JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Electrodeposited Cobalt-Sulfide Catalyst for Electrochemical and Photoelectrochemical Hydrogen Generation from Water

Yujie Sun,[†,∥,∇,◆] Chong Liu,[†,◆] David C. Grauer,[†,⊥] Junko Yano,[⊗] Jeffrey R. Long,*[,†,⊥] Peidong Yang,*[,†,#] and Christopher J. Chang*[,†,‡,§,∥]

Departments of [†]Chemistry and [‡]Molecular and Cell Biology and [§]the Howard Hughes Medical Institute, University of California, Berkeley, California 94720, United States

[∥]Chemical Sciences Division, [⊥]Materials Sciences Division, and [⊗]Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[#]Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

Supporting Information

ABSTRACT: A cobalt-sulfide (Co−S) film prepared via electrochemical deposition on conductive substrates is shown to behave as an efficient and robust catalyst for electrochemical and photoelectrochemical hydrogen generation from neutral pH water. Electrochemical experiments demonstrate that the film exhibits a low catalytic onset overpotential (η) of 43 mV, a Tafel slope of 93 mV/dec, and near 100% Faradaic efficiency in pH 7 phosphate buffer. Catalytic current densities can approach 50 mA/cm^2 and activity is maintained for at least 40 h. The catalyst can also be electrochemically coated on silicon, rendering a water-compatible photoelectrochemical system for hydrogen production under simulated 1 sun illumination. The facile preparation of this Co−S film, along with its low overpotential, high activity, and long-term aqueous stability, offer promising features for potential use in solar energy applications.

Hydrogen, when generated directly from water or through other carbon-neutral processes, is a promising chemical fuel for sustainable energy applications.[1] As such, the development of synthetic hydrogen evolution reaction (HER) catalysts that functionally mimic the elegant water reduction chemistry of hydrogenase enzymes have attracted broad interest,[2−4] but creating molecular systems that utilize earth-abundant elements and achieve high efficiency and activity, a low overpotential for hydrogen production, and long-term stability in green aqueous media remains a significant challenge.[5] Several aqueous compatible and water-soluble molecular HER catalysts have been reported;[5] nevertheless, they usually suffer from a large overpotential and/or low stability.[6] Solid-state inorganic compounds offer an alternative strategy to meet this goal and a number of interesting materials have emerged as earth-abundant platinum replacements for HER catalysis, including metal alloys,[7] nitrides,[8] borides,[9] carbides,[9] chalcogenides,[10] and phosphides,[11] but the vast majority of these systems are limited to use in strongly acidic media. Our laboratory[12] and others[4a,5l,7,13] have sought to develop HER catalysts for use in neutral pH water to avoid the use of strong acids and bases, thus reducing their environmental impact and increasing their biocompatibility. In particular, we have recently exploited polypyridine ligand platforms to support molecular molybdenum and cobalt systems that exhibit robust electrochemical and photochemical HER catalysis in water.[14] As a complementary approach to these molecular efforts, we now report that an electrodeposited cobalt−sulfide (Co−S) film is an efficient and robust HER catalyst in aqueous media. This catalyst maintains its activity for at least 40 h in neutral pH water and exhibits a low catalytic onset overpotential (η) of 43 mV, a Tafel slope of 93 mV/dec, and near 100% Faradaic efficiency in pH 7 water, with current densities that can approach 50 mA/cm^2. Moreover, the Co−S film is easily coated on semiconductor substrates, resulting in a water-compatible system for photoelectrochemical hydrogen evolution under simulated 1 sun irradiation, establishing its utility for solar energy applications.

