Solar Hydrogen

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Solar Hydrogen Generation by Silicon Nanowires Modified with Platinum Nanoparticle Catalysts by Atomic Layer Deposition**

*Pengcheng Dai, Jin Xie, Matthew T. Mayer, Xiaogang Yang, Jinhua Zhan, and Dunwei Wang**

As a material candidate for solar-energy-conversion applications of the next generation, Si nanowires (SiNWs) are easy to prepare,[1–3] more tolerant to impurities than planar Si,[4,5] and have attracted significant research attention. Prototype devices such as solid-junction solar cells[6,7] and photoelectrochemical (PEC) cells[8–12] have been developed. As the conduction band edge of Si (ca. 4.05 V vs. vacuum)[13] is more negative than the water reduction potential (ca. 4.51 V vs. vacuum at pH 0),[14] there has been great interest in using Si for the production of solar hydrogen.[15,16] One important challenge in doing so is the use of hydrogen evolution reaction (HER) catalysts, which are necessary because the exchange current density of Si for H_2 production ($j_0 \approx 10^{-8}\,\mathrm{A\,cm^{-2}}$ for $2\,H^+ + 2\,e^- \rightarrow H_2$) is insufficient to sustain a photocurrent that matches the solar flux without the need for large overpotentials.[17,18] Existing catalyst-deposition techniques are typically not optimized for high-aspect-ratio structures such as SiNWs. They are either limited by their line-of-sight nature (for example, evaporation)[15] or by diffusion in solution (for example, electrochemical or electroless deposition),[16] and tend to produce a non-uniform catalyst distribution, so that most catalyst particles aggregate on the tips of the NWs, where the space is most accessible for catalyst deposition (Figure 1). Such a catalyst profile is not ideal for solar H_2 production. In order for most photoelectrons generated away from the tips of the NWs to reach the catalyst sites, a long charge diffusion distance is required. This requirement dictates that crystals of very high purity and high quality are required for high performance, leading to high costs of material preparation.

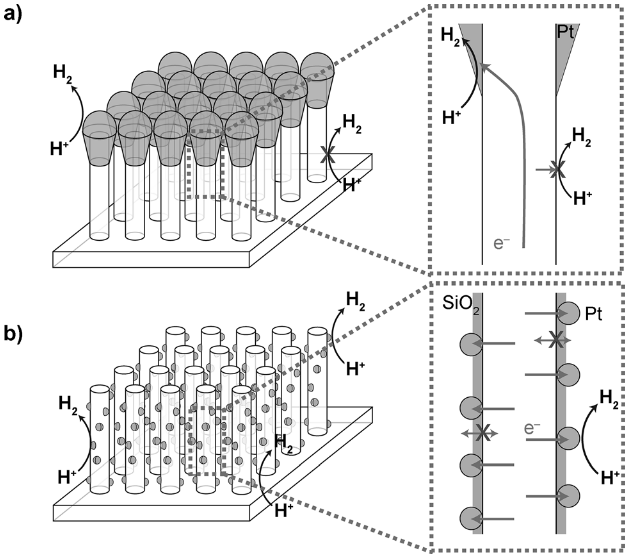

Figure 1. The differences between Pt nanoparticle catalysts produced by other techniques (a) and by ALD (b). When the catalysts predominantly reside on the tips of the NWs, effective charge collection requires a long diffusion distance, as shown in the magnified, cross-sectional view on the right. Charges trapped on the side walls of the NW do not contribute to the HER. The ALD method, by contrast, offers a uniform catalyst profile on the NW surfaces that addresses this problem. Furthermore, the surface of Si is oxidized during Pt growth to yield a protection layer, as is shown in the magnified view on the right.

From the perspective of device physics, the key to realizing full potentials held by the NW design is to ensure effective charge collection in the radial direction.[5] For a PEC cell, we thus desire a catalyst distribution profile that is uniform on the NW surfaces, so as to facilitate the transfer of the photogenerated charge from NW to solution. Herein, we show that such an objective can be achieved by growing Pt nanoparticles using atomic layer deposition (ALD).[19] Pt was used because it is a HER catalyst with very high activities. Indeed, the resulting SiNW/Pt materials enable high-performance H_2O reduction reactions. With a conformal catalyst coverage, the strategy also allowed us to understand the design advantages and caveats of SiNWs for H_2O reduction applications.

