

Efficient Electrochemical and Photoelectrochemical H₂ Production from Water by a Cobalt Dithiolene One-Dimensional Metal–Organic Surface

Courtney A. Downes and Smaranda C. Marinescu*

Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

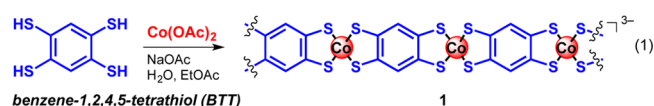
S Supporting Information

ABSTRACT: Solar-driven hydrogen evolution from water has emerged as an important methodology for the storage of renewable energy in chemical bonds. Efficient and practical clean-energy devices for electrochemical or photoelectrochemical splitting of water require the immobilization of stable and active hydrogen-evolving catalysts onto electrode or photocathode materials, which remains a significant challenge. Here we show that cobalt(II) reacts with benzene-1,2,4,5-tetrathiol in the presence of base to form a cobalt dithiolene polymer **1**. The generated polymer is immobilized onto glassy carbon electrodes (GCE) to generate a metal–organic surface (MOS 1|GCE), which displays efficient H₂-evolving activity and stability in acidic aqueous solutions. Moreover, the generated polymer is integrated with planar p-type Si to generate very efficient photocathode materials (MOS 1|Si) for solar-driven hydrogen production from water. Photocurrents up to 3.8 mA/cm² at 0 V vs RHE were achieved under simulated 1 Sun illumination. MOS 1|Si photocathodes operate at potentials 550 mV more positive than MOS 1|GCE cathodes to reach the same activity for H₂ evolution from water (1 mA/cm²).

Solar-driven hydrogen production through the reduction of water has emerged as an important strategy for the development of clean-energy technologies.¹ The hydrogen evolution reaction (HER) is efficiently catalyzed by noble metals, such as Pt, which generate large cathodic currents at low overpotentials. However, their scarcity and high cost limit widespread use. Replacement of Pt with nonprecious metal catalysts would be desirable for practical applications and global scalability of such potential clean-energy technologies. These considerations have led to the development of homogeneous² and heterogeneous³ catalysts that employ nonprecious metals. Efficient and practical clean-energy devices for HER require the immobilization onto electrodes of catalytically active species, based on inexpensive metals that can operate and are robust under acidic aqueous conditions, under which proton exchange membrane-based electrolysis is operational.⁴ Molecular catalysts are attractive because the ligand environment allows for tuning of their reduction potentials and chemical properties. However, the reported methods for the immobilization of molecular catalysts onto electrodes are scarce and suffer from low surface coverage.^{4a,5} Of particular interest for practical artificial photosynthesis devices are integrated photoelectrochemical (PEC)

systems that couple light harvesting and solar fuel production to enable direct solar-to-hydrogen production. Silicon is an excellent candidate as a light absorber in a PEC system due to its ideal band gap ($E_g = 1.12$ eV) for the absorption of low-energy sunlight to drive HER. Several photocathodes based on heterogeneous noble^{6,7} and nonprecious⁸ metal catalysts for solar-driven HER have been recently reported. In the realm of molecular catalysts, p-type silicon has been used as a photocathode with drop-casted⁹ or free catalysts in solution¹⁰ or with grafted molecular catalysts,¹¹ with the latter two displaying low activity for HER.^{10a,11} Although new methodologies for the modification of silicon surfaces through covalent attachment of molecular species show great promise,¹² the development of molecular catalysts|Si integrated photocathode materials with efficient activity for the solar-driven HER remains a major challenge. We have recently reported that cobalt dithiolene units can be incorporated into two-dimensional (2D) metal–organic surfaces (MOS), which display efficient electrocatalytic H₂-evolving activity and stability in acidic aqueous solutions.¹³ We extend here the methodology to the formation of cobalt dithiolene MOS based on benzene-1,2,4,5-tetrathiolate (BTT) frameworks and report their applications as electrode materials for efficient electrochemical and PEC HER. These studies demonstrate the broad scope of MOS synthesis with cobalt dithiolene units and, for the first time, their integration with planar p-type Si to generate very efficient photocathode materials for solar-driven HER from water.