In the context of our investigations of molecular mimics of molybdenum-sulfide edge sites,[15] we were inspired by Hu's work showing that cobalt additives could improve the HER performance of molybdenum-sulfide films in acidic media,[16] as well as the redox activity of cobalt-sulfide films and their use in dye-sensitized solar cells,[17,18] and thus sought to explore cobalt sulfides for HER catalysis. With the use of fluorine-doped tin oxide (FTO) as both the working and counter electrodes with a Ag/AgCl reference electrode (Figure S1), a cobalt-sulfide (Co−S) film was deposited electrochemically on FTO from $CoCl_2$ and thiourea precursors. During progression of the deposition process, the exposed area of the transparent FTO working electrode took on a nearly black color. Scans of a typical potentiodynamic deposition of Co−S film are shown in Figure S2. After rinsing thoroughly with water and acetone, the dried Co−S/FTO electrode was annealed at 300 °C under argon for 2 h. Figure 1 displays a scanning electron microscopy (SEM) image of the annealed Co−S film, and its amorphous nature is confirmed by X-ray diffraction data, as shown in Figure S3. The presence of Co and S in the film was identified by energy dispersive X-ray spectroscopy (EDX) (Figure S4) and further

Received: September 12, 2013
Published: November 13, 2013

   dx.doi.org/10.1021/ja4094764 | J. Am. Chem. Soc. 2013, 135, 17699−17702

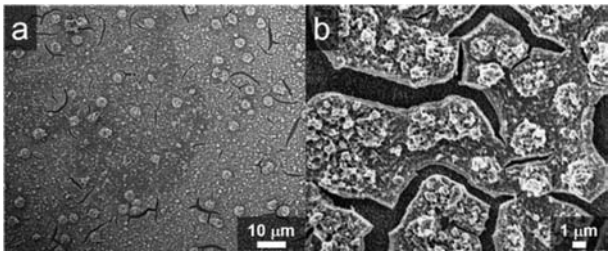

Figure 1. Representative SEM images of the annealed Co−S film on FTO.

confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). We note that the Co/S ratio of ∼1.4 remains constant for both the as-prepared and annealed Co−S films (Table S1), indicating that its composition is not pure CoS but also likely contains $CoO/Co(OH)_2$, which is in line with previous observations.[17] X-ray photoelectron spectroscopy (XPS) data summarized in Figures S5−S9 provide further support for this hypothesis. Indeed, a Co 2p peak at 781.2−781.4 eV with a shoulder at ∼786 eV indicates a Co^{2+} oxidation state with a mixed composition of CoS and $CoO/Co(OH)_2$ (Figure S7).[17−21] Similarly, the S 2p peak at 161−163 eV suggests a S^{2-} oxidation state (Figure S8).[17,22] Importantly, the oxidation states of both Co and S remain constant before and after annealing, as evidenced by their similar XPS spectra. The comparison of the XANES and EXAFS results of the Co−S/FTO sample with CoO further confirms the Co^{2+} oxidation state and its dominating composition as CoS (Figures S10−S11, Table S2).[13,23]

The annealed Co−S film is an active HER catalyst in neutral pH water, as illustrated in Figure S12. After electrolysis at η = 287 mV for 3 h, the polarization curve of the Co−S film is shown in Figure 2. Under these conditions, the catalytic current rises at a low onset overpotential of 43 mV, accompanied by H_2 bubbles evolving from the electrode surface. Catalytic current densities approaching 50 mA/cm^2 can be achieved at η = 397 mV. For comparison, amorphous MoS_2 films prepared by a similar potentiodynamic deposition show a current density of 7 mA/cm^2 at the same pH and overpotential (pH 7, η = 400 mV).[10h] In addition, an elegant Janus cobalt catalyst for water splitting reported recently achieves current densities of 0.5 and 2 mA/cm^2 for H_2 production at overpotentials of 270 and 385 mV;[13] at these same overpotentials, the Co−S film exhibits current densities of 29 and 48 mA/cm^2, respectively. To achieve a moderate current density of 2 mA/cm^2, the Co−S film needs an overpotential of only 85 mV, while other earth-abundant solid-state catalysts typically require an overpotential of 100−200 mV (Table S3).