As-grown Pt nanoparticles on SiNWs were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Pt nanoparticles (average diameters ca. 3 nm for a typical 50-cycle ALD growth) are randomly distributed on the surface of SiNWs (Figure 2). The catalyst profile is in stark contrast to Pt catalysts prepared by evaporation[15] or chemical deposition[16] methods (Supporting Information, Figure S1). HRTEM studies (Figure 2b) revealed that the as-grown Pt nanoparticles are single-crystalline in nature. They make direct contact with

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[*] P. Dai, J. Xie, M. T. Mayer, Dr. X. Yang, Prof. Dr. D. Wang
Department of Chemistry, Merkert Chemistry Center, Boston College, 2609 Beacon St., Chestnut Hill, MA 02467 (USA)
E-mail: dunwei.wang@bc.edu
Homepage: http://www2.bc.edu/dunwei-wang

P. Dai, Prof. Dr. J. Zhan
Department of Chemistry, Shandong University
27 South Shanda Road, Jinan, Shandong, 250100 (P. R. China)

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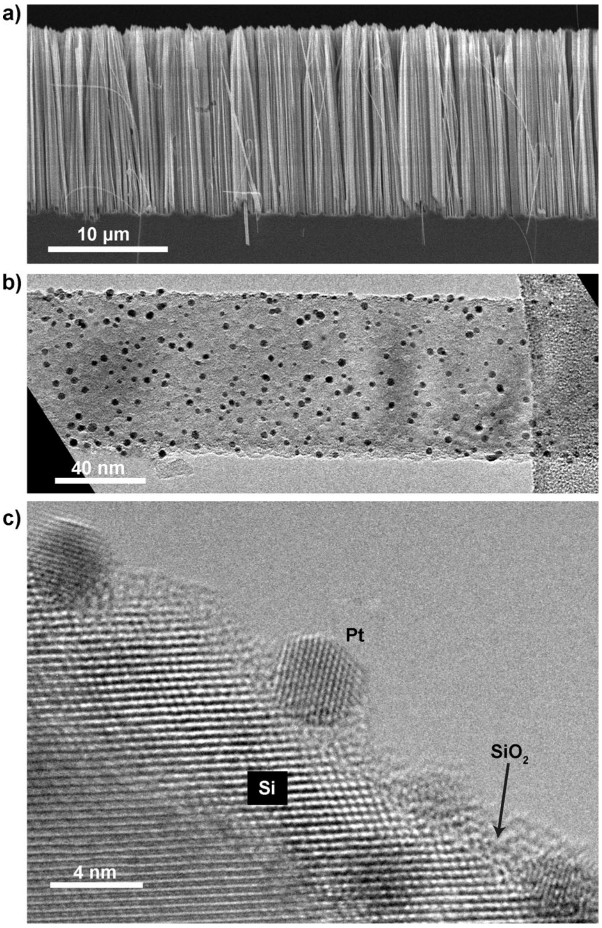

Figure 2. Electron micrographs of SiNWs decorated with ALD Pt. a) Cross-sectional scanning electron micrograph (SEM) showing no obvious catalyst aggregation. b) Low-magnification transmission electron micrograph (TEM) showing the distribution and uniformity of ALD Pt. c) High-resolution TEM showing the crystalline quality of Pt particles grown on the SiNW surface by ALD. The existence of amorphous SiO_2 is indicated by an arrow.