Cobalt dithiolene species are among the most efficient molecular catalysts for HER.¹⁴ A cobalt dithiolene polymer can be accessed from a cobalt(II) starting material and a dinucleating conjugated ligand, benzene-1,2,4,5-tetrathiol, in the presence of a base and through a liquid–liquid interfacial process (eq 1). An



ethyl acetate solution of BTT was gently layered on top of an aqueous solution of cobalt(II) acetate and sodium acetate. The organic solvents were allowed to evaporate over 1 h, leaving behind a black solid (**1**) at the gas–liquid interface. Immersion of a glassy carbon electrode (GCE) face down into the reaction mixture leads to the deposition of **1** generating MOS 1|GCE,

Received: July 6, 2015

Published: October 7, 2015

which is washed and dried. Alternatively, the black solid **1** was collected, washed, suspended in water, and dropcast onto freshly etched Si(100) electrodes to generate MOS 1Si.

The measured elemental composition of **1** corresponds to a molecular formula of $[\text{Co}(\text{C}_6\text{H}_2\text{S}_4)][\text{Na}]$. The FTIR spectrum of **1** shows the disappearance of the strong signal present in the benzene-1,2,4,5-tetrathiol starting material at 2500 cm^{-1} , which corresponds to the S–H stretching vibration (Figure S3). XPS analysis of MOS 1/GCE reveals the presence of Co, S, and Na (Figure S4), analogous with the 2D cobalt dithiolene MOS based on benzenehexathiolate and triphenylene-2,3,6,7,10,11-hexathiolate frameworks.¹³ Two sets of peaks are observed in the cobalt region, with binding energies of $\sim 780\text{ eV}$ and $\sim 795\text{ eV}$, which correspond to the $2p_{3/2}$ and $2p_{1/2}$ levels in the expected 2:1 ratio. Deconvolution of these signals generates four peaks; the peaks at 778.9 and 794.1 eV are assigned to Co^{III} , whereas the peaks at 780.1 and 795.1 eV are assigned to Co^{II} .¹⁵ The $\text{Co}^{\text{III}}:\text{Co}^{\text{II}}$ ratio observed is 1:1. This assignment is in agreement with the electronic structure of cobalt bisdithiolene complexes, which are best represented by the resonances $[\text{Co}^{\text{III}}(\text{bdt})_2]^{-1} \leftrightarrow [\text{Co}^{\text{II}}(\text{bdt})(\text{bdt}\bullet)]^{-1}$ ($\text{bdt} = 1,2\text{-benzenedithiolate}$).¹⁶ Three additional peaks are observed for MOS 1/GCE with binding energies of 1071.4, ~ 228 , and $\sim 163\text{ eV}$, which correspond to Na 1s, S 2s, and S 2p, respectively. The broad peaks at 230.0 and 166.0 eV are assigned to the shakeup satellites, which are often observed in bisdithiolene complexes.¹⁷ XPS analysis of MOS 1Si revealed similar peaks with the ones observed for MOS 1/GCE (Figure S5). These data support assignment of the MOS with cobalt dithiolene moieties linked by tetrathiolate nodes.

The electrochemistry of MOS 1/GCE was investigated by cyclic voltammetry (CV). Maximum average surface catalyst concentrations of $5.5(6) \times 10^{-7}\text{ mol}_{\text{Co}}/\text{cm}^2$ are estimated from the integration of the electrochemical wave at pH 10.0. Similar values are obtained from inductively coupled plasma (ICP) measurements of the sonicated and digested catalyst **1**, suggesting that the majority of the cobalt centers are electrochemically active. As the pH of the aqueous solution is lowered, an increase in current is observed (Figures 1 and S7), indicating

