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Hierarchically Porous Calcium-containing Manganese Dioxide Nanorod Bundles with Superior Photoelectrochemical Activity

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Bioinspired by the composition of the oxygen evolving complex and the fundamental role of calcium for catalysis, we have synthesized calcium-manganese oxides as promising photoelectrodes. We report the first demonstration of hierarchically porous Ca-containing MnO_2 nanorod (NR) bundles as visible-light-sensitive photofunctional nanoelectrodes to fundamentally improve the performance of MnO_2 for photoelectrochemical hydrogen generation. A substantial amount of Ca (up to 7.8 atom %) can be in situ incorporated into the MnO_2 lattice by a simple electroplating technique because of the exceptionally small feature sizes of several nanorods. The maximum photocurrent could be successfully achieved as high as 0.42 mAcm⁻², which is the best value for a MnO_2 photoanode

to date. Significantly, Ca-containing MnO_2 photoanodes illustrated striking photoelectrochemical activity in response to visible light with a high incident photon-to-current conversion efficiency of 7% at a monochromatic wavelength of 450 nm. The improvement in photoactivity of photoelectrochemical response may be attributed to the enhanced visible-light absorption, increased charge-carrier densities, and large contact area with electrolyte owing to the synergistic effects of Ca incorporation and specific mesopore networks, thus contributing to photocatalysis. The new design of constructing highly photoactive Ca-containing MnO_2 nanorod bundles sheds light on developing high-efficiency photoelectrodes for solar hydrogen generation.

Introduction

The dream goal of energy research is to make an artificial device whereby the photocatalytic splitting of water is finalized to give a continuous production of oxygen and hydro-

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gen.^[1,2] Success in this task would guarantee the generation of hydrogen as a carbon-free fuel to satisfy our energy demands at no environmental cost. In comparison to catalytic reforming of hydrocarbon fuels,^[3-5] hydrogen generation from photoelectrochemical (PEC) water decomposition by solar illumination is much simpler and also more environmentally friendly. Highperformance PEC systems based on single-crystalline III-V semiconductors have been demonstrated in laboratories,^[6] but they are neither chemically stable nor economically viable to be utilized in commercial applications. Earth-abundant metal oxides with narrow band gaps, such as hematite and tungsten trioxide, have attracted intensive attention owing to their visible-light response, but they only exhibit good photochemical stability in base or acid aqueous solution, respectively.^[7-9] Thus, the search for cost-effective PEC photoelectrodes that efficiently split water under visible-light irradiation and benign condition remains one of the most challenges for solar-energy utilization.

In nature, photosystem II has the unique capability to oxidize water to molecular oxygen by a metal-oxo Mn₄Ca complex housed in a special protein environment.^[10] In the past, there has been a major research effort studying the synthesis of various manganese compounds aimed at mimicking the oxygen evolving complex of photosystem II.^[11] Of these manganese compounds, particular attention has been given to the manganese oxides, which have been shown to be multifunctional for applications of battery, supercapacitors, oxygen electrochemistry, and especially visible-light-driven catalysis.^[12-15]

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Therefore, the low costs of manganese and the envisioned biomimetic character make the development of manganese oxide based photoelectrodes for solar hydrogen application especially desirable. Sakai et al. reported the first observation of photocurrent generation by self-assembled manganese oxide nanosheets under visible-light irradiation.^[16] Recently, Hsu et al. showed that addition of an efficient hole acceptor in the electrolyte was found to improve PEC activities.^[17] However, to date, the PEC activity of manganese oxide is still low owing to poor carrier separation and transport. Historically, numerous endeavors have been devoted to combat these two intrinsic limitations through doping and nanostructuring strategies.^[18-21] 1D nanorod/nanowire-arrayed photoelectrodes with large surface areas and short diffusion distances for photogenerated minority carriers are expected to facilitate the charge separation.^[22,23] Meanwhile, heteroatom doping into oxide semiconductors can remarkably increase the electronic conductivity of the semiconductor.^[19,20,22,24] For example, the incorporation of nitrogen or carbon into 1D ZnO nanostructures were found to ensure rapid electronic transport, efficient charge separation, and even enhanced visible-light absorption.^[20, 22, 24] Interestingly, recent studies demonstrated that incorporation of calcium into binary manganese oxides significantly improved their photocatalytic activities of water oxidation in the presence of [Ru(bipyridine)₃]²⁺.^[25] Many biomimetic water oxidation experiments are performed in the presence of $[Ru(bipyridine)_3]^{2+}$ as a photosensitizer, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ or $\text{S}_2\text{O}_8^{-2-}$ as an electron acceptor, and visible light with the aim of studying a model for a photoredox chain.^[26-28] Specifically, in the presence of a water-oxidizing catalyst the photosensitizer is recycled and oxygen evolution is detected. Nevertheless, the present achievements are distant from the demands of nontoxicity and environmental friendliness. Therefore, it is imperative to explore 1D calcium-manganese oxide nanostructures for next-generation PEC devices that could benefit from the light-scattering ability of highaspect-ratio nanostructures and the unique properties of Ca incorporation. In addition, the overall PEC reaction should be accomplished in an aqueous electrolyte without photosensitizer reagents.