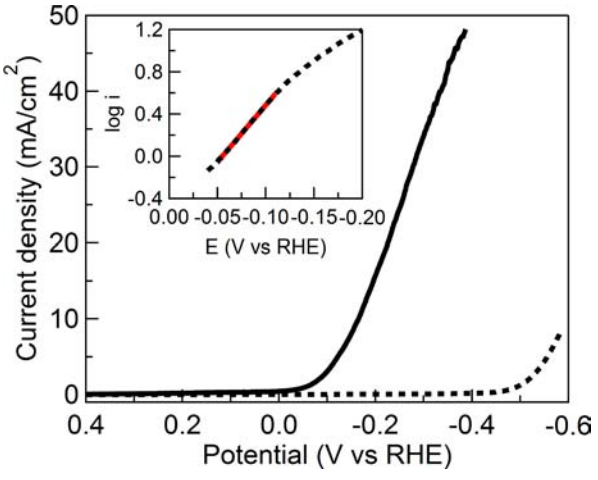

Figure 2. Polarization curves of annealed Co−S/FTO (solid) after controlled potential electrolysis at η = 287 mV for 3 h and blank FTO (dotted) in 1.0 M potassium phosphate buffer of pH 7 water (scan rate: 5 mV/s). Inset: Tafel plot of the Co−S/FTO electrode under the same conditions (black dotted) and linear fitting curve (red solid), rendering a Tafel slope of 93 mV/dec. The unit of log i is log(mA/cm^2).

The Tafel slope value of 93 mV/dec, calculated from data displayed in the inset of Figure 2, does not match any of the three principle steps for hydrogen evolution (29, 38, or 116 mV/dec),[24] but is comparable to values reported for other amorphous M-MoS_3 (M = Fe, Co, or Ni) films[16] and crystalline Cu_2MoS_4[25] (86−96 mV/dec) HER catalysts at pH 7 (Table S3). In addition to its low onset overpotential and high activity, the Co−S catalyst operates at virtually 100% Faradaic efficiency, as determined by direct quantification of the H_2 produced over a 3-h controlled potential electrolysis using gas chromatography (Figures S13−S14). Finally, ICP-OES analysis of the Co−S film after this 3-h electrolysis shows a Co/S ratio of nearly 1 (Table S1), suggesting the possible dissolution of $CoO/Co(OH)_2$ while maintaining the integrity of CoS during electrocatalysis. The SEM images of this postelectrolysis Co−S/FTO electrode are shown in Figure S15.

The durability of the Co−S film in neutral pH water was further assessed in a longer-duration controlled potential electrolysis experiment. As depicted in Figure 3, the catalyst

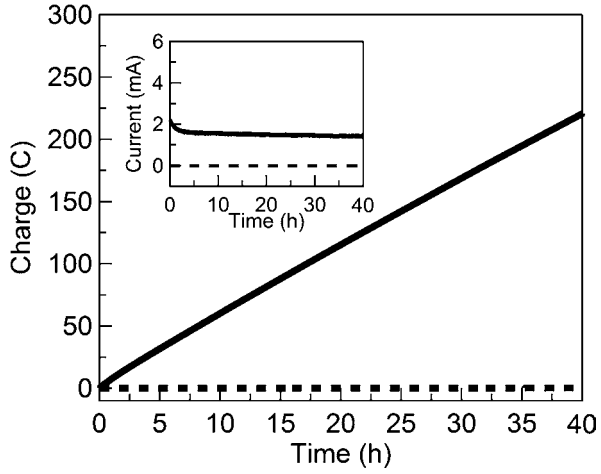

Figure 3. Extended controlled potential electrolysis shows the accumulated charge versus time for annealed Co−S/FTO (solid) and a blank FTO electrode (dotted) in 1.0 M potassium phosphate buffer of pH 7 at η = 187 mV. Inset: current versus time during the long-term controlled potential electrolysis of Co−S/FTO (solid) and blank FTO (dotted).