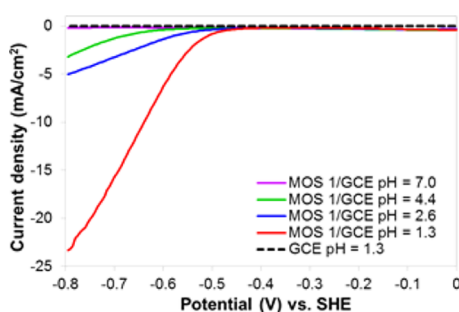


Figure 1. Polarization curves of MOS 1/GCE ($5.5(6) \times 10^{-7}\text{ mol}_{\text{Co}}/\text{cm}^2$) in 0.1 M NaClO_4 aqueous solutions at pH 7.0 (purple), 4.4 (green), 2.6 (blue), 1.3 (red), and of blank GCE at pH 1.3 (dashed black); scan rate: 20 mV/s.

that a catalytic reaction is taking place. A potential value of -0.64 V vs SHE (-0.56 V vs RHE) was required to reach a current density of $10\text{ mA}/\text{cm}^2$ at pH 1.3. This potential value is similar to the one reported for 2D cobalt dithiolene MOS based on a triphenylene-2,3,6,7,10,11-hexathiolate framework (-0.53 V vs RHE) and $\sim 0.2\text{ V}$ more negative than the benzenehexathiolate system,¹³ indicating that these MOS are indeed tunable, an advantageous characteristic of molecular catalysts. The modified

electrodes do not generate any soluble materials responsible for catalysis, as indicated by negligible currents observed in the CV studies of the solutions resulted after the electrochemical studies of MOS 1/GCE and by negligible soluble cobalt concentrations determined from ICP measurements. GCE modified with only starting materials (cobalt(II) acetate or benzene-1,2,4,5-tetrathiol) or with $[\text{Co}(\text{bdt})_2]^{-}$ displays insignificant increases in current densities (Figure S8), indicating that the catalytic activity results from MOS **1**.

Controlled potential electrolysis (CPE) of MOS 1/GCE in pH 1.3 H_2SO_4 solution, measured at -0.8 V vs SHE, consumed 32 coulombs of charge after 2 h (Figure S9). Analysis of the gas mixture in the headspace of the working compartment of the electrolysis cell by gas chromatography confirmed production of H_2 with a Faradaic yield of $97 \pm 3\%$. The durability of MOS 1/GCE in pH 2.6 aqueous solution was further assessed in a longer-duration CPE experiment. MOS 1/GCE affords a continuous increase in charge build-up over a 10 h CPE at -0.55 V vs SHE (Figure S10), however with moderate stability. The observed decrease in activity over time is attributed to delamination of the catalyst due to H_2 bubble formation. XPS analyses of MOS 1/GCE after electrochemical studies display peaks similar to the ones observed before electrolysis, suggesting that the material left on GCE is stable under reductive and acidic conditions (Figure S11). Catalytic current densities of MOS 1/GCE, measured at potentials of -0.80 V vs SHE and pH 1.3, increase linearly with catalyst loading (Figure S12).

The photoelectrochemistry of MOS 1Si was investigated by linear sweep voltammetry in pH 1.3 H_2SO_4 aqueous solution under $100\text{ mW}/\text{cm}^2$ of simulated air mass (AM)1.5G (1 Sun) illumination. The surface concentration of MOS 1Si was controlled by varying the amount of MOS **1** that was dropcast onto freshly etched Si(100) electrodes. The surface concentrations of MOS 1Si were obtained from ICP measurements of the sonicated and digested catalyst **1**. The maximum surface concentration of MOS 1Si is $6.3(6) \times 10^{-6}\text{ mol}_{\text{Co}}/\text{cm}^2$, which is an order of magnitude higher than the surface concentration of MOS 1/GCE. Under 1 Sun illumination, MOS 1Si photocathodes with a surface concentration as little as $0.5(1) \times 10^{-6}\text{ mol}_{\text{Co}}/\text{cm}^2$ display a significant improvement in both the onset of photocurrent as well as the current density compared to that of bare p-Si(100) (Figure 2a). Negligible current densities are observed in the absence of light for MOS 1Si photocathodes. Gradually increasing the surface concentrations of MOS 1Si further shifts the onset of photocurrent to an even more positive value and improves the current density at 0 V vs RHE to $3.8\text{ mA}/\text{cm}^2$ for $4.0(4) \times 10^{-6}\text{ mol}_{\text{Co}}/\text{cm}^2$. Further increasing the surface concentration to $6.3(6) \times 10^{-6}\text{ mol}_{\text{Co}}/\text{cm}^2$ leads to a decrease in catalytic activity (Figure S15), likely due to blockage of the light absorption, as reported for photocathodes based on MoS_2 .^{8g} The light-limited current density of MOS 1Si ($J_{\text{ph}} \approx 21\text{ mA}/\text{cm}^2$; Figure S16b) is less than the value anticipated from the band gap of Si due to losses associated with absorption of the incident photons by the black MOS **1** catalyst. A 430 mV positive shift in the onset of activity to reach $1\text{ mA}/\text{cm}^2$ is observed for MOS 1Si with the optimal surface concentration of $4.0(4) \times 10^{-6}\text{ mol}_{\text{Co}}/\text{cm}^2$ compared with the activity of the bare Si (Figure S16). Moreover, to reach the same activity for H_2 evolution from water ($1\text{ mA}/\text{cm}^2$), MOS 1Si photocathodes operate at potentials 550 mV more positive as compared to MOS 1/GCE cathodes (Figure 2b).