Recently, heterogeneous calcium-manganese oxide catalysts that had been synthesized by high-temperature-heating of calcium and manganese carbonates were shown to be effective for water oxidation.^[25] However, annealing at such high temperatures may lead to unwanted side effects, such as degradation of the transparent conductive substrate, defect formation within calcium-manganese oxide lattice, and sintering of the nanostructure. Fabricating 1D nanostructured calcium-manganese oxides through rapid and economic alternative routes is of great interest for developing high-performing CaMn-based photoelectrodes. From this point of view, a simple and cost-effective electrodeposition technique is very promising. In this work, we demonstrate a facile and reliable procedure for fabrication of vertically aligned Ca-containing MnO₂ nanorod (NR) bundles with unprecedented small feature sizes of several nanorods at approximately 3.5-5 nm in diameter. The Ca-containing MnO₂ NR bundle arrays were grown on indium tin oxide (ITO) glass substrates by using an in situ electrodeposition method at room temperature. These well-characterized NR bundles consist of highly specific mesopore networks, which can significantly improve the confinement and localization of incident light, thus enhancing the effective interaction of light with photoactive materials. The PEC performance of porous Ca-containing MnO₂ NR bundle nanosystems in solar hydrogen production with sacrificial reagents was systematically evaluated. Furthermore, we also performed microstructural characterization, elemental analysis, and electrochemical impedance spectroscopy (EIS) on the Ca-containing MnO₂ nanoelectrodes to confirm the Ca intercalation and understand the correlation with the improved PEC performance and surface photochemistry of MnO₂. To the best of our knowledge, this is the first demonstration of realizing 1D mesoporous calciummanganese oxide NR bundle arrayed photoanodes for solar photoelectrochemistry under neutral condition in the absence of a photosensitizer.

Results and Discussion

In Figure 1 a, a typical SEM image of pristine MnO_2 films is displayed grown on ITO substrate under cyclic voltammetric conditions using only manganese acetate as a precursor. The re-



Figure 1. SEM micrographs of the a) pristine and b) Ca-containing MnO_2 samples on ITO substrate. c–g) Elemental mapping images of Ca, Mn, and O.

sulting film with sheet-like structure of uniform distribution was obtained. Interestingly, if calcium nitrate was introduced as insertion source for the in situ growth of Ca-containing MnO₂, different morphologies were observed, ranging from sheet-like to rod-like structure (Figure 1 b). More detailed SEM images with energy-dispersive X-ray elemental mapping of Mn, O, and Ca are shown in Figure 1 c-g, which confirm the presence of uniformly dispersed Ca atoms inside the MnO₂. A typical TEM image of Ca-containing MnO₂ is presented in Figure 2a, which exhibits 1D bundle arrays of 70 ± 10 nm in diameter and 160 ± 30 nm in length. Additionally, several disordered

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Figure 2. a–c) Typical TEM images and d) high-resolution TEM image, as well as SAED pattern (inset in part c) of Ca-containing $MnO_2 NR$ bundles.

wormhole-like mesopores (indicated by the circles) can also be seen to be present. One of the most significant advantages of the porous nanoarchitectures, which are clearly distinct from that of the traditional photoelectrodes, is that hierarchical pore-channel networks offer effective contact between incident light and the surface of the photoelectrodes. Besides, each bundle was found to consist of several nanorods of 3.5– 5 nm in diameter (Figure 2b). The XRD patterns (Supporting Information, Figure S1) of the porous Ca-containing MnO₂ NR bundles did not display any visible diffraction peaks corresponding to MnO₂; all of the strong diffraction peaks are associated with ITO substrate. This indicates a lack of long-rangeorder nature of NR bundles.

