonia was detected in all illuminated solutions containing FeMoS-chalcogel saturated with nitrogen, and its concentration continuously increased with irradiation time (Figure 4A). The UV−vis spectra showing indophenol are
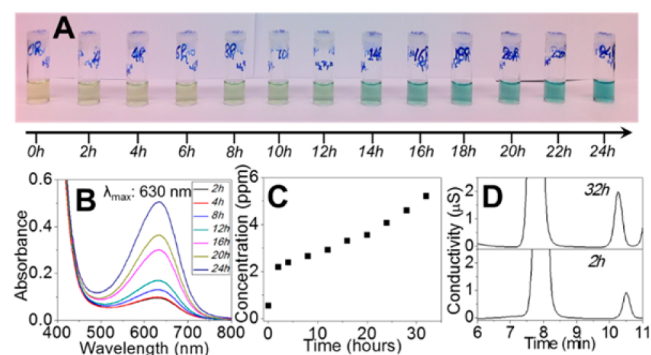

Figure 4. Catalytic nitrogen-fixation. (A) Photos of aliquots obtained during nitrogen-fixation catalysis, after performing the indophenol test. Note the steady increase in the intensity of blue color with time. (B) UV−vis absorption spectra of indophenol assays, showing the characteristic absorption maximum at 630 nm of indophenol. (C) Kinetic plot of NH₃ concentration evolution in the assayed aliquots with time, using ion chromatography. (D) Representative ion chromatographs of aliquots obtained during nitrogen-fixation at 2 and 32 h showing increasing concentration of $[NH_4]^+$ ions. The Na⁺ ions are from ascorbate.

shown in Figure 4B, and the ion chromatographs of the aliquots are shown in Figure 4D, respectively. Figure 4C is a kinetic plot showing rising ammonia production as determined from ion chromatography. In a separate experiment run for 72 h, we measured 12 μmol produced using ∼1.5 μmol of catalyst. Thus, for each equivalent of total catalyst, approximately 8 equiv of ammonia was obtained, clearly indicating the catalytic nature of the reaction. Reactions were monitored for a maximum of 72 h, and during this time no degradation or loss of activity of the catalyst was observed.

In control experiments, chalcogel-containing reaction solutions kept in darkness or solutions without chalcogels showed no NH₃ formation. Illuminated chalcogel samples containing the proton and electron sources but lacking nitrogen gas (saturated with argon) also showed no detectable NH₃. Finally, samples that were not illuminated or illuminated under nitrogen but lacked either the proton or the electron source show no NH₃ formation either. Preliminary experiments performed with ligands that can potentially bind to the metals and act as inhibitors show that the activity of the FeMoS clusters can be blocked. For example, we observed that the NH₃ production appears to be inhibited by alkyl phosphines known to bind to either Fe or Mo (Supporting Information Figure S5).

To prove that nitrogen gas is the source of ammonia in our experiments, we used isotopic labeling experiments. We thus performed two types of isotope labeling experiments. One type

involved the use of ^{15}N-labeled pyridinium and the other type ^{15}N$_2$ gas. The use of ^{15}N-labeled pyridinium chloride yielded ^{14}NH$_3$ ammonia, which was confirmed by the LC−MS of the indophenol anion detected at 198 m/z and the absence of enhanced peak at 199 m/z. This eliminates the possibility of a hydrodenitrogenation-type reaction of the pyridine ring to yield NH$_3$. The other type was the use of ^{15}N$_2$ gas in the photochemical reaction. These experiments yielded ^{15}NH$_3$. We used two independent methods to confirm the formation of ^{15}NH$_3$. First, we used 2D ^{1}H−^{15}N heteronuclear single quantum coherence (HSQC) NMR spectroscopy where $[^{15}$NH$_4]^+$ was clearly identified in solution with its characteristic ^{15}N−^{1}H coupling $^1J_{N-H}$ = 72 Hz (Figure 5A,B). Second,