CPE studies performed at -0.12 V vs RHE in pH 1.3 H_2SO_4 solution under simulated 1 Sun illumination show that the

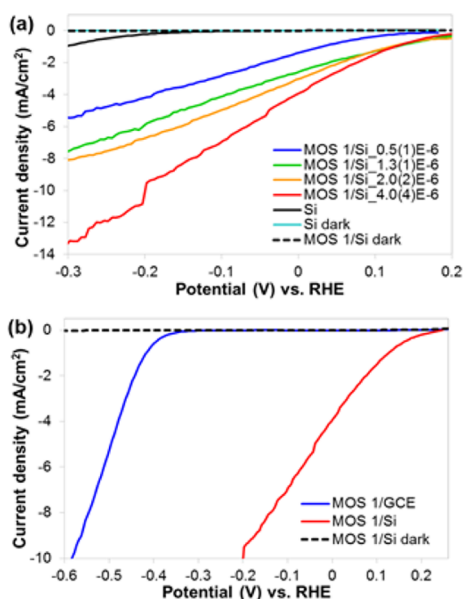


Figure 2. (a) Polarization curves of MOS 1/Si with varying surface concentrations ranging between $0.5(1)$ and $4.0(4) \times 10^{-6} \text{ mol}_{\text{Co}}/\text{cm}^2$ in pH 1.3 H_2SO_4 solutions (blue–red) and of bare Si (black) measured under simulated 1 Sun illumination. Polarization curves of MOS 1/Si (dashed black) and bare Si (cyan) measured in the absence of light. (b) Polarization curves of illuminated (red) and dark (dashed black) MOS 1/Si ($4.0(4) \times 10^{-6} \text{ mol}_{\text{Co}}/\text{cm}^2$) and MOS 1/GCE ($7.6(7) \times 10^{-7} \text{ mol}_{\text{Co}}/\text{cm}^2$, blue) in pH 1.3 H_2SO_4 solution.

current produced with MOS 1/Si photocathode is stable for 20 min (Figure 3a). Analysis of the gas mixture in the headspace of the working compartment of the photoelectrolysis cell confirmed production of H_2 with a Faradaic yield of $80 \pm 3\%$. By comparison, unmodified Si photocathodes display very little H_2 -evolving activity. Negligible current densities are observed for