However, TEM and Raman microscopy indicated the presence of short-range order in these NR bundles, presumably as amorphous or nanocrystalline materials. From TEM micrographs and their corresponding selected area electron diffraction patterns (SAED), their nanocrystalline nature can be confirmed (Figure 2 c). The high-resolution TEM image of intercalated sample is presented in Figure 2d yielding the spacing of the (121) lattice plane of the α -MnO₂ crystal to be 0.238 nm. To gain further insight into microstructural changes of MnO₂ with Ca insertion, micro-Raman analyses were performed as presented in Figure 3a. The spectra of pristine MnO₂ reveal the presence of a dominant A_g mode at 640 cm⁻¹, which is associated with symmetric stretching vibration (Mn-O) of the MnO₆ octahedron.^[29] A Todorokite-type MnO₂ with tunnel structure can be concluded (Figure S2). In the case of Ca-containing MnO₂, two strong peaks at 650 cm⁻¹ and 580 cm⁻¹ are associated with Mn–O vibrations that are orthogonal and along the direction of the MnO₆ octahedral double chains, respectively.^[30] The band positions of Ca-containing MnO₂ are in good agreement with Cryptomelane-type octahedral molecular sieves structure, which consists of MnO_6 octahedron forming 2×2 tunnels (Figure S2).^[31] Clearly, the microstructural and morphological change can be attributed to introduction of calcium nitrate for the in situ intercalation of Ca atoms into the MnO_2 lattice. However, the intercalation mechanism may be more complicated and more research is needed to elucidate it. The investigation on this issue is still in progress.

To verify that Ca incorporation has an enhancement effect on the light harvesting, Tauc plots of Ca-containing MnO₂ nanoelectrodes are shown in Figure 3b. In comparison to pristine MnO₂, Ca-containing MnO₂ clearly exhibits a significant enhancement in absorption of visible light. This finding could be attributed to the redshift of the band gap in the ternary calcium-manganese oxide. Furthermore, X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface bonding and element oxidation state of Ca-containing MnO₂. In Figure 3 c, the Mn 2p core level XP spectra of calcium-manganese oxide nanocomposites are depicted. To differentiate between the oxidation states of Mn, the main peak of the Mn 2p_{3/2} core level spectra was fitted with two components at 641.5 and 643.2 eV corresponding to Mn^{III} and Mn^{IV} species, respectively.^[32] It can be seen that a large fraction of Mn^{III} is present after insertion of Ca into the nanocomposites. The XPS spectra for Ca2p are also presented in the inset of Figure 3c, revealing the intercalated Ca forms Ca^{II} species on nanocomposites.^[33] In addition, he O1s core level spectra of Ca-containing MnO₂ NR bundles in Figure 3d illustrate a main peak at 530.3 eV, which could be further deconvoluted into two peaks. The low binding energy at 529.7 eV, denoted by O1, corresponds to Mn-O-Mn bonding, and the higher one of 531.4 eV (O2) is attributed to the Mn–OH bonding.^[17] Finally, the Ca concentration in the intercalated MnO₂ NR bundles is also estimated by XPS measurement to be approximately 7.8 atom %. Such a substantial amount of Ca can be incorporated into the MnO₂ lattice by a simple electroplating technique because of the exceptionally small feature sizes of several nanorods.

To understand the electronic structures of the Ca-containing MnO₂ NR bundles, systematic X-ray absorption spectroscopy (XAS) studies were performed as shown in Figure 4. X-ray absorption near-edge structure (XANES) spectra of the synthetic Ca-containing samples are presented in Figure 4a together with those of Mn oxides of known Mn oxidation states serving as reference compounds. The Mn oxidation state can be estimated from the XANES data by a calculation of the characteristic edge-position energy and a following comparison to reference compounds as recorded in Figure 4b and Table 1. For the average oxidation states of Ca-containing samples, the values between 3 and 4 in this way could be obtained. This means that the insertion of Ca into MnO₂ channels decreases the oxidation state of Mn as a result of charge transfer from Ca to Mn. Not only an average oxidation state but also the relative fractions of $\mathsf{Mn}^{\mathbb{W}}$ and $\mathsf{Mn}^{\mathbb{W}}$ ions in the synthetic oxides could be determined (Table 1). Apparently, the fraction of Mn^{III} ions increases strongly through intercalation of Ca into MnO₂ lattices. This is in good agreement with XPS results. Moreover, in Figure 4c O K-edge XANES spectra of ternary nanocompositions

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Figure 3. a) Micro-Raman spectra of pure MnO_2 and Ca-containing samples. b) Tauc plots for determining the indirect band gaps of pure MnO_2 and Ca-containing samples. c) $Mn 2p_{3/2}$ and d) O1s XPS spectra of the Ca-containing sample. Inset in part c: XPS spectra of Ca 2p transitions for the Ca-containing sample.

