Photoelectrochemical Cells

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A Photoelectrochemical Solar Cell Consisting of a Cadmium Sulfide Photoanode and a Ruthenium–2,2′-Bipyridine Redox Shuttle in a Non-aqueous Electrolyte**

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Abstract: *A photoelectrochemical (PEC) cell consisting of an n-type CdS single-crystal electrode and a Pt counter electrode with the ruthenium–2,2′-bipyridine complex* $[Ru(bpy)_3]^{2+/3+}$ *as the redox shuttle in a non-aqueous electrolyte was studied to obtain a higher open-circuit voltage* (V_{OC}) *than the onset voltage for water splitting. A* V_{OC} *of 1.48 V and a short-circuit current* (I_{SC}) *of* $3.88\ mA\,cm^{-2}$ *were obtained under irradiation by a 300 W Xe lamp with 420–800 nm visible light. This relatively high voltage was presumably due to the difference between the Fermi level of photo-irradiated n-type CdS and the redox potential of the Ru complex at the Pt electrode. The smooth redox reaction of the Ru complex with one-electron transfer was thought to have contributed to the high* V_{OC} *and* I_{SC}*. The obtained* V_{OC} *was more than the onset voltage of water electrolysis for hydrogen and oxygen generation, suggesting prospects for application in water electrolysis.*

Photoelectrochemical (PEC) cells for electric power generation have attracted great attention as candidates for low-cost photovoltaics (PVs) with the capacity to supersede conventional solid-state PVs such as Si, $Cu(Ga,In)Se_2$, and CdTe.[1,2] One such PEC PV, the dye-sensitized solar cells (DSSCs), have been successfully developed.[3–5] DSSCs offer such advantages as simplicity of cell fabrication, abundance of starting materials, and an efficiency comparable to that of solid-state PVs.[5,6] The efficiency of DSSCs has been improved with application of organic–inorganic perovskite compounds to photoabsorbers. As such, perovskite PVs have led to a new concept in solid-state solar cells.[7,8] PVs are generally designed to optimize the material properties so as to obtain the maximum electric power, and thus the band gap of the semiconductor should be designed to be 1.4–1.5 eV for the generation of an open-circuit voltage (V_{OC}) of 0.8–0.9 V. This conventional design, which is based on the theory of the Shockley–Queisser limit,[9] has typically yielded the maximum electrical power.

The production of chemical energy carriers from solar energy is of great importance because of the daily, seasonal, and meteorological fluctuations in solar irradiation. The conversion of unstable natural energy into storable chemicals is poised to become a key technology in future human society.[10] Water splitting into hydrogen and oxygen under the standard conditions of 297 K and 101.3 kPa requires a voltage of 1.23 V thermodynamically as the difference in the equilibrium potentials between the anode and cathode, which yields a ΔG° estimate of $247\ kJ\,mol^{-1}$ for this reaction. If a PV can generate over 1.23 V, it can split water simply with a single photon excitation on the basis of thermodynamics. Since an additional overpotential is, of course, required for electrocatalysis in the electrolyzer, 1.5–1.6 V output will be needed for the electrolysis of water.[11] As mentioned above, typical PVs are designed to generate only 0.8–0.9 V; therefore, they cannot electrolyze water without a series circuit of two or three PVs or the electric circuit of a voltage converter.[8,11] Thus, approaches to developing a PEC PVs with a high output voltage for direct connection to a water electrolyzer have rarely been reported.[12–14]

PEC and photocatalytic (PC) water splitting for the direct production of hydrogen and oxygen from an aqueous electrolyte is strongly expected to become a new energy technology in the near future.[15,16] Disadvantages of direct water splitting by the PEC and PC methods are: 1) the semiconductors have to be able to function in aqueous solutions without any degradation; 2) the energy levels of the conduction band minimum (CBM) and valence band maximum (VBM) have to exceed the hydrogen and oxygen evolution potentials, respectively; and 3) photoexcited minority carriers have to perform the multi-electron processes of hydrogen (two-electron) and oxygen (four-electron) evolution at the interface. Because of these requirements, the efficiency of PEC or PC water splitting has remained limited, and only a few examples have been reported for PEC and PC water splitting with one-step excitation by visible light irradiation.[13,15,16]