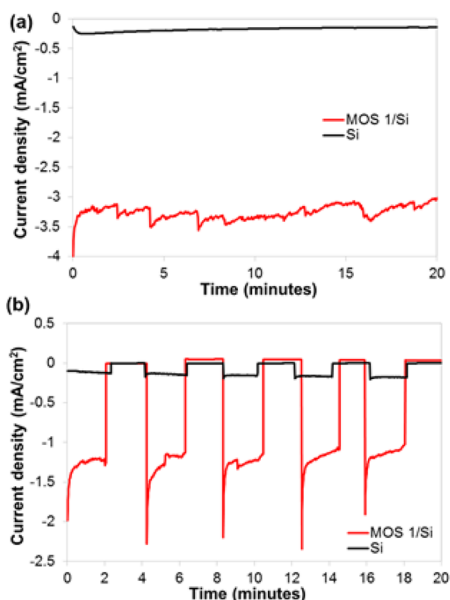


Figure 3. (a) CPE studies of MOS 1/Si ($0.9(1) \times 10^{-6} \text{ mol}_{\text{Co}}/\text{cm}^2$, red) and bare Si (black) at -0.12 V vs RHE in pH 1.3 H_2SO_4 solutions under simulated 1 Sun illumination. (b) CPE studies of MOS 1/Si ($0.6(1) \times 10^{-6} \text{ mol}_{\text{Co}}/\text{cm}^2$, red) and bare Si (black) at -0.12 V vs RHE in pH 1.3 H_2SO_4 solutions under chopped (light on/light off) 1 Sun illumination.

CPE studies performed in the absence of light (Figure 3b). Si photocathodes modified with starting materials only (cobalt(II)acetate or benzene-1,2,4,5-tetrathiol) or with $[\text{Co}(\text{bdt})_2]^-$, by the drop-casting method or in solution display insignificant current densities (Figure S17). The durability of MOS 1/Si at -0.12 V vs RHE in pH 1.3 H_2SO_4 solution was further assessed in a longer-duration CPE experiment. MOS 1/Si affords a continuous increase in charge build-up over a 2 h CPE at -0.12 V vs RHE (Figure S18), however with moderate stability, due to delamination of the catalyst from the Si surface, as described above for MOS 1/GCE. XPS analyses of MOS 1/Si after PEC studies display peaks similar to the ones observed before, suggesting that the material left on the Si support is stable during photocatalysis (Figure S19). Si 2p core level XPS spectra of Si and MOS 1/Si contain peaks at ~ 99 and $\sim 102 \text{ eV}$, indicative of Si–H and Si–O, respectively, terminated surfaces (Figure S22). The presence of an interfacial oxide on both the bare Si and MOS 1/Si photocathodes before and after PEC studies is attributed to the Si oxidation in air during the samples preparation and loading before XPS analysis or during the longer-duration CPE experiments. Si–Me passivated photocathodes will be explored in the future due to their increased stability toward oxidation.

The MOS generated here operates under fully aqueous conditions. Photocurrents up to $3.8 \text{ mA}/\text{cm}^2$ at 0 V vs RHE were achieved using MOS 1/Si photocathodes under simulated 1 Sun illumination, which is among the highest photocurrents reported for an immobilized molecular catalysts/Si integrated photocathode materials. Moreover, the maximum surface concentration of MOS 1/Si is $6.3(6) \times 10^{-6} \text{ mol}_{\text{Co}}/\text{cm}^2$, which is 4 orders of magnitude higher than the one reported for the covalently attached nickel phosphine H_2 -evolving catalyst.¹¹ To reach a current density of $1 \text{ mA}/\text{cm}^2$, MOS 1/Si photocathodes require potentials 550 mV less negative than MOS 1/GCE cathodes (photovoltage). Similar values were reported for the photovoltage of several free catalysts in solution.¹⁰ Other photocathode materials, such as InP,¹⁸ GaP,^{5e,f,19} or water-solubilized CdSe quantum dots,^{14d,20} have been investigated for their ability to interface with molecular systems, and, despite their great promise, their chemical stability and PEC performance needs to be improved. The generated MOS 1/Si photocathodes display increased activity and stability.

In summary, we demonstrate here the successful integration of cobalt dithiolene catalysts with glassy carbon or Si electrodes to generate MOS-modified cathodes. MOS 1/Si is an efficient photocathode material for solar-driven hydrogen production from water, achieving photocurrents of $3.8 \text{ mA}/\text{cm}^2$ at 0 V vs RHE under simulated 1 Sun illumination. The generated MOS display current densities much higher than those of the molecular complex, suggesting that immobilization provides a significant increase in efficiency and stability for these cobalt catalysts and thus paves the way toward development of practical devices.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.5b07020](https://doi.org/10.1021/jacs.5b07020).