Table 1. Characteristics of pristine and Ca-containing MnO2 samples.						
Sample composition	[Ca ²⁺] initial content [м]	Ca/Mn atomic ratio ^[a]	Mean Mn oxidation state ^[b]	Mn ³⁺ /Mn ⁴⁺ element ratio ^[b]		
MnO ₂	_	0:1	4	0		
Ca _{0.12} MnO _{1.98}	0.5	0.12:1	3.75	0.33		
Ca _{0.17} MnO _{1.98}	1	0.17:1	3.61	0.64		
Ca _{0.25} MnO _{1.94}	1.5	0.25:1	3.37	1.7		
[a] Atomic ratios were determined by inductively coupled plasma optical emission spectroscopy. [b] Valence states and element ratios were calcu- lated by using XAS.						

are shown. The broad peak at approximately 545 eV on the side of high energy corresponds to the O1s to Mn 4sp transition, whereas the features around 531 eV on the side of low energy correspond to the transition from O1s to the mixing bands of O2p and Mn 3d.^[34] Significantly, the intensity of the $t_{2g}\downarrow$ and/or $e_g\uparrow$ orbital decreases and that of the $e_g\downarrow$ orbital increases if the Ca ion was gradually incorporated into the samples. This implies that the Mn^{III} Jahn–Teller ion arises accompanying insertion of Ca ion, and, therefore, the local structure

surrounding the $\mathsf{Mn}^{\mathsf{IV}}$ ion is distorted from octahedral symmetry.

To confirm the further applicability of Ca-containing MnO₂ NR bundles in solar-to-fuel conversion (Figure 5a), the photoresponse analysis was performed in a 0.1 M aqueous solution of Na_2SO_4 with a trace level of H_2O_2 (as hole acceptor) at pH 7. The hole acceptor will bring about a reduction in the surface recombination loss, leading to the promotion of hydrogen evolution by electrons and avoiding photocorrosion of the photoanode itself. The photocurrent-time responses of MnO₂ and various Ca-containing MnO₂ were determined by chronoamperometry under simulated AM 1.5 illuminations (100 mW cm⁻²) with 0.9 V bias potential (vs. Ag/AgCl reference electrode). After subtracting baselines, the comparison of photocurrents is shown in Figure 5b. Clearly, the Ca-containing MnO₂ NR bundles manifest a pronounced photocurrent, which increases to 0.42 mA cm⁻² under illumination. In addition, photocurrent density of Ca-containing MnO₂ hybrid nanoelectrodes is approximately 4 times higher than that of pristine MnO₂, suggesting that MnO₂ incorporated with Ca can effectively improve PEC activity. This result is even superior to the performances of many MnO2-based photoanodes in recent re-



Figure 4. a) Mn K-edge XANES spectra of pure MnO₂ and various Ca-containing samples. b) Relation between edge position and Mn average oxidation state for various Ca-containing samples. c) O K-edge XAS spectra of pure MnO₂ and various Ca-containing samples.