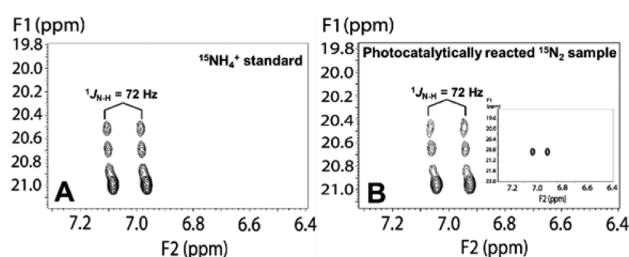**Figure 5. NMR spectroscopic detection of $[^{15}$NH$_4]^+$ in the reaction solution.** (A) ^{1}H−^{15}N HSQC NMR data of standard $[^{15}$NH$_4]^+$ solution in 10% D$_2$O/H$_2$O. The peaks are from a statistical mixture of $[^{15}$NH$_{4-x}$D$_x]^+$ species (x = 0−4). (B) ^{1}H−^{15}N HSQC NMR data of $[^{15}$NH$_4]^+$ obtained from photocatalytic ^{15}N$_2$-fixation (spectra taken in 10% D$_2$O/H$_2$O). Inset shows the corresponding spectra of the $[^{15}$NH$_4]^+$ containing product solution with DMSO-d_6 added to avoid H−D exchange. The observed doublet is from ^{15}N−H coupling with $^1J_{N-H}$ = 72 Hz. Experiments with $[^{14}$NH$_4]^+$ solutions showed no such spectra.

indophenol assays of photocatalytically reacted ^{15}N$_2$ samples showed a strong ^{15}N-labeled indophenol anion mass spectroscopy signal at 199 m/z in LC−MS studies (Supporting Information Figure S6), having relative intensities considerably higher than the natural abundance ratio of ^{14}N:^{15}N nuclei.

We have shown here that solid chalcogels containing FeMoS clusters are capable of light-driven nitrogen fixation and conversion to ammonia not only under ambient conditions of temperature and pressure but also in aqueous media. Although the $[Mo_2Fe_6S_8(SPh)_3Cl_6]^{3-}$ clusters are not exact FeMoS cofactor analogues, when part of the chalcogel structure they seem capable of acting in a fashion similar to that of the biological systems. This is the first time a structural analogue of the nitrogenase enzyme is shown to also be a functional analogue at least in a qualitative sense. These chalcogels feature multiple immobilized FeMoS active sites in a design that features a very high spatial density of such sites all closely and densely integrated into a three-dimensional matrix. The high density of clusters in the material enhances the prospect of multielectron transformations, particularly those that are photodriven as light energy accumulates creating highly excited cluster states. In that sense, our photoactive chalcogels are a good mimic of nitrogenases but with the added property of strong light absorption that is generally a characteristic of photosynthetic centers and semiconductors. The ease with which the amorphous FeMoS-chalcogel converts nitrogen to ammonia in aqueous solution at ambient temperature and pressure in the presence of light, protons, and mild reducing agents raises intriguing implications for such activity occurring

in nature, especially in environments where mineral sulfide surfaces with the proper transition metal ingredients are adventitiously present. Although such evidence has yet to be presented, such occurrence may be particularly relevant to the less oxidizing conditions of the early earth where ammonia generation may have been catalyzed in this fashion on a global scale.