affords a robust and essentially linear charge build-up over time, with no substantial loss in activity over the course of at least 40 h. In contrast, negligible charge was passed when a blank FTO electrode was used as the working electrode under the same conditions. To estimate lower bounds for the turnover frequency (TOF) and turnover number (TON) for HER during the 40-h electrolysis, we assumed all of the loaded Co contributed to the overall catalysis. On the basis of catlyst loadings measured by bulk ICP-OES (Co = 1.35 μmol/cm^2,

dx.doi.org/10.1021/ja4094764 | J. Am. Chem. Soc. 2013, 135, 17699−17702

Table S3), a TOF of 0.017 s^{-1} and a TON of 2420 are estimated. However, we note that these values represent an underestimated activity of the Co−S film, since only surface-exposed sites are expected to be responsible for catalysis. Significantly, the low overpotential, high activity, and long-term stability of the Co−S film compares quite favorably to related solid-state HER catalysts for use in neutral pH water, including MoS_2,[10] M-MoS_2 (M = Mn, Fe, Co, Ni, Cu, and Zn),[16] MoS_2/MoO_3,[10] Cu_2MoS_4,[25] MoN,[8] $NiMoN_x$/C,[8] and Ni_2P[11] systems collated in Table S2.

We next investigated the HER performance of the Co−S catalyst at extreme pH values. In 0.5 M H_2SO_4, a rapid catalytic current rises when scanning beyond −0.05 V vs RHE with a Tafel slope of 56 mV/dec (Figure S18), with H_2 generation confirmed by gas chromatography; however, subsequent cathodic sweeps led to a quick deactivation of the film, which is most likely due to the dissolution of CoS in strong acidic media as the FTO electrode returns to a transparent color after these cathodic scans. On the other hand, in 1.0 M KOH, the Co−S film exhibits robust HER activity, with a catalytic onset of η = 100 mV and nearly linear charge accumulation during a 25-h controlled potential electrolysis (Figure S19). The Co−S film is also compatible with seawater, the most abundant proton source on earth. Figure S20 (top) compares the polarization curves of Co−S/FTO and blank FTO in seawater with 1.0 M $NaClO_4$ as a supporting electrolyte. Only the former shows a catalytic onset at −0.6 V vs SHE followed by a rapid current rise, and the activity persists for at least 20 h as established by a long-term controlled potential electrolysis (Figure S20 (bottom)). Taken together, these results establish the robust HER activity of the Co−S catalyst for a wide range of pH values and aqueous reaction media.

We then proceeded to assemble a system for photoelectrochemical hydrogen evolution by electrochemically depositing the Co−S catalyst on a planar n^+/p-Si electrode. Figure 4 compares the photocurrent densities of n^+/p-Si electrodes coated with Co−S by different cycles of preparation. Indeed, the presence of the Co−S catalyst significantly enhances the photocurrent densities of the planar n^+/p-Si electrodes under simulated 1 sun irradiation in pH 7 buffer.

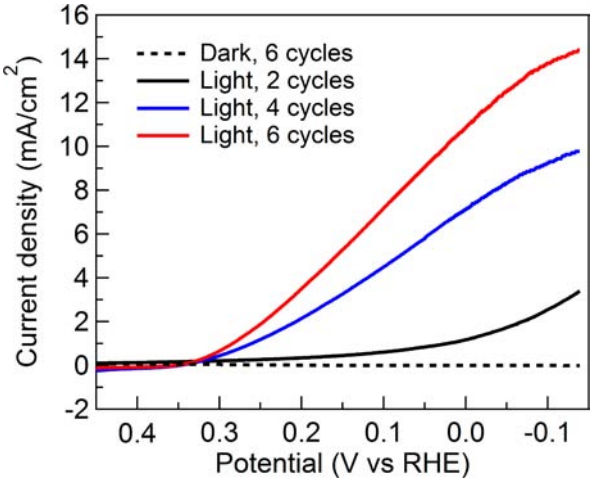

Figure 4. Polarization curves of Co−S deposited on planar n^+/p-Si photoelectrodes with different preparation cycles in 1.0 M potassium phosphate buffer of pH 7. Light source: 100 mW/cm^2 AM 1.5 G illumination via a 300 W xenon lamp. Scan rate: 10 mV/s.

With increasing deposition cycles from 2 to 6, the photocurrent density rises from ∼1 to ∼11 mA/cm^2 at 0 V vs RHE, and the onset also shifts to ∼320 mV vs RHE. Further cycles of Co−S deposition do not improve the photocurrent response (Figure S21), presumably due to inner-filter effects of the catalyst upon light absorption by Si (Figure S22). Nevertheless, the data show the compatibility of the Co−S catalyst for solar energy applications in neutral pH water.