ports.^[16, 17, 35–37] Moreover, the rate of H_2 evolution measured for our Ca-containing MnO₂ hybrid nanocomposites was approximately 9.5 μ mol h⁻¹. As MnO₂ is visible-light sensitive, we also evaluated the PEC properties of MnO₂ and Ca-containing MnO₂ photoelectrodes under visible-light irradiation ($\lambda > 400$ nm), which is presented in Figure S3. In this case, noteworthy photocurrent responses are still observed for each switch-on/off in the case of Ca-containing MnO₂ photoelectrodes, which confirms high photoactivity of Ca-containing hybrid nanoelectrodes under visible light. Besides, to quantify the photoconversion performance, measurements of incident photon-to-current conversion efficiency (IPCE) were performed for pristine and Ca-containing MnO₂ nanoelectrodes as a function of incident light wavelength (Figure 5 c). Surprisingly, the Ca-containing sample displays substantial photoactivity in the visible-light region from 400 to 550 nm in addition to strong photoresponse in the near-UV region. Particularly, the IPCE of Ca-containing MnO₂ photoelectrodes at the monochromatic wavelength of 450 nm is approximately 7%. It should be noted that Ca insertion substantially improves the light utilization and conversion efficiency in the visible region of interest in comparison with the pure MnO₂ structure. These results are in good agreement with the Tauc plots. To understand the intrinsic electronic properties of ternary Ca-containing MnO_2 NR bundles in the electrolyte solution, we performed EIS in the dark coupled with Mott-Schottky analysis commonly used to determine both donor density and flat-band potential at semiconductor/liquid contacts. In Figure 5d a Mott-Schottky-type plot of data is shown analyzed by using the complex nonlinear least squares fitting method based on an equivalent circuit, as shown in the inset.^[17] All samples exhibit a positive slope in the Mott-Schottky plots, as expected for n-type semiconducshift of the Fermi level facilitates the charge separation at the semiconductor/electrolyte interface, by increasing the degree of band bending at MnO₂ surface. Therefore, the porous features, the reduced band gap, and increased carrier concentration are believed to be the major reasons for the improvement in photocatalytic activities of PEC response based on Ca-containing MnO₂ NR bundle photoelectrodes.

Conclusions

The efficient solar hydrogen system was successfully developed based on porous Ca-containing MnO₂ photoelectrodes. Our strategy was to mimic essential components of the calcium-manganese oxide complex in the photosynthetic water oxidizing center. Using this water oxidizing center as a blueprint for materials design, hierarchically porous nanorod (NR) bundle arrays of Ca-containing MnO₂ with nanocrystalline nature were in situ grown on the ITO substrate by means of a cost-effective and simple electroplating technique. This is the first example of realizing 1D mesoporous Ca-containing MnO₂ NR bundles for photoelectrochemical (PEC) hydrogen generation under neutral conditions in the absence of photosensitizer. Relative to pristine MnO₂ photoanodes, the photocurrent of Ca-containing MnO₂ NR bundles increased substantially with up to approximately 300% of photocurrent increase. Most importantly, Ca-containing MnO₂ photoanodes illustrated striking PEC activity in response to visible light with a high incident photon to current conversion efficiency of 7% at a monochromatic wavelength of 450 nm. The improvement in photoactivity of PEC response may be attributed to the enhanced visiblelight absorption, increased charge-carrier densities, and large contact area with electrolyte owing to the synergistic effects of

tors. The estimated flat-band potentials of the pure MnO₂ and Ca-containing MnO₂ are 0 V and -0.1 V, respectively. Apparently, Ca-containing MnO₂ has a more negative flat-band potential than pure MnO₂ on account of the Ca-intercalating effect. In addition, the calculated donor densities of the pure MnO₂ and Cacontaining MnO_2 are 2.5×10^{20} and 6.2×10^{21} cm⁻³, respectively. The enhanced donor density is mainly owing to the incorporation of Ca, which could be an electron donor for MnO₂ systems. The increased donor density improves the charge transport in MnO₂, as well as the electron transfer at the interface between MnO₂ and ITO substrate. Moreover, the increased electron density is expected to shift the Fermi level of MnO₂ toward the conduction band. The upward

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Figure 5. a) Schematic illustration of the PEC process on Ca-containing $MnO_2 NR$ bundles. b) Photocurrent-time behavior of pristine and Ca-containing MnO_2 photoelectrodes after subtracting baselines. c) Measured IPCE spectra of pristine and Ca-containing MnO_2 photoelectrodes in the region of 300–600 nm at a potential of 0.9 V (vs. Pt) in two-electrode system. d) Mott–Schottky plots for pristine and Ca-containing MnO_2 samples in 0.1 M Na₂SO₄ (C=capacitance of the semiconductor). Inset: equivalent circuit.

Ca incorporation and specific mesopore networks, thus contributing to photocatalysis. As the Ca-containing MnO_2 NR bundle photoanodes are convenient to fabricate and highly active, they can serve as a good substitution for MnO_2 in a variety of solar-energy-driven applications including PEC hydrogen generation, photocatalysis, and solar cells.