Herein we introduce a newly designed PEC PV capable of generating sufficient voltage for water splitting. Voltages above 1.23 V cannot be generated in the aqueous electrolyte of a PEC PV because of the potential window; thus the combination of a non-aqueous electrolyte and a metal complex redox shuttle with one-electron transfer was employed. An n-type CdS single-crystal electrode was chosen as the photoanode because it has an essentially high CBM and strongly absorbs visible light.[17–20] While CdS photoanodes

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are well known to degrade by photocorrosion in aqueous media,[21,22] a remarkable durability can be expected in a non-aqueous medium. The equilibrium potential of the redox reaction between ruthenium–2,2′-bipyridine complex as $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{3+}$ is known to be around 1.26 V_{NHE},[23,24] which is comparable to (slightly higher than) the oxygen evolution potential. The band diagram of the present PV cell is illustrated in Figure 1. A relatively high output voltage can be expected by the combination of CdS and $[Ru(bpy)_3]^{2+/3+}$ in a non-aqueous medium. The aim of the present study is to demonstrate the PEC properties of this system.

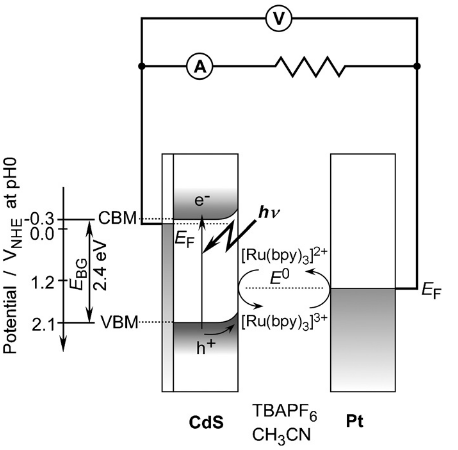

Figure 1. Band diagram for the CdS photoanode and $[Ru(bpy)_3]^{2+/3+}$ redox shuttle in acetonitrile solution.

A commercially available CdS single-crystal (10 × 10 mm, 1 mm thick, Crystal Base Co. Ltd.), which was cut into pieces of 5 × 5 mm in size, was used for the photoanode, and wiring was produced using a vacuum-deposited indium layer and indium soldering on the backside of the CdS. The back and sides of the crystal were then covered with epoxy resin (Nichiban Co. Ltd.). The CdS surface was cleaned by immersion of the CdS electrode in concentrated HCl solution. Tris(2,2′-bipyridine)ruthenium(II) dihexafluorophosphate, $[Ru(bpy)_3](PF_6)_2$ (Aldrich), was used for the redox shuttle as purchased. The $[Ru(bpy)_3]^{3+}$ complex was obtained by electrochemical oxidation of the $[Ru(bpy)_3]^{2+}$ complex. During the electrolysis of the $[Ru(bpy)_3]^{2+}$ complex with a Pt working electrode, a Pt wire counter electrode was placed in a compartment separated from the main cell by a frit. A total concentration of 2 mM Ru complexes was used, with a $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ ratio of one. Anhydrous acetonitrile (Wako Chemicals) was used as a solvent for all electrochemical measurements, and 100 mM tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Wako Chemicals) was used as the supporting electrolyte. For PEC measurements, Pt black deposited on a Pt wire (0.5 mm diameter, ca. 90 mm length) was used as the counter electrode in the three-electrode setup. To determine the redox potential of $[Ru(bpy)_3]^{2+/3+}$, a Pt disk electrode (BAS Co. Ltd.) was used as the working electrode. The potential was measured by a Ag/AgCl reference electrode constructed in-house with an acetonitrile electrolyte junction, which had double bridges to avoid leakage of Cl^- and aqueous solution to the main vessel. In the two-electrode setup, CdS and Pt black deposited on a Pt wire were used as the working and counter electrodes, respectively. All PEC measurements were performed while stirring the electrolyte and purging the air in the cell with Ar before each measurement. As a light source, a 300-W Xe lamp (420–800 nm) was used with a cutoff filter and a cold mirror. Further details are provided in the Supporting Information.