the crystalline part of the SiNWs, with no obvious amorphous layers in between. This feature ensures efficient electron transfer between the SiNWs and the Pt nanoparticles. The good contact is of great importance to the H_2O reduction performance, because otherwise a significant drop in potential may occur at the SiNW/Pt interface. The growth of Pt is based on the oxidation of the Pt precursor $[(MeCp)PtMe_3]$ (Cp = cyclopentadienyl).[19] The deposition of Pt was found to depend on whether the surface of Si is preoxidized or not. A pretreatment of SiNWs with HNO_3 (70%) for 30 min (Figure S2) was necessary for a high yield of Pt growth. Few Pt nanoparticles were observed on SiNWs without this treatment (Figure S3). It is not entirely clear how the preformed amorphous layer disappeared at the site where Pt nanoparticles grew. We suggest that it was removed by reacting with $MeCpPtMe_3$. A thin (0.8 ± 0.2 nm) amorphous oxide coating was observed on the other parts of the SiNWs (Figure 2c). The coating serves as a protection layer against further oxidation when SiNWs are immersed in H_2O; this will be discussed in more detail below.

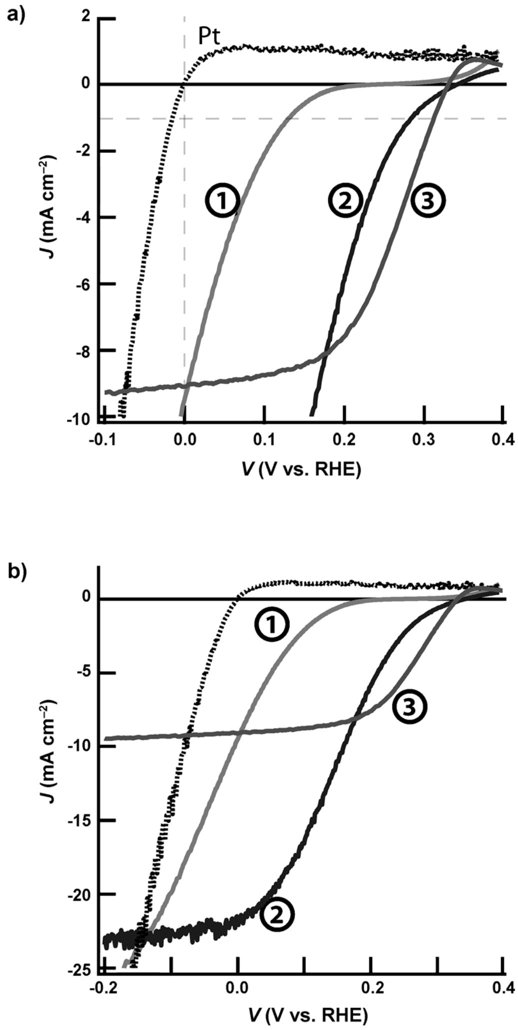

Figure 3. Polarization curves of various eletrodes in HER environments. a) Magnified view for a comparison of the kinetic regions. 1 = bare SiNWs, 2 = SiNWs with ELD Pt, 3 = SiNWs with ALD Pt. The dotted horizontal line marks the 1 mA cm^{-2} current density used to define the turn-on potential. The vertical dotted line marks the equlibrium potential for HER. b) Overall view of the polarization curves where the highest fill factor is obtained on SiNWs with ALD Pt.

Once prepared, the Pt-coated SiNWs were readily fashioned into photoelectrodes for PEC water reduction reactions. In this section, we compare three types of substrates, bare SiNWs, SiNWs with electroless-deposited (ELD) Pt, and SiNWs with ALD Pt (Figure 3). All measurements were carried out in H_2-saturated ($P = 1$ atm) solutions at room temperature (see the Experimental Section). Three regions of the polarization curves are of interest to our discussions. First, let us focus on the low-current, kinetic region, whose magnified view is shown in Figure 3a. We immediately notice a stark difference for the bare SiNWs and for those with Pt catalysts, as the former shows significantly lower turn-on potentials (0.13 V vs. RHE (reversible hydrogen electrode), at 1 mA cm^{-2} current density). This is due to the small exchange current density of Si for HER (ca. 10^{-5} mA cm^{-2}), and a significant overpotential is needed to enable a current density of 1 mA cm^{-2}. Although SiNWs with ELD Pt and ALD Pt both show more positive turn-on potentials and, hence, reduced overpotential requirements, their characteristics are distinctly different. SiNWs decorated with ALD Pt exhibit better charge collection as indicated by the steep transition from cathodic to anodic currents. On the basis that the nominal exchange current density of Pt for HER is approximately 1.0 mA cm^{-2}, we defined the turn-on voltage as the potential at which a current density of 1.0 mA cm^{-2} was measured. Turn-on potentials of 0.28 V and 0.31 V were measured for SiNW photoelectrodes with ELD Pt and ALD Pt catalysts, respectively. This result establishes ALD Pt as an effective catalyst for PEC water reduction reactions. The voltages at which there is no net exchange current (the cathodic current equals the anodic current) are 0.24, 0.34, and 0.33 V for bare SiNWs, SiNWs with ELD Pt, and SiNWs with ALD Pt, respectively.