Experimental procedures, spectroscopic characterization, and electrochemical data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*smarines@usc.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the University of Southern California (USC) and the Office of the Provost of USC (Zumberge Individual award to S.C.M.) for funding. We thank Prof. Richard Brutchey and Haipeng Lu for providing access to the Si reference cell and for assistance with the calibration of the light intensity. XPS and SEM data were collected at the Center for Electron Microscopy and Microanalysis, USC. We are grateful to the Anton Burg Foundation for their sponsorship of the elemental analysis instrument.

REFERENCES

- (1) (a) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729. (b) Gray, H. B. *Nat. Chem.* **2009**, *1*, 7.
- (2) (a) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995. (b) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238. (c) Du, P.; Eisenberg, R. *Energy Environ. Sci.* **2012**, *5*, 6012. (d) McKone, J. R.; Marinescu, S. C.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Chem. Sci.* **2014**, *5*, 865. (e) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388. (f) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3683. (g) Helm, M. L.; Stewart, M. P.; Bullock, R. M.; DuBois, M. R.; DuBois, D. L. *Science* **2011**, *333*, 863.
- (3) Cook, T. R.; Dogutan, D. K.; Reece, S. Y.; Surendranath, Y.; Teets, T. S.; Nocera, D. G. *Chem. Rev.* **2010**, *110*, 6474.
- (4) (a) Le Goff, A.; Artero, V.; Jusselme, B.; Tran, P. D.; Guillet, N.; Metaye, R.; Fihri, A.; Palacin, S.; Fontecave, M. *Science* **2009**, *326*, 1384. (b) Hamburger, M.; Gervaldo, M.; Svedruzic, D.; King, P. W.; Gust, D.; Ghirardi, M.; Moore, A. L.; Moore, T. A. *J. Am. Chem. Soc.* **2008**, *130*, 2015.
- (5) (a) Andreiadis, E. S.; Jacques, P.-A.; Tran, P. D.; Leyris, A.; Chavarot-Kerlidou, M.; Jusselme, B.; Matheron, M.; Pécourt, J.; Palacin, S.; Fontecave, M.; Artero, V. *Nat. Chem.* **2013**, *5*, 48. (b) Tran, P. D.; Le Goff, A.; Heidkamp, J.; Jusselme, B.; Guillet, N.; Palacin, S.; Dau, H.; Fontecave, M.; Artero, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 1371. (c) Blakemore, J. D.; Gupta, A.; Warren, J. J.; Brunschwig, B. S.; Gray, H. B. *J. Am. Chem. Soc.* **2013**, *135*, 18288. (d) Das, A. K.; Engelhard, M. H.; Bullock, R. M.; Roberts, J. A. S. *Inorg. Chem.* **2014**, *53*, 6875. (e) Krawicz, A.; Yang, J.; Anzenberg, E.; Yano, J.; Sharp, I. D.; Moore, G. F. *J. Am. Chem. Soc.* **2013**, *135*, 11861. (f) Krawicz, A.; Cedeno, D.; Moore, G. F. *Phys. Chem. Chem. Phys.* **2014**, *16*, 15818.
- (6) (a) Reece, S. Y.; Hamel, J. A.; Sung, K.; Jarvi, T. D.; Esswein, A. J.; Pijpers, J. J. H.; Nocera, D. G. *Science* **2011**, *334*, 645. (b) Boettcher, S. W.; Spurgeon, J. M.; Putnam, M. C.; Warren, E. L.; Turner-Evans, D. B.; Kelzenberg, M. D.; Maiolo, J. R.; Atwater, H. A.; Lewis, N. S. *Science* **2010**, *327*, 185. (c) Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. *J. Am. Chem. Soc.* **2011**, *133*, 1216.