■ METHODS SUMMARY

Clusters (NBu$_4$)$_3$[Mo$_2$Fe$_6$S$_8$(SPh)$_9$] (**1**) and (NBu$_4$)$_3$[Mo$_2$Fe$_6$S$_8$(SPh)$_3$Cl$_6$] (**2**), as well as Na$_4$Sn$_2$S$_6$·14H$_2$O, were synthesized according to literature procedures.[17] Chalcogels were synthesized in a nitrogen-filled glovebox by slowly adding a solution of 250 mg of cluster **2** (0.13 mmol) in 1.5 mL N,N'-dimethylformamide to a solution of 150 mg of Na$_4$Sn$_2$S$_6$·14 H$_2$O (0.195 mmol) in 1.5 mL of N-methylformamide, with the mixture being manually shaken after each drop, so that the entire addition took place over 30−45 min. After all of **2** was added, the reaction mixture was black and viscous. The reaction was covered and left undisturbed under nitrogen for 15−20 days, after which the viscous solution hardened into a rigid black chalcogel. The chalcogels were then subjected to solvent exchange by washing with a mixture of ethanol and water (4:1, v/v) four times, followed by pure ethanol three times. The chalcogels were subjected to supercritical drying with carbon dioxide for surface area measurements; otherwise, the gels were stored under ethanol.

Ammonia evolution experiments were performed in sealed vials with pieces of the chalcogel (approximately 180−200 mg of wet-gel per trial) immersed in an aqueous solution containing pyridinium hydrochloride (50 mM) and sodium ascorbate (5 mM). Nitrogen was continually bubbled through the solution, which was illuminated with the light from a 150 W xenon lamp. Aliquots of the solution were taken regularly for a period of 32 h and assayed for NH$_3$ by ion chromatography,[14] and the indophenol method.[15] Experiments requiring the estimation of TON were performed with minimalistic amount of catalyst (less than 5 mg) with aliquots collected at the beginning and after 72 h.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Detailed experimental procedures, including the synthesis of chalcogels, catalysis experiments, and analytical techniques for catalytic product determination and estimation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Dos Santos, P. C.; Igarashi, R. Y.; Lee, H. I.; Hoffman, B. M.; Seefeldt, L. C.; Dean, D. R. *Acc. Chem. Res.* **2005**, *38*, 208−214. (b) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983−3011. (c) Seefeldt, L. C.; Hoffman, B. M.; Dean, D. R. *Annu. Rev. Biochem.* **2009**, *78*, 701−722.

(2) (a) Barney, B. M.; Yang, T. C.; Igarashi, R. Y.; Dos Santos, P. C.; Laryukhin, M.; Lee, H. I.; Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. *J. Am. Chem. Soc.* **2005**, *127*, 14960−14961. (b) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120−125. (c) Lukoyanov, D.; Yang, Z. Y.; Barney, B. M.; Dean, D. R.; Seefeldt, L. C.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 5583−5587. (d) Rittle, J.; Peters, J. C. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15898−15903. (e) Yang, Z. Y.; Khadka, N.; Lukoyanov, D.; Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 16327−16332.

(3) (a) Youngblood, W. J.; Lee, S. H. A.; Maeda, K.; Mallouk, T. E. *Acc. Chem. Res.* **2009**, *42*, 1966−1973. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2009**, *42*, 1890−1898. (c) Maeda, K.; Teramura, K.; Lu, D. L.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *Nature* **2006**, *440*, 295−295.

(4) (a) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696−1700. (b) Hu, Y. L.; Fay, A. W.; Lee, C. C.; Yoshizawa, J.; Ribbe, M. W. *Biochemistry* **2008**, *47*, 3973−3981. (c) Barney, B. M.; Igarashi, R. Y.; Dos Santos, P. C.; Dean, D. R.; Seefeldt, L. C. *J. Biol. Chem.* **2004**, *279*, 53621−53624. (d) Howard, J. B.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17088−17093.

(5) (a) Mascharak, P. K.; Papaefthymiou, G. C.; Armstrong, W. H.; Foner, S.; Frankel, R. B.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 2851−2858. (b) Koutmos, M.; Georgakaki, I. P.; Coucouvanis, D. *Inorg. Chem.* **2006**, *45*, 3648−3656. (c) Demadis, K. D.; Coucouvanis, D. *Inorg. Chem.* **1995**, *34*, 436−448. (d) Palermo, R. E.; Singh, R.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2600−2612. (e) Roth, L. E.; Nguyen, J. C.; Tezcan, F. A. *J. Am. Chem. Soc.* **2010**, *132*, 13672−13674. (f) Roth, L. E.; Tezcan, F. A. *ChemCatChem* **2011**, *3*, 1549−1555. (g) Roth, L. E.; Tezcan, F. A. *J. Am. Chem. Soc.* **2012**, *134*, 8416−8419. (h) Kanatzidis, M. G.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A.; Papefthymiou, V. *J. Am. Chem. Soc.* **1985**, *107*, 4925−4935. (i) Coucouvanis, D.; Kanatzidis, M.; Simhon, E.; Baenziger, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 1874−1882.