In summary, we have discovered that a Co−S film prepared by simple potentiodynamic deposition is an active, efficient, and robust HER catalyst in neutral pH water, as well as other aqueous media, featuring a low onset overpotential, 100% Faradaic efficiency, and high current densities that can persist for at least 40 h. Moreover, this Co−S catalyst can be easily deposited on silicon electrodes, resulting in a photoelectrochemical system for proton production from water under simulated 1 sun illumination. These results provide a starting point for further structure/activity investigations of Co−S films and related metal chalcogenides for HER and other energy catalysis applications.

■ ASSOCIATED CONTENT

Supporting Information

Details for catalyst preparation and additional characterization, electrochemistry, and photoelectrochemistry data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

chrischang@berkeley.edu; p_yang@berkeley.edu; jrlong@berkeley.edu

Present Address

[▽]Y.S.: Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322.

Author Contributions

[◆]Y.S. and C.L. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The catalyst preparation, characterization, and electrochemistry work was supported by DOE/LBNL Grant 403801 (C.J.C.) and the DoE/LBNL Helios Solar Energy Research Center 51HE112B (C.J.C. and Y.S.). J.R.L. was supported by the US DOE, Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Program. The photoelectrochemistry work was supported by KAU (P.Y.). XAS experiments were performed at the Advanced Light Source (BL 10.3.2), Berkeley, under Contract DE-AC02-05CH11231. C.J.C. is an Investigator with the Howard Hughes Medical Institute.

■ REFERENCES

(1) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Turner, J. A. *Science* **2004**, *305*, 972. (c) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729. (d) Gray, H. B. *Nat. Chem.* **2009**, *1*, 7.

(2) (a) Evans, D. J.; Pickett, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268. (b) Tye, J. W.; Hall, M. B.; Darensbourg, M. Y. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 16911. (c) Barton, B. E.; Olsen, M. T.; Rauchfuss, T. B. *Curr. Opin. Biotechnol.* **2010**, *21*, 292.

(3) (a) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995. (b) Rakowski Dubois, M.; Dubois, D. L. *Acc. Chem. Res.* **2009**, *42*, 1974. (c) Rakowski DuBois, M.; DuBois,

D. L. *Chem. Soc. Rev.* **2009**, *38*, 62. (d) Gloaguen, F.; Rauchfuss, T. B. *Chem. Soc. Rev.* **2009**, *38*, 100. (e) Ogo, S. *Chem. Commun.* **2009**, 3317. (f) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238. (g) Wang, M.; Chen, L.; Sun, L. *Energy Environ. Sci.* **2012**, *5*, 6763. (h) Inglis, J. L.; MacLean, B. J.; Pryce, M. T.; Vos, J. G. *Coord. Chem. Rev.* **2012**, *256*, 2571. (i) Du, P.; Eisenberg, R. *Energy Environ. Sci.* **2012**, *5*, 6012.

(4) (a) Le Goff, A.; Artero, V.; Jousselme, B.; Tran, P. D.; Guillet, N.; Métayé, R.; Fihri, A.; Palacin, S.; Fontecave, M. *Science* **2009**, *326*, 1384. (b) Helm, M. L.; Stewart, M. P.; Bullock, R. M.; DuBois, M. R.; DuBois, D. L. *Science* **2011**, *333*, 863. (c) Wang, F.; Wang, W.-G.; Wang, X.-J.; Wang, H.-Y.; Tung, C.-H.; Wu, L.-Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 3193. (d) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. *Science* **2012**, *338*, 1321. (e) McCrory, C. C. L.; Uyeda, C.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 3164. (f) Anxolabéhère-Mallart, E.; Costentin, C.; Fournier, M.; Nowak, S.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2012**, *134*, 6104. (g) McNamara, W. R.; Han, Z.; Alperin, P. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *J. Am. Chem. Soc.* **2012**, *133*, 15368. (h) Marinescu, S. C.; Winkler, J. R.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15127. (i) Andreiadis, E. S.; Jacques, P.-A.; Tran, P. D.; Leyris, A.; Chavarot-Kerlidou, M.; Jousselme, B.; Matheron, M.; Pécaut, J.; Palacin, S.; Fontecave, M.; Artero, V. *Nat. Chem.* **2013**, *5*, 48.