Second, the efficacies of charge collection by various photocathodes were further studied by measuring the fill factors. In doing so, we treated the system as a regenerative solar cell with H^+/H_2 as the electron shuttle and used the RHE potential as the short-circuit condition (see the Supporting Information).[20] These assumptions permitted us to consider the PEC cell as a diode-based solar cell. Characterizations of the diode behaviors describe the energetic and kinetic nature of the semiconductor/electrolyte interface. A fill factor of 21 % was measured on bare SiNWs, consistent with the fact that Si is not a good catalyst for HER. The addition of catalysts, such as Pt, improved charge collection, and fill factors of 28 % and 55 % were measured on SiNWs decorated with ELD Pt and ALD Pt, respectively. As ALD-grown Pt is uniformly distributed on the surface of SiNWs from tip to base, they ensure effective collection of photogenerated electrons in the radial direction (also see Figure 1 b). Pt particles prepared by ELD, by contrast, predominantly reside on the tips of SiNWs because of the diffusion limitations of the Pt precursor (H_2PtCl_6). For photogenerated electrons to transfer to Pt, where the HER take place, they need to diffuse along the longitudinal direction to the tip. Surface trapping/recombination that does not contribute to the HER negatively affects current collection, and leads to poorer fill factors.

Szklarczyk et al. have shown that when Pt catalysts are present, no electron transfer takes place between Si and H_2O, and the function of Si is primarily confined to providing an additional voltage (photovoltage).[18] If we define the difference between the turn-on potential and the potential, at which a current density of 1 mA cm^{-2} is measured at the Pt electrode, as the photovoltage, a nominal 0.32 V is obtained for SiNWs with ALD Pt. This is slightly smaller than the expected maximum band bending of 0.38 V (calculated based on p-type Si with a doping level of 10^{15} cm^{-3}). Note that the estimated band bending is also based on the likely assumption that the introduction of Pt does not change the energetic nature of the Si/H_2O interface, which has been discussed by Szklarczyk and Bockris.[18] The measured photovoltage is similar to the best reported performance by bare p-type Si.[20] To further improve it, a change in the surface doping profile of Si would be necessary, for instance by forming an n^+ overlayer.[15,20] The ALD Pt deposition described herein is expected to be compatible with these treatments.

Third, we examined the saturation current region. For a semiconductor-based PEC system, the current reaches saturation because of a limitation of the ionic diffusion in the electrolyte, or because of electronic limitation in the semiconductor, or both. Previous research by us and others have shown that SiNWs can deliver photocurrent densities >30 mA cm^{-2}, when effective redox species are present.[11,12,21,22] The same holds true for planar Si and SiNWs without catalyst at low applied bias (Figure S4). The introduction of ELD Pt led to a reduction of saturation current densities of ca. 8.0 mA cm^{-2} (from 31 mA cm^{-2} to 23 mA cm^{-2}). We measured the optical reflectance of SiNWs with and without ELD Pt in an integration sphere and did not observe measureable differences to account for the 26 % drop in photocurrents (Figure S6). This result suggests that poor ionic and molecular diffusion on the rough surface of the Pt catalyst may be a reason for the lower saturation photocurrents, although more research is needed to fully understand the origin of these differences.