Experimental Section

The Ca-containing MnO₂ NR bundle arrays were in situ grown on the ITO glass as a substrate and working electrode by typical electrodeposition method. A piece of Pt foil and a standard Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Aqueous 0.1 $\,$ Mn(CH₃COO)₂ solutions with 0.5–2 $\,$ M Ca(NO₃)₂ were used as electrolytes. Then, the cyclic voltammetric approach was operated between 0 and 0.7 V versus Ag/AgCl for 30 min under a scan rate of 500 mV s⁻¹ and the deposition temperature was maintained at RT. Finally, the resulting Ca-containing MnO₂ NR bundle arrays were heated in vacuum to 300 °C for 10 h. The reference MnO₂ was obtained under same cyclic voltammetric conditions in 0.1 $\,$ Mn(CH₃COO)₂ mixed with 0.1 $\,$ Na₂SO₄ solution.

For material characterization, SEM measurements were conducted on a JEOL 6700 filed-emission SEM. For obtaining TEM images, the Ca-containing MnO₂ NR bundle products on the ITO substrate were scratched and dispersed on a carbon-coated Cu grid, and analyzed using a JEOL JEM-2100 TEM system. The XRD analyses were performed on a Bruker D8 Advance diffractometer with Cu (40 kV, 40 mA) radiation. Micro-Raman analyses were performed on a Jobin Yivon Labram HR800 spectrometer. XPS spectra were obtained using a Microlab 350 system. XAS analyses were performed in Argonne National Laboratory and National Synchrotron Radiation Research Center. UV/Vis absorption spectra were performed with a JASCO V-670 instrument. Inductively coupled plasma-optical emission spectroscopy data were collected by using PerkinElmer Optima 3000DV system. In PEC reaction, a Ca-containing MnO₂ photoanode was used as the working electrode with a surface area of 1 cm², a platinum plate as a counter electrode, and Ag/AgCl as a reference electrode. All PEC studies were operated in a 0.1 M Na_2SO_4 solution with 4.4 mM H_2O_2 additives (pH 7) as supporting electrolyte medium by using Electrochemical Multichannel Solartron Analytical System. The PEC photoelectrode was illuminated with the AM 1.5G simulated solar light at 100 mW cm⁻². This illumination source matches the shape and intensity of the Air Mass 1.5 Global (AM 1.5 G) G173 standard set forth by the American Society of Testing and Materials. The IPCE was calculated by using Equation (1):

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$$IPCE [\%] = \frac{1240 \times photocurrent \ density \ [mA \ cm^{-2}]}{wavelength \ [nm] \times photon \ flux \ [mW \ cm^{-2}]} \times 100$$
(1)

IPCE measurements were performed by a 2-electrode system under monochromatic irradiation, emitted from a 150 W Xe lamp equipped with band-pass filters and a variable neutral density filter. Monochromatic photon fluxes at each wavelength were measured using an optical photodiode power meter and were adjusted to around 0.1 mW cm⁻² using the neutral density filter.

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- [1] A. J. Bard, M. A. Fox, Acc. Chem. Res. 1995, 28, 141-145.
- [2] N. S. Lewis, D. G. Nocera, Proc. Natl. Acad. Sci. USA 2006, 103, 15729– 15735.
- [3] Y. G. Lin, Y. K. Hsu, S. Y. Chen, Y. K. Lin, L. C. Chen, K. H. Chen, Angew. Chem. Int. Ed. 2009, 48, 7586–7590; Angew. Chem. 2009, 121, 7722– 7726.
- [4] Y. G. Lin, Y. K. Hsu, S. Y. Chen, L. C. Chen, K. H. Chen, J. Mater. Chem. 2010, 20, 10611–10614.
- [5] Y. G. Lin, Y. K. Hsu, S. Y. Chen, L. C. Chen, K. H. Chen, J. Mater. Chem. 2011, 21, 324–326.
- [6] O. Khaselev, J. A. Turner, Science 1998, 280, 425-427.
- [7] S. D. Tilley, M. Cornuz, K. Sivula, M. Grätzel, Angew. Chem. Int. Ed. 2010, 49, 6405–6408; Angew. Chem. 2010, 122, 6549–6552.
- [8] Y. Lin, G. Yuan, S. Sheehan, S. Zhou, D. Wang, Energy Environ. Sci. 2011, 4, 4862–4869.
- [9] J. Su, X. Feng, J. D. Sloppy, L. Guo, C. A. Grimes, Nano Lett. 2011, 11, 203–208.
- [10] J. P. McEvoy, G. W. Brudvig, Chem. Rev. 2006, 106, 4455-4483.
- [11] C. W. Cady, R. H. Crabtree, G. W. Brudvig, Coord. Chem. Rev. 2008, 252, 444–455.
- [12] A. R. Armstrong, P. G. Bruce, *Nature* **1996**, *381*, 499–500.
- [13] Y. Gorlin, T. F. Jaramillo, J. Am. Chem. Soc. 2010, 132, 13612-13614.
- [14] F. Jiao, H. Frei, Energy Environ. Sci. 2010, 3, 1018–1027.