Figure 2 A shows the potential–current curves for a CdS photoelectrode in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile obtained with a sweep rate of 10 mV s^{-1}, using a three-electrode setup. The photoanodic current for the CdS electrode appeared at −0.2 V vs. Ag/AgCl ($V_{Ag/AgCl}$) when the CdS electrode was irradiated. Under both irradiation and darkness, a cathodic current was observed below −0.2 $V_{Ag/AgCl}$, indicating that the flat band potential for the CdS electrode was about −0.2 $V_{Ag/AgCl}$ in this acetonitrile electrolyte. The photoanodic current saturated at 0.85 $V_{Ag/AgCl}$ and reached 7.1 mA cm^{-2} at 1.4 $V_{Ag/AgCl}$ under stirring. The CBM for CdS is known to be around −0.4 to −0.7 V vs. the normal hydrogen electrode (V_{NHE}) as conversion into pH 0 condition, and the Fermi level (E_F) for CdS should be about 0.2 V more positive than the CBM ($E_F \approx -0.2$ to -0.5 V_{NHE}).[21,25] These potentials pertain to aqueous electrolytes. In non-aqueous electrolytes such as an acetonitrile solution, it is hard to define the standard potential. However, the potential of

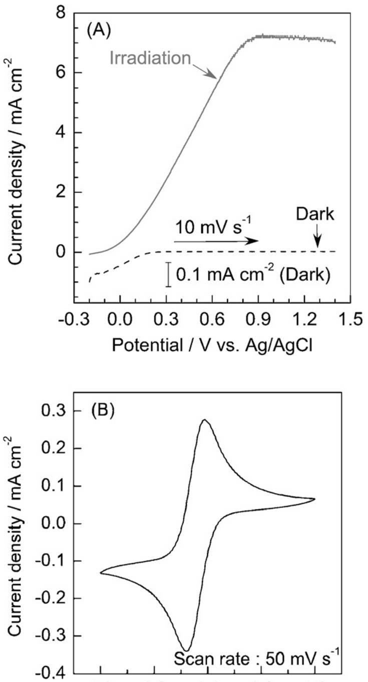

Figure 2. Potential–current curves for A) CdS and B) Pt electrodes in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile. The CdS was irradiated by a 300 W Xe lamp (420–800 nm) or not irradiated (dark). The potential of the CdS electrode was swept at 10 mV s^{-1} anodically, and that of the Pt electrode was swept cyclically at 50 mV s^{-1}. The current density under dark conditions (-----) in (A) was magnified by 10 times.

$-0.2\ V_{Ag/AgCl}$ for acetonitrile in the present results can be considered to be equivalent to $E_F \approx -0.2$ to $-0.5\ V_{NHE}$ in an aqueous solution. As a reference, the redox potential of ferrocene in $TBAPF_6$/acetonitrile was $0.47\ V_{Ag/AgCl}$ against the present Ag/AgCl electrode, as shown in the Supporting Information. The photocurrent fluctuated slightly, as seen in Figure 2 A and Figure 3, which was caused by the stirring of the solution under illumination as mentioned in the Supporting Information. The cathodic dark current was observed in the low-potential region as shown in Figure 2 A, which was negligibly small as compared to the photocurrent.

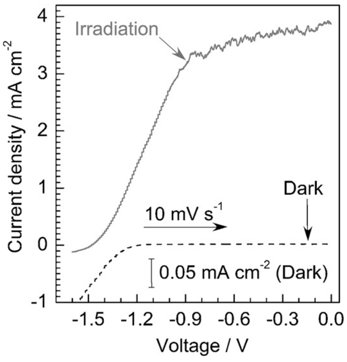

Figure 3. Voltage–current curves for a PEC PV cell with a CdS photoanode and Pt-black electrode in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile. The voltage of the cell was swept from negative to positive at $10\ mV s^{-1}$. A 300 W Xe lamp (420–800 nm) was used as a light source. The current density under dark conditions (-----) was magnified by 10 times.

A cyclic voltammogram (CV) for a Pt electrode in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile was obtained at a scan rate of $50\ mV s^{-1}$ (see Figure 2 B). The redox equilibrium potential (E_0) for $[Ru(bpy)_3]^{2+/3+}$ was estimated to be $1.4\ V_{Ag/AgCl}$ from the midpoint between the reduction and oxidation waves. Thus, the difference between E_0 at the Pt electrode surface and the onset potential for CdS for photoanodic current was 1.6 V, which is expected to be the V_{OC} for a PV cell made of CdS and Pt. The diffusion limiting current of $[Ru(bpy)_3]^{2+/3+}$ was estimated to be about $0.1\ mA cm^{-2}$ from the current at 1.0 and $1.8\ V_{Ag/AgCl}$. The redox currents in this CV converge on the diffusion limiting current at sufficiently high or low potential. Therefore, Pt black with an exceedingly large surface area was used as a counter electrode in the two-electrode setup presented below.