- (7) (a) Dominey, R. N.; Lewis, N. S.; Bruce, J. A.; Bookbinder, D. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 467. (b) Oh, I.; Kye, J.; Hwang, S. *Nano Lett.* **2012**, *12*, 298. (c) Dasgupta, N. P.; Liu, C.; Andrews, S.; Prinz, F. B.; Yang, P. *J. Am. Chem. Soc.* **2013**, *135*, 12932. (d) Zhao, Y.; Anderson, N. C.; Zhu, K.; Aguiar, J. A.; Seabold, J. A.; van de Lagemaat, J.; Branz, H. M.; Neale, N. R. *Nano Lett.* **2015**, *15*, 2517. (e) Seo, J.; Kim, H. J.; Pekarek, R. T.; Rose, M. J. *J. Am. Chem. Soc.* **2015**, *137*, 3173.
- (8) (a) McKone, J. R.; Warren, E. L.; Bierman, M. J.; Boettcher, S. W.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. *Energy Environ. Sci.* **2011**, *4*, 3573. (b) Warren, E. L.; McKone, J. R.; Atwater, H. A.; Gray, H. B.; Lewis, N. S. *Energy Environ. Sci.* **2012**, *5*, 9653. (c) Berglund, S. P.; He, H.; Chemelewski, W. D.; Celio, H.; Dolocan, A.; Mullins, C. B. *J. Am. Chem. Soc.* **2014**, *136*, 1535. (d) Seger, B.; Laursen, A. B.; Vesborg, P. C. K.; Pedersen, T.; Hansen, O.; Dahl, S.; Chorkendorff, I. *Angew. Chem., Int. Ed.* **2012**, *51*, 9128. (e) Sun, Y.; Liu, C.; Grauer, D. C.; Yano, J.; Long, J. R.; Yang, P.; Chang, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 17699. (f) Sim, U.; Yang, T. Y.; Moon, J.; An, J.; Hwang, J.; Seo, J. H.; Lee, J.; Kim, K. Y.; Lee, J.; Han, S.; Hong, B. H.; Nam, K. T. *Energy Environ. Sci.* **2013**, *6*, 3658. (g) Ding, Q.; Meng, F.; English, C. R.; Cabañ-Acevedo, M.; Shearer, M. J.; Liang, D.; Daniel, A. S.; Hamers, R. J.; Jin, S. *J. Am. Chem. Soc.* **2014**, *136*, 8504. (h) Roske, C. W.; Popczun, E. J.; Seger, B.; Read, C. G.; Pedersen, T.; Hansen, O.; Vesborg, P. C. K.; Brunschwig, B. S.; Schaak, R. E.; Chorkendorff, I.; Gray, H. B.; Lewis, N. S. *J. Phys. Chem. Lett.* **2015**, *6*, 1679. (i) Morales-Guio, C. G.; Thorwarth, K.; Niesen, B.; Liardet, L.; Patscheider, J.; Ballif, C.; Hu, X. *J. Am. Chem. Soc.* **2015**, *137*, 7035. (j) Basu, M.; Zhang, Z.-W.; Chen, C.-J.; Chen, P.-T.; Yang, K.-C.; Ma, C.-G.; Lin, C. C.; Hu, S.-F.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2015**, *54*, 6211. (k) Tran, P. D.; Pramana, S. S.; Kale, V. S.; Nguyen, M.; Chiam, S. Y.; Batabyal, S. K.; Wong, L. H.; Barber, J.; Loo, J. *Chem. - Eur. J.* **2012**, *18*, 13994.
- (9) Hou, Y. D.; Abrams, B. L.; Vesborg, P. C. K.; Bjorketun, M. E.; Herbst, K.; Bech, L.; Setti, A. M.; Damsgaard, C. D.; Pedersen, T.; Hansen, O.; Rossmel, J.; Dahl, S.; Nørskov, J. K.; Chorkendorff, I. *Nat. Mater.* **2011**, *10*, 434.
- (10) (a) Kumar, B.; Beyler, M.; Kubiak, C. P.; Ott, S. *Chem. - Eur. J.* **2012**, *18*, 1295. (b) Kumar, B.; Smieja, J. M.; Kubiak, C. P. *J. Phys. Chem. C* **2010**, *114*, 14220. (c) Kumar, B.; Smieja, J. M.; Sasayama, A. F.; Kubiak, C. P. *Chem. Commun.* **2012**, 48, 272.