(5) (a) Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7361. (b) Houlding, V.; Geiger, T.; Kolle, U.; Gratzel, M. *Chem. Commun.* **1982**, 681. (c) Kellett, R. M.; Spiro, T. G. *Inorg. Chem.* **1985**, *24*, 2373. (d) Koelle, U.; Paul, S. *Inorg. Chem.* **1986**, *25*, 2689. (e) Collin, J. P.; Jouaiti, A.; Sauvage, J. P. *Inorg. Chem.* **1988**, *27*, 1986. (f) Bernhardt, P. V.; Jones, L. A. *Inorg. Chem.* **1999**, *38*, 5086. (g) Mejia-Rodriguez, R.; Chong, D.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004. (h) Begum, A.; Moula, G.; Sarkar, S. *Chem.—Eur. J.* **2010**, *16*, 12324. (i) Voloshin, Y. Z.; Dolganov, A. V.; Varzatskii, O. A.; Bubnov, Y. N. *Chem. Commun.* **2011**, *47*, 7737. (j) Kilgore, U. J.; Roberts, J. A. S.; Pool, D. H.; Appel, A. M.; Stewart, M. P.; DuBois, M. R.; Dougherty, W. G.; Kassel, W. S.; Bullock, R. M.; DuBois, D. L. *J. Am. Chem. Soc.* **2012**, *133*, 5861. (k) Stubbert, B. D.; Peters, J. C.; Gray, H. B. *J. Am. Chem. Soc.* **2012**, *133*, 18070. (l) Singh, W. M.; Baine, T.; Kudo, S.; Tian, S.; Ma, X. A. N.; Zhou, H.; DeYonker, N. J.; Pham, T. C.; Bollinger, J. C.; Baker, D. L.; Yan, B.; Webster, C. E.; Zhao, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 5941. (m) Quentel, F.; Passard, G.; Gloaguen, F. *Energy Environ.Sci.* **2012**, *5*, 7757.

(6) Artero, V.; Fontecave, M. *Chem. Soc. Rev.* **2013**, *42*, 2338.

(7) 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.

(8) Chen, W.-F.; Sasaki, K.; Ma, C.; Frenkel, A. I.; Marinkovic, N.; Muckerman, J. T.; Zhu, Y.; Adzic, R. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 6131.

(9) (a) Vrubel, H.; Hu, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 12703. (b) Scanlon, M. D.; Bian, X.; Vrubel, H.; Amstutz, V.; Schenk, K.; Hu, X.; Liu, B.; Girault, H. H. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2847.

(10) (a) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jorgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Norskov, J. K. *J. Am. Chem. Soc.* **2005**, *127*, 5308. (b) Jaramillo, T. F.; Jorgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. *Science* **2007**, *317*, 100. (c) Jaramillo, T. F.; Bonde, J.; Zhang, J.; Ooi, B.-L.; Andersson, K.; Ulstrup, J.; Chorkendorff, I. *J. Phys. Chem. C* **2008**, *112*, 17492. (d) Bonde, J.; Moses, P. G.; Jaramillo, T. F.; Norskov, J. K.; Chorkendorff, I. *Farad. Discuss.* **2009**, *140*, 219. (e) Chen, Z.; Cummins, D.; Reinecke, B. N.; Clark, E.; Sunkara, M. K.; Jaramillo, T. F. *Nano Lett.* **2011**, *11*, 4168. (f) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. *Nat. Mater.* **2012**, *11*, 963. (g) Laursen, A. B.; Kegnæs, S.; Dahl, S.; Chorkendorff, I. *Energy Environ. Sci.* **2012**, *5*, 5577. (h) Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. *Chem. Sci.* **2011**, *2*, 1262. (i) Merki, D.; Hu, X. *Energy Environ. Sci.* **2011**, *4*, 3878. (j) Vrubel, H.; Merki, D.; Hu, X. *Energy Environ. Sci.* **2012**, *5*, 6136. (k) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. *J. Am. Chem. Soc.* **2011**, *133*, 7296. (l) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. *J. Am. Chem. Soc.* **2013**, *135*, 10274.