Voltage–current curves for a PEC PV cell in a two-electrode setup with a CdS photoanode and Pt-black counter electrode in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile are shown in Figure 3. As discussed in the previous paragraph, the onset potential of CdS was $-0.2\ V_{Ag/AgCl}$, and the redox potential of $[Ru(bpy)_3]^{2+/3+}$ at the Pt electrode was $1.4\ V_{Ag/AgCl}$. Thus, as expected from the results for the three-electrode setup, a V_{OC} of 1.48 V was obtained with the two-electrode setup. I_{SC} and the fill factor (FF) were found to be $3.88\ mA cm^{-2}$ and 0.49, respectively, under irradiation by a 300 W Xe lamp with 420–800 nm visible light. The irradiation of used 300 W Xe lamp was estimated to have power of about 9.7 times of AM 1.5 G in the visible light region as shown in the Supporting Information. Even if the light source was intense, V_{OC} of 1.48 V is clearly higher than the V_{OC} for conventional DSSCs, in which dye-modified TiO_2 photoelectrodes and I^-/I_3^- redox shuttles are utilized.[3–5] Looking at solid-state PVs[5–8] and other types of PEC PVs,[20,26–29] a V_{OC} of 1.48 V is unique.

The incident-photon-to-current conversion efficiency (IPCE) of this PEC PV cell was measured under short-circuit conditions in the two-electrode setup, using band-pass filters (Figure 4). $[Ru(bpy)_3]^{2+}$ is known to have absorption bands at 280 and 450 nm and to evolve oxygen from aqueous media when photoexcited under irradiation.[27,30,31] The decrease in the IPCE at 420-460 nm in Figure 4 was presumably caused by the absorption of $[Ru(bpy)_3]^{2+}$ in the electrolyte solution at the front of the photoelectrode. However, the IPCE curve was found to correspond to the absorption spectrum of CdS, indicating that this PEC cell was driven by band-gap excitation in the electronic structure of CdS. Although $[Ru(bpy)_3]^{2+}$ is known to be a metal complex photocatalyst for oxygen evolution,[27,30,31] this IPCE curve indicated that the photoprocess (photoexcitation) of $[Ru(bpy)_3]^{2+}$ did not contribute to the present PEC properties. The decrease in IPCE at 420–460 nm clearly indicates that the photoexcitation of $[Ru(bpy)_3]^{2+}$ was not included in the present PEC process.

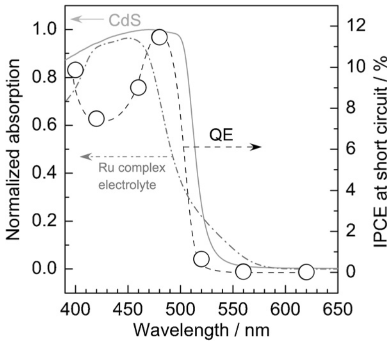

Figure 4. Incident-photon-to-current conversion efficiency (IPCE) spectrum of the PEC PV cell under short-circuit conditions in a two-electrode setup with a CdS photoanode and Pt-black counter electrode (right). The diffusion reflection spectrum (DRS) of CdS and the absorption spectrum of $[Ru(bpy)_3]^{2+}$ in acetonitrile are shown as normalized absorption (left). A 300 W Xe lamp with a band-pass filter was used as a light source.

The time course of the current density for the PEC PV cell with a CdS photoanode and Pt-black electrode at an output of 1.23 V is plotted in Figure 5. The current decayed during the irradiation, dropping to about 50 % of its initial value after 2 h of irradiation. The total Faradaic number for the current in Figure 5 was estimated to be 13.7 μmol of electrons. This is much larger than that for the atoms on a CdS surface, which is on the order of $nmol cm^{-2}$. Thus, the photoanodic current mostly originated from the oxidation of $[Ru(bpy)_3]^{2+}$, rather than the degradation of CdS. Nevertheless, the degradation was significant enough to warrant establishing stability improvement as a topic of future study. Since the early days