Compared with bare SiNWs and those decorated with ELD Pt, the saturation current density of SiNWs with ALD Pt is drastically lower, only reaching approximately 9.0 mA cm^{-2}. Weaker light absorption by SiNWs with ALD Pt is an unlikely reason for the difference because comparable photovoltages were measured on both types of photoelectrodes. For the same reason, we exclude poorer charge transfer kinetics as a reason. Instead, we propose that poor diffusion of H^+ or H_2 or both through the densely packed SiNWs is the main reason for the reduced saturation current densities.

To understand this hypothesis, we compared the morphologies of SiNWs with ELD Pt and ALD Pt. As ELD Pt particles mostly reside on the tips of SiNWs, the HER chiefly takes place on the top surface of the photoelectrode. With a non-uniform catalyst profile as shown in Figure 1 a, the SiNWs would thus function like a planar photoelectrode, only with improved light trapping.[23] To measure a high performance on these photoelectrodes, a long charge diffusion distance is needed. These requirements are met by our SiNWs as they are prepared from high-quality Si substrates. In principle, comparable performance can be measured on SiNWs with lower qualities in terms of purity or defect density, if radial charge collection is enabled.[5] For this purpose, however, we need a uniform catalyst distribution profile.

When a significant portion of electron transfer occurs at locations away from the tip of the packed NWs, ionic and gas diffusion may become limiting factors.[24] This is particularly true for SiNWs with high packing densities, such as those used in our study. We therefore understand the low saturation current density by SiNWs with ALD Pt as a result of poor ionic or molecular diffusion. Control experiments showed a systematic dependence of the saturation current density on the NW length (see the Supporting Information). This result highlights one important caveat of densely packed SiNWs. The same conclusion had previously been drawn by using a non-aqueous model regenerative redox system,[8] but it had not been verified in a realistic water-splitting environment where a catalyst is needed. Our study corrects this deficiency.

One important concern in using Si for water splitting is the oxidation of the photoelectrode.[15] Without protection, SiNWs and those with ELD Pt indeed degraded relatively quickly. For instance, the performance as measured by the saturation current of SiNWs with ELD Pt drops from 23 mA cm^{-2} to 19 mA cm^{-2}, five days after preparation (see the Supporting Information). One design advantage as shown in Figure 1 b is that the SiNWs are covered by an oxide layer. As a result, the performance of these photoelectrodes does not show measureable degradation up to 50 days after preparation. Another concern of using Si for water splitting lies in the small band gap, which is inadequate to power complete water splitting. This challenge may be addressed by forming multi-junction cells to increase the photovoltage[25] or by coupling the photocathode with a wide-band-gap photocathode.[26] Again, our ALD Pt deposition is expected to be compatible with these photoelectrode preparation methods.

Lastly, we present and discuss the different turn-on characteristics of planar Si and SiNWs. Under the same lighting conditions, high-quality planar Si should exhibit a better performance in terms of photovoltage, photocurrent, and fill factors. In this study, however, we consistently observed better turn-on characteristics with SiNWs (Figure 4; Supporting Information, Figure S5). Better light absorption by SiNWs alone cannot account for the differences (see the Supporting Information). Another reason proposed in the literature is that SiNWs are of different flatband potentials (V_{fb}).[16] This possibility was ruled out by our previous work showing comparable V_{fb} values in Mott–Schottky measurements.[12] Our attention was then turned to the difference in charge transfer kinetics. In essence, we understand that for the same measured current density (over projected area), the actual current density as defined by the real surface area can be dramatically different. For example, a projected current density of 1 mA cm^{-2} would translate to an actual current density of 0.01 mA cm^{-2} for SiNWs with a surface roughening factor of 100. To measure the same projected current density, a significantly smaller overpotential is required for SiNWs. Based on this understanding, we obtain a difference of 112 mV for planar Si and SiNWs with a surface roughening factor of 100, which is in reasonable agreement with the 96 mV measured (Figure 4). Here we compared planar Si with ELD Pt and SiNWs with ALD Pt, because each provides the highest performance in terms of turn-on characteristics for its type. For instance, planar Si with ALD Pt showed a significantly poorer performance owing to low catalyst loading and surface oxidation. Efforts to quantitatively compare this structure with SiNWs with ALD Pt were hindered by complications. The above-presented discussion is subject to criticism, as a high surface area of SiNWs would promote surface recombination, thereby reducing V_{ph}. Owing to the availability of SiO_2 passivation as shown in Figure 1 and Figure 2, we consider this effect less significant for samples studied in this work.