(11) Popczun, E. J.; McKone, J. R.; Read, C. G.; Biacchi, A. J.; Wiltrout, A. M.; Lewis, N. S.; Schaak, R. E. *J. Am. Chem. Soc.* **2013**, *135*, 9267.

(12) (a) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388. (b) Karunadasa, H. I.; Chang, C. J.; Long, J. R. *Nature* **2010**, *464*, 1329.

(13) Cobo, S.; Heidkamp, J.; Jacques, P.-A.; Fize, J.; Fourmond, V.; Guetaz, L.; Jousselme, B.; Ivanova, V.; Dau, H.; Palacin, S.; Fontecave, M.; Artero, V. *Nat. Mater.* **2012**, *11*, 802.

(14) (a) Bigi, J. P.; Hanna, T. E.; Harman, W. H.; Chang, A.; Chang, C. J. *Chem. Commun.* **2010**, *46*, 958. (b) Sun, Y.; Bigi, J. P.; Piro, N. A.; Tang, M. L.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 9212. (c) Sun, Y.; Sun, J.; Long, J. R.; Yang, P.; Chang, C. J. *Chem. Sci.* **2013**, *4*, 118. (d) King, A. E.; Surendranath, Y.; Piro, N. A.; Bigi, J. P.; Long, J. R.; Chang, C. J. *Chem. Sci.* **2013**, *4*, 1578. (e) Nippe, M.; Khnayzer, R. S.; Panetier, J. A.; Zee, D. Z.; Olaiya, B. S.; Head-Gordon, M.; Chang, C. J.; Castellano, F. N.; Long, J. R. *Chem. Sci.* **2013**, *4*, 3934.

(15) Karunadasa, H. I.; Montalvo, E.; Sun, Y.; Majda, M.; Long, J. R.; Chang, C. J. *Science* **2012**, *335*, 698.

(16) Merki, D.; Vrubel, H.; Rovelli, L.; Fierro, S.; Hu, X. *Chem. Sci.* **2012**, *3*, 2515.

(17) Spataru, N.; Banica, F. G. *Analyst* **2001**, *126*, 1907.

(18) (a) Wang, M.; Anghel, A. M.; Marsan, B.; Ha, N.-L. C.; Pootrakulchote, N.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2009**, *131*, 15976. (b) Lin, J.-Y.; Liao, J.-H.; Chou, S.-W. *Electrochim. Acta* **2011**, *56*, 8818.

(19) McIntyre, N. S.; Cook, M. G. *Anal. Chem.* **1975**, *47*, 2208.

(20) Tan, B. J.; Klabunde, K. J.; Sherwood, P. M. A. *J. Am. Chem. Soc.* **1991**, *113*, 855.

(21) de Jong, A. M.; de Beer, V. H. J.; van Veen, J. A. R.; Niemantsverdriet, J. W. *J. Phys. Chem.* **1996**, *100*, 17722.

(22) Kivel, J.; Sallo, J. S. *J. Electrochem. Soc.* **1965**, *112*, 1201.

(23) Vissenberg, M. J.; de Bont, P. W.; Arnouts, J. W. C.; van de Ven, L. J. M.; de Haan, J. W.; van der Kraan, A. M.; de Beer, V. H. J.; van Veen, J. A. R.; van Santen, R. A. *Catal. Lett.* **1997**, *47*, 155.

(24) Bockris, J. O. M.; Potter, E. C. *J. Electrochem. Soc.* **1952**, *99*, 169.

(25) Tran, P. D.; Nguyen, M.; Pramana, S. S.; Bhattacharjee, A.; Chiam, S. Y.; Fize, J.; Field, M. J.; Artero, V.; Wong, L. H.; Loo, J.; Barber. *J. Energy Environ. Sci.* **2012**, *5*, 8912.