- [15] Y. K. Hsu, Y. C. Chen, Y. G. Lin, L. C. Chen, K. H. Chen, Chem. Commun. 2011, 47, 1252–1254.
- [16] N. Sakai, Y. Ebina, K. Takada, T. Sasaki, J. Phys. Chem. B 2005, 109, 9651– 9655.
- [17] Y. K. Hsu, Y. C. Chen, Y. G. Lin, L. C. Chen, K. H. Chen, J. Mater. Chem. 2012, 22, 2733–2739.
- [18] G. Wang, H. Wang, Y. Ling, Y. Tang, X. Yang, R. C. Fitzmorris, C. Wang, J. Z. Zhang, Y. Li, *Nano Lett.* **2011**, *11*, 3026–3033.
- [19] S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, Nano Lett. 2012, 12, 26–32.
- [20] Y. Qiu, K. Yan, H. Deng, S. Yang, Nano Lett. 2012, 12, 407-413.
- [21] Y. G. Lin, Y. K. Hsu, Y. C. Chen, S. B. Wang, J. T. Miller, L. C. Chen, K. H. Chen, *Energy Environ. Sci.* 2012, *5*, 8917–8922.
- [22] X. Yang, A. Wolcott, G. Waang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang, Y. Li, *Nano Lett.* 2009, *9*, 2331–2336.
- [23] Y. J. Hwang, A. Boukai, P. D. Yang, Nano Lett. 2009, 9, 410-415.
- [24] Y. G. Lin, Y. K. Hsu, Y. C. Chen, L. C. Chen, S. Y. Chen, K. H. Chen, Nanoscale 2012, 4, 6515–6519.
- [25] M. M. Najafpour, T. Ehrenberg, M. Wiechen, P. Kurz, Angew. Chem. Int. Ed. 2010, 49, 2233-2237; Angew. Chem. 2010, 122, 2281-2285.
- [26] M. M. Najafpour, Chem. Commun. 2011, 47, 11724-11726.
- [27] D. M. Robinson, Y. B. Go, M. Mui, G. Gardner, Z. Zhang, D. Mastrogiovanni, E. Garfunkel, J. Li, M. Greenblatt, G. C. Dismukes, J. Am. Chem. Soc. 2013, 135, 3494–3501.
- [28] V. B. R. Boppana, S. Yusuf, G. S. Hutchings, F. Jiao, Adv. Funct. Mater. 2013, 23, 878-884.
- [29] H. S. Kim, P. C. Stair, J. Phys. Chem. B 2004, 108, 17019-17026.
- [30] R. M. Potter, G. R. Rossman, Am. Mineral. 1979, 64, 1199-1218.
- [31] A. Iyer, J. Del-Pilar, C. K. King'ondu, E. Kissel, H. F. Garces, H. Huang, A. M. El-Sawy, P. K. Dutta, S. L. Suib, J. Phys. Chem. C 2012, 116, 6474– 6483.
- [32] F. Wang, H. X. Dai, J. G. Deng, G. M. Bai, K. M. Ji, Y. X. Liu, Environ. Sci. Technol. 2012, 46, 4034–4041.
- [33] Y. Y. Kim, D. Williams, F. C. Meldrum, D. Walsh, Small 2013, 9, 61-66.
- [34] F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, H. Petersen, Phys. Rev. B 1989, 40, 5715-5723.
- [35] R. Brimblecombe, G. F. Swiegers, G. C. Dismukes, L. Spiccia, Angew. Chem. Int. Ed. 2008, 47, 7335–7338; Angew. Chem. 2008, 120, 7445– 7448.
- [36] R. Brimblecombe, A. Koo, G. C. Dismukes, G. F. Swiegers, L. Spiccia, J. Am. Chem. Soc. 2010, 132, 2892–2894.
- [37] B. A. Pinaud, Z. Chen, D. N. Abram, T. F. Jaramillo, J. Phys. Chem. C 2011, 115, 11830-11838.

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