- (11) Seo, J.; Pekarek, R. T.; Rose, M. J. *Chem. Commun.* **2015**, *51*, 13264.
- (12) (a) Moore, G. F.; Sharp, I. D. *J. Phys. Chem. Lett.* **2013**, *4*, 568. (b) Lattimer, J. R. C.; Blakemore, J. D.; Sattler, W.; Gul, S.; Chatterjee, R.; Yachandra, V. K.; Yano, J.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. *Dalton Trans.* **2014**, 43, 15004. (c) O'Leary, L. E.; Rose, M. J.; Ding, T. X.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. *J. Am. Chem. Soc.* **2013**, *135*, 10081. (d) Lattimer, J. R. C.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. *J. Phys. Chem. C* **2013**, *117*, 27012. (e) Liu, W.; Sharp, I. D.; Tilley, T. D. *Langmuir* **2013**, *30*, 172. (f) Li, F.; Basile, V. M.; Pekarek, R. T.; Rose, M. J. *ACS Appl. Mater. Interfaces* **2014**, *6*, 20557.
- (13) Clough, A. J.; Yoo, J. W.; Mecklenburg, M. H.; Marinescu, S. C. *J. Am. Chem. Soc.* **2015**, *137*, 118.
- (14) (a) McNamara, W. R.; Han, Z.; Alperin, P. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *J. Am. Chem. Soc.* **2011**, *133*, 15368. (b) McNamara, W. R.; Han, Z.; Yin, C.-J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15594. (c) Eckenhoff, W. T.; McNamara, W. R.; Du, P.; Eisenberg, R. *Biochim. Biophys. Acta, Bioenerg.* **2013**, *1827*, 958. (d) Han, Z.; Eisenberg, R. *Acc. Chem. Res.* **2014**, *47*, 2537. (e) Letko, C. S.; Panetier, J. A.; Head-Gordon, M.; Tilley, T. D. *J. Am. Chem. Soc.* **2014**, *136*, 9364. (f) Eady, S. C.; Peczonczyk, S. L.; Maldonado, S.; Lehnert, N. *Chem. Commun.* **2014**, *50*, 8065.
- (15) Chuang, T. J.; Brundle, C. R.; Rice, D. W. *Surf. Sci.* **1976**, *59*, 413.
- (16) Sproules, S.; Wieghardt, K. *Coord. Chem. Rev.* **2011**, *255*, 837.
- (17) (a) Kambe, T.; Sakamoto, R.; Hoshiko, K.; Takada, K.; Miyachi, M.; Ryu, J. H.; Sasaki, S.; Kim, J.; Nakazato, K.; Takata, M.; Nishihara, H. *J. Am. Chem. Soc.* **2013**, *135*, 2462. (b) Lui, S.-G.; Liu, Y.-Q.; Zhu, D.-B. *Synth. Met.* **1997**, *89*, 187. (c) Zhou, S.; Ichimura, K.; Inokuchi, H. *J. Mater. Chem.* **1995**, *5*, 1725. (d) Matsuo, R.; Sakamoto, R.; Kambe, T.; Takada, K.; Kusamoto, T.; Nishihara, H. *Chem. Commun.* **2014**, *50*, 8137.
- (18) Nann, T.; Ibrahim, S. K.; Woi, P.-M.; Xu, S.; Ziegler, J.; Pickett, C. *J. Angew. Chem., Int. Ed.* **2010**, *49*, 1574.
- (19) Cedeno, C.; Krawicz, A.; Doak, P.; Yu, M.; Neaton, J. B.; Moore, G. F. *J. Phys. Chem. Lett.* **2014**, *5*, 3222.
- (20) (a) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. *Science* **2012**, *338*, 1321. (b) Das, A.; Han, Z.; Haghighi, M. G.; Eisenberg, R. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 16716. (c) Ruberu, T. P. A.; Dong, Y.; Das, A.; Eisenberg, R. *ACS Catal.* **2015**, *5*, 2255. (d) Wang, M.; Han, K.; Zhang, S.; Sun, L. *Coord. Chem. Rev.* **2015**, *287*, 1.