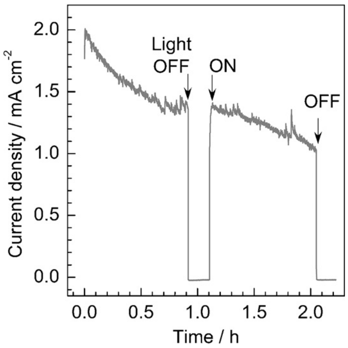

Figure 5. Time course of the current density for the PEC PV cell with a CdS photoanode and Pt-black electrode at an output of 1.23 V in 2 mM $[Ru(bpy)_3]^{2+/3+}$ and 100 mM $TBAPF_6$ in acetonitrile. A 300 W Xe lamp (420–800 nm) was used as a light source.

of the electrochemistry of CdS photoelectrodes,[17,32–34] photocorrosion of CdS has been thought to occur according to the following chemical equation:[21,22]

$$CdS \xrightarrow{h\nu} Cd^{2+} + S^{(0)} + 2\,e^-$$

The Gibbs free energy for the transfer of Cd^{2+} from water to acetonitrile has been reported to be in the 17–42 kJ mol^{-1} range.[35–37] This indicates that Cd^{2+} is less stable in acetonitrile than the aqueous electrolyte, resulting in the suppression of photocorrosion.

The proposed band diagram has been briefly explained above, in connection with Figure 1. Cd compounds are known to have large negative CBM potentials relative to those of typical semiconductors for photoanodes.[26,38,39] In this case, the onset potential for the photocurrent of CdS in a non-aqueous electrolyte, which was observed at $-0.2\ V_{Ag/AgCl}$, was almost equivalent to the Fermi level for the intrinsic band position. The redox potential of $[Ru(bpy)_3]^{2+/3+}$ was observed to be 1.4 $V_{Ag/AgCl}$ on the Pt electrode. The smooth reaction with one-electron transfer shows a steeper I–E slope than the redox of oxygen, which has a large over-potential for surface reaction. Thus, a V_{OC} of 1.48 V between the CdS and Pt electrodes was achieved. As another candidate of redox shuttle, PEC cell with CdS photoanode in $Fe^{2+/3+}$ perchlorate complexes were also found to have relatively high V_{OC}, which will be reported elsewhere. However, $[Ru(bpy)_3]^{2+/3+}$ has been shown the highest V_{OC} and I_{SC} at present.

Although a variety of PEC PVs have been developed to maximize electric power,[4–6,9] the present work demonstrates an alternative direction for the development of PEC PVs to obtain a target output voltage, such as water electrolysis. One shortcoming of this cell is the strong visible light absorption of the $[Ru(bpy)_3]^{2+/3+}$ complex. $[Ru(bpy)_3]^{2+}$ has absorption peaks at 280 and 450 nm, and $[Ru(bpy)_3]^{3+}$ has a peak at 310 nm.[23,24,27,30,31] Because the absorption edge for CdS is at 520 nm,[17–20,32–34] the absorption of 450 nm light by $[Ru(bpy)_3]^{2+}$ interfered with the irradiation of CdS.

In conclusion, the present PEC cell with a CdS photoanode and Pt-black counter electrode in a non-aqueous electrolyte with a $[Ru(bpy)_3]^{2+/3+}$ redox couple showed a V_{OC} of 1.48 V and an I_{SC} of 3.88 mA cm^{-2} under visible light irradiation by a 300 W Xe lamp. This output voltage was obtained thanks to the relatively negative potential of the conduction band for CdS and the positive potential of the redox potential of $[Ru(bpy)_3]^{2+/3+}$. The use of acetonitrile as a solvent enabled the photocorrosion of CdS to be suppressed. The higher output voltage compared to the thermodynamic voltage for water electrolysis of 1.23 V suggests the feasibility of water electrolysis by one-step photoexcitation in the present semiconductor.

Keywords: cadmium sulfide · photoanodes · redox complexes · ruthenium · water electrolysis