(6) (a) Shima, T.; Hu, S. W.; Luo, G.; Kang, X. H.; Luo, Y.; Hou, Z. M. *Science* **2013**, *340*, 1549−1552. (b) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955−962. (c) Tanaka, K.; Hozumi, Y.; Tanaka, T. *Chem. Lett.* **1982**, 1203−1206. (d) Askevold, B.; Nieto, J. T.; Tussupbayev, S.; Diefenbach, M.; Herdtweck, E.; Holthausen, M. C.; Schneider, S. *Nat. Chem.* **2011**, *3*, 532−537. (e) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84−88. (f) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Tanaka, H.; Kamaru, N.; Yoshizawa, K.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2014**, *136*, 9719−9731. (g) Kitano, M.; Inoue, Y.; Yamazaki, Y.; Hayashi, F.; Kanbara, S.; Matsuishi, S.; Yokoyama, T.; Kim, S. W.; Hara, M.; Hosono, H. *Nat. Chem.* **2012**, *4*, 934−940.

(7) (a) Ileperuma, O. A.; Weerasinghe, F. N. S.; Bandara, T. S. L. *Sol. Energy Mater.* **1989**, *19*, 409−414. (b) Schrauzer, G. N.; Guth, T. D. *J. Am. Chem. Soc.* **1977**, *99*, 7189−7193. (c) Hoshino, K. *Chem.—Eur. J.* **2001**, *7*, 2727−2731. (d) Rusina, O.; Linnik, O.; Eremenko, A.; Kisch, H. *Chem.—Eur. J.* **2003**, *9*, 561−565.

(8) Zhu, D.; Zhang, L.; Ruther, R. E.; Hamers, R. J. *Nat. Mater.* **2013**, *12*, 836−841.

(9) Nishibayashi, Y.; Saito, M.; Uemura, S.; Takekuma, S.; Takekuma, H.; Yoshida, Z. *Nature* **2004**, *428*, 279−280.

(10) (a) Bag, S.; Trikalitis, P. N.; Chupas, P. J.; Armatas, G. S.; Kanatzidis, M. G. *Science* **2007**, *317*, 490−493. (b) Bag, S.; Gaudette, A. F.; Bussell, M. E.; Kanatzidis, M. G. *Nat. Chem.* **2009**, *1*, 217−224.

(11) Rao, P. V.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527−559.

(12) Yuhas, B. D.; Smeigh, A. L.; Samuel, A. P. S.; Shim, Y.; Bag, S.; Douvalis, A. P.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 7252−7255.

(13) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603−619.

(14) Weiss, J.; Weiss, T. *Handbook of Ion Chromatography*, 3rd ed.; Wiley-VCH: Weinheim, 2004.

(15) (a) Scheiner, D. *Water Res.* **1976**, *10*, 31−36. (b) Searle, P. L. *Analyst* **1984**, *109*, 549−568.

(16) Ngo, T. T.; Phan, A. P. H.; Yam, C. F.; Lenhoff, H. M. *Anal. Chem.* **1982**, *54*, 46−49.

(17) (a) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2820−2831. (b) Christou, G.; Garner, C. D. *J. Chem. Soc., Chem. Commun.* **1980**, 613−614. (c) Krebs, B.; Pohl, S.; Schiwy, W. *Z. Anorg. Allg. Chem.* **1972**, *393*, 241−252.