In conclusion, we demonstrated a catalyst deposition technique that can produce a uniform Pt nanoparticle catalyst coverage on the surface of SiNWs. The resulting catalyst profile permits efficient collection of photogenerated charges across the radial direction, which is desired to fulfil the design advantages of NWs for solar energy harvesting applications. The high packing density of SiNWs presents a challenge in terms of ionic and molecular diffusion. Furthermore, a better performance was obtained on SiNWs than on planar Si in terms of turn-on characteristics, and the phenomenon was attributed to improved charge transfer owing to the high surface area of SiNWs. Importantly, the study was carried out in a realistic water reduction environment. Future research efforts will be directed towards applying these techniques to other catalyst systems, such as the MoS_x[20] or Ni-Mo based systems.[27]

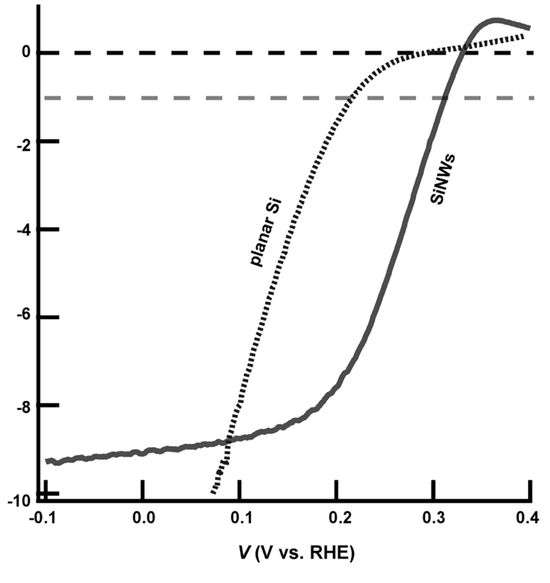

Figure 4. Comparison of turn-on characteristics of planar Si and SiNWs. Here, planar Si refers to Si with ELD Pt, and SiNWs refer to those with ALD Pt. See the main text for detailed explanations.

Experimental Section

Pt nanoparticle deposition: Pt nanoparticle catalysts were deposited in an Arradiance (Gemstar) atomic layer deposition (ALD) system. The reaction took place at 250 °C with $[(MeCp)PtMe_3]$ (heated to 75 °C) and compressed air (at room temperature) as the precursors. For a 50-cycle growth, each growth cycle consisted of four repeated pulse and purge steps for $[(MeCp)PtMe_3]$ to enhance its surface adsorption and one pulse and purge step for O_2 to remove the remaining ligands on the Pt cluster.

Photoelectrochemical characterizations: PEC characterizations were carried out using a potentiostat/galvanostat (CH Instruments CHI604C) in a three-electrode configuration. SiNWs-based photoelectrodes served as the working electrodes, with a Ag/AgCl wire soaked in a 1 M KCl aqueous solution as the reference, and a Pt wire as the counter electrode. The electrolyte was a Na_2SO_4 solution (0.5 M); pH 1 was achieved by adding concentrated H_2SO_4. The light source for the data presented in this work was an AM 1.5 solar simulator (100 mW cm^{-2}, Newport Oriel 96000). In a typical J–V experiment, the voltage was swept linearly from negative to positive at a rate of

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50 mV s^{-1}. H_2 was continuously bubbled through the solution as well to maintain the partial pressure of H_2 at 1 atm.