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[1] R. B. Bergmann, *Appl. Phys. A* **1999**, *69*, 187–194.
[2] B. Parida, S. Iniyan, R. Goic, *Renewable Sustainable Energy Rev.* **2011**, *15*, 1625–1636.
[3] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737–740.
[4] H. Choi, C. Nahm, J. Kim, C. Kim, S. Kang, T. Hwang, B. Park, *Curr. Appl. Phys.* **2013**, *13*, S2–S13.
[5] J. Gong, J. Liang, K. Sumathy, *Renewable Sustainable Energy Rev.* **2012**, *16*, 5848–5860.
[6] B. Li, L. Wang, B. Kang, P. Wang, Y. Qiu, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 549–573.
[7] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**, *499*, 316–319.
[8] J. Luo, J. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. Park, S. D. Tilley, H. J. Fan, M. Grätzel, *Science* **2014**, *345*, 1593–1596.
[9] M. Kouhnavard, S. Ikeda, N. A. Ludin, N. B. Ahmad Khairudin, B. V. Ghaffari, M. A. Mat-Teridi, M. A. Ibrahim, S. Sepeai, K. Sopian, *Renewable Sustainable Energy Rev.* **2014**, *37*, 397–407.
[10] J. Newman, P. G. Hoertz, C. A. Bonino, J. A. Trainham, *J. Electrochem. Soc.* **2012**, *159*, A1722–A1729.
[11] K. Onda, T. Murakami, T. Hikosaka, M. Kobayashi, R. Notu, K. Ito, *J. Electrochem. Soc.* **2002**, *149*, A1069.
[12] J. H. Park, A. J. Bard, *Electrochem. Solid-State Lett.* **2006**, *9*, E5–E8.
[13] K. Maeda, K. Domen, *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.
[14] T. J. Jacobsson, V. Fjällström, M. Edoff, T. Edvinsson, *Sol. Energy Mater. Sol. Cells* **2015**, *134*, 185–193.
[15] T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* **2014**, *43*, DOI: 10.1039/C3CS60378D.
[16] A. A. Ismail, D. W. Bahnemann, *Sol. Energy Mater. Sol. Cells* **2014**, *128*, 85–101.
[17] A. B. Ellis, S. W. Kaiser, M. S. Wrighton, *J. Am. Chem. Soc.* **1976**, *98*, 1635–1637.
[18] A. B. Ellis, S. W. Kaiser, J. M. Bolts, M. S. Wrighton, *J. Am. Chem. Soc.* **1977**, *99*, 2839–2848.
[19] R. N. Noufi, P. A. Kohl, A. J. Bard, *J. Electrochem. Soc.* **1978**, 125, 375—379.
[20] R. N. Noufi, P. A. Kohl, J. W. Rogers, J. M. White, A. J. Bard, *J. Electrochem. Soc.* **1979**, *126*, 949–954.
[21] T. Inoue, *J. Electrochem. Soc.* **1977**, *124*, 719.
[22] D. Meissner, R. Memming, B. Kastening, *J. Phys. Chem.* **1988**, *92*, 3476–3483.
[23] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244.
[24] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.
[25] X. Yong, M. A. A. Schoonen, *Am. Mineral.* **2000**, *85*, 543–556.
[26] M. J. Price, S. Maldonado, *J. Phys. Chem. C* **2009**, *113*, 11988–11994.

[27] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322 – 5363.
[28] Q. Mi, R. H. Coridan, B. S. Brunschwig, H. B. Gray, N. S. Lewis, *Energy Environ. Sci.* **2013**, *6*, 2646.
[29] J.-B. Jiang, Y.-Y. Wu, P. Wang, P. Huo, Q.-Y. Zhu, J. Dai, *Dye. Pigment.* **2014**, *107*, 153 – 160.
[30] A. Lewandowska-Andralojc, D. E. Polyansky, *J. Phys. Chem. A* **2013**, *117*, 10311 – 10319.
[31] A. Lewandowska-Andralojc, D. E. Polyansky, R. Zong, R. P. Thummel, E. Fujita, *Phys. Chem. Chem. Phys.* **2013**, *15*, 14058 – 14068.
[32] R. Tenne, *Appl. Phys.* **1981**, *25*, 13 – 16.
[33] M. Matsumura, M. Hiramoto, T. Iehara, H. Tsubomura, *J. Phys. Chem.* **1984**, *88*, 248 – 250.
[34] H.-D. Rubin, B. D. Humphrey, A. B. Bocarsly, *Nature* **1984**, *308*, 339.
[35] G. R. Hedwig, D. A. Owensy, A. J. Parker, *J. Am. Chem. Soc.* **1975**, *97*, 3888 – 3894.
[36] Y. Marcus, *Pure Appl. Chem.* **1983**, *55*, 977 – 1021.
[37] G. Gritzner, F. Hörzenberger, *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 3013.
[38] P. A. Kohl, A. J. Bard, *J. Am. Chem. Soc.* **1977**, 99, 7531 – 7539.
[39] K. Nakatani, H. Tsubomura, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 783.

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