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[1] A. I. Hochbaum, P. Yang, *Chem. Rev.* **2010**, *110*, 527.
[2] A. Levine, G. Yuan, J. Xie, D. Wang, *Sci. Adv. Mater.* **2010**, *2*, 463.
[3] K. Peng, Y. Xu, Y. Wu, Y. Yan, S.-T. Lee, J. Zhu, *Small* **2005**, *1*, 1062.
[4] A. Boukai, P. Haney, A. Katzenmeyer, G. M. Gallatin, A. A. Talin, P. Yang, *Chem. Phys. Lett.* **2011**, *501*, 153.
[5] B. M. Kayes, H. A. Atwater, N. S. Lewis, *J. Appl. Phys.* **2005**, *97*, 114302.
[6] B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, C. M. Lieber, *Nature* **2007**, *449*, 885.
[7] E. C. Garnett, P. Yang, *J. Am. Chem. Soc.* **2008**, *130*, 9224.
[8] A. P. Goodey, S. M. Eichfeld, K. K. Lew, J. M. Redwing, T. E. Mallouk, *J. Am. Chem. Soc.* **2007**, *129*, 12344.
[9] J. R. Maiolo, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater, N. S. Lewis, *J. Am. Chem. Soc.* **2007**, *129*, 12346.
[10] G. Yuan, H. Zhao, X. Liu, Z. S. Hasanali, Y. Zou, A. Levine, D. Wang, *Angew. Chem.* **2009**, *121*, 9860; *Angew. Chem. Int. Ed.* **2009**, *48*, 9680.
[11] R. Liu, G. Yuan, C. L. Joe, T. E. Lightburn, K. L. Tan, D. Wang, *Angew. Chem.* **2012**, *124*, 6813; *Angew. Chem. Int. Ed.* **2012**, *51*, 6709.
[12] R. Liu, C. Stephani, J. J. Han, K. L. Tan, D. Wang, *Angew. Chem.* **2013**, *125*, 4319; *Angew. Chem. Int. Ed.* **2013**, *52*, 4225.
[13] S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, Wiley, Hoboken, NJ, **2007**.
[14] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, **2001**.
[15] S. W. Boettcher et al., *J. Am. Chem. Soc.* **2011**, *133*, 1216.
[16] I. Oh, J. Kye, S. Hwang, *Nano Lett.* **2012**, *12*, 298.
[17] R. N. Dominey, N. S. Lewis, J. A. Bruce, D. C. Bookbinder, M. S. Wrighton, *J. Am. Chem. Soc.* **1982**, *104*, 467.
[18] M. Szklarczyk, J. O. M. Bockris, *J. Phys. Chem.* **1984**, *88*, 1808.
[19] J. Xie, X. Yang, B. Han, Y. S. Horn, D. Wang, *ACS Nano* **2013**, *7*, 6337.
[20] B. Seger, A. B. Laursen, P. C. Vesborg, T. Pedersen, O. Hansen, S. Dahl, I. Chorkendorff, *Angew. Chem.* **2012**, *124*, 9262; *Angew. Chem. Int. Ed.* **2012**, *51*, 9128.
[21] G. Yuan, K. Aruda, S. Zhou, A. Levine, J. Xie, D. Wang, *Angew. Chem.* **2011**, *123*, 2382; *Angew. Chem. Int. Ed.* **2011**, *50*, 2334.
[22] X. Wang, K. Q. Peng, X. J. Pan, X. Chen, Y. Yang, L. Li, X. M. Meng, W. J. Zhang, S. T. Lee, *Angew. Chem.* **2011**, *123*, 10035; *Angew. Chem. Int. Ed.* **2011**, *50*, 9861.
[23] E. Garnett, P. D. Yang, *Nano Lett.* **2010**, *10*, 1082.
[24] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, **1980**.
[25] S. Y. Reece, J. A. Hamel, K. Sung, T. D. Jarvi, A. J. Esswein, J. J. H. Pijpers, D. G. Nocera, *Science* **2011**, *334*, 645.
[26] M. T. Mayer, C. Du, D. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 12406.
[27] E. L. Warren, J. R. McKone, H. A. Atwater, H. B. Gray, N. S. Lewis, *Energy Environ. Sci.* **2012**, *5*, 9653.

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