Windowsill Hydrogen Production under Daylight Irradiation

Bertrand Vileno, Philippe Turek, Jean Weiss, David Martel

▶ **To cite this version:**

Bertrand Vileno, Philippe Turek, Jean Weiss, David Martel. Windowsill Hydrogen Production under Daylight Irradiation. ChemPlusChem, 2013. hal-03810217

HAL Id: hal-03810217
https://cnrs.hal.science/hal-03810217

Submitted on 11 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Windowsill Hydrogen Production under Daylight Irradiation

Bertrand Vileno,[b] Philippe Turek,[b] Jean Weiss,[c] and David Martel*[a, d]

[a] Dr. D. Martel Institut de Chimie, UMR 7177 CNRS/Université de Strasbourg 1 rue Blaise Pascal, 67000 Strasbourg (France) E-mail: dmartel@unistra.fr
[b] Dr. B. Vileno, Prof. P. Turek Propriétés Optiques et Magnétiques des Architectures Moléculaires (POMAM), Institut de Chimie UMR 7177 CNRS/Université de Strasbourg 4 rue Blaise Pascal, 67000 Strasbourg (France)
[c] Dr. J. Weiss Chimie des Ligands _ Architecture Contrôlée (CLAC) Institut de Chimie, UMR 7177 CNRS/Université de Strasbourg 1 rue Blaise Pascal, 67000 Strasbourg (France)
[d] Dr. D. Martel Centre National de la Recherche Scientifique, UPR22 Institut Charles Sadron, 23 rue du loess, BP 84047 67034 Strasbourg cedex 2 (France)

Supporting information for this article, including the experimental details, is available on the WWW under http://dx.doi.org/10.1002/ cplu.201300201.

Abstract

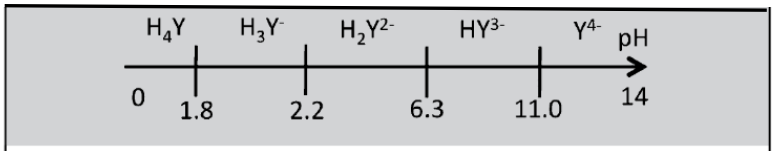
Hydrogen can be produced on a windowsill under daylight irradiation of TiO_2-supported platinum by using a self-buffered electron-donor solution that optimizes the interfacial processes.

The fundamentals of light-induced hydrogen production from water were initially outlined by Fujishima and Honda,[1] and further developed by several groups[2, 3] in the early 1980s. Since these pioneering studies, efficient pathways of hydrogen generation have attracted the attention of many scientists who have aimed to develop clean energy sources. In particular, efforts have focused on improving the three major components involved in the photosensitized hydrogen production systems: 1) the dye or photosensitizer (PS), 2) the semiconducting (SC) support associated with a catalyst, and 3) the nature of the electron-donating (ED) molecule that allows the monitoring of H_2 generation regardless of any other coupled processes (e.g., O_2 production). The development of new dyes has been motivated by increasing the efficiency in the range of absorbed wavelengths, in conjunction with research on dye-sensitized solar cells (DSSCs).[4] For economical reasons, the use of inexpensive metals rather than ruthenium and its coordination complexes has been the primary focus.[4–7] One alternative is to take advantage of the accessible bandgap in inorganic semiconductors; thus,

various combinations of metals and semiconductors have been studied during the last decade.[8, 9] The substitution of platinum as a heterogeneous catalyst responsible for proton reduction has been investigated, but replacement of Pt without loss of efficiency remains a challenge.[10] Finally, the thermodynamically favored back-transfer of electrons to the dye can be precluded by the use of electron donors, and therefore different donors have been investigated to control and improve the photocatalytic activity of given PS/SC–metal combinations.[3, 9,11] Surprisingly, other chemical parameters and components involved in light-induced hydrogen production systems have attracted much less attention.

Among these parameters, the role and nature of the buffer required to control the pH has never been emphasized, although a recent study singled out the influence of the presence and absence of phosphate buffer (PB) for H_2 production.[12] In this study, the presence of phosphate was believed to block the adsorption sites used by the molecular catalyst component, and thus to reduce the efficiency of H_2 generation.

Herein, we report significant daylight-sensitized evolution of hydrogen, which was observed during a systematic investigation of buffers used in the photogeneration of H_2 with donor/ TiO_2/Pt combinations. This study shows that a very simple two-component system that contains an electron donor, which acts as a buffer, and a suspension of TiO_2/Pt produces dihydrogen under neutral aqueous conditions. Although far from being optimized, the simplicity of the system offers new insights into the interfacial processes involved in the photoproduction of hydrogen.



	pK_a (25 °C)
H_4Y/H_3Y	1.8
H_3Y^-/H_2Y^{2-}	2.2
H_2Y^{2-}/HY^{3-}	6.3
$HY^{3-}/Y4^-$	11.0

Table 1. *pK_a values for the EDTA (Y) system[14] and the distribution of species as a function of the pH.*

Ethylenediamine tetraacetic acid (EDTA) and triethanolamine (TEOA) are among the most frequently utilized electron donors. On the basis of the various pK_a values of EDTA (**Table 1**) and that of TEOA (pK_a=7.74),[13] we reasoned that EDTA (or TEOA) could be used as a buffer, in the pH range of 6.5–7, rather than the traditional phosphate buffer. This reasoning prompted us to study catalytic systems in which EDTA would act as both the donor and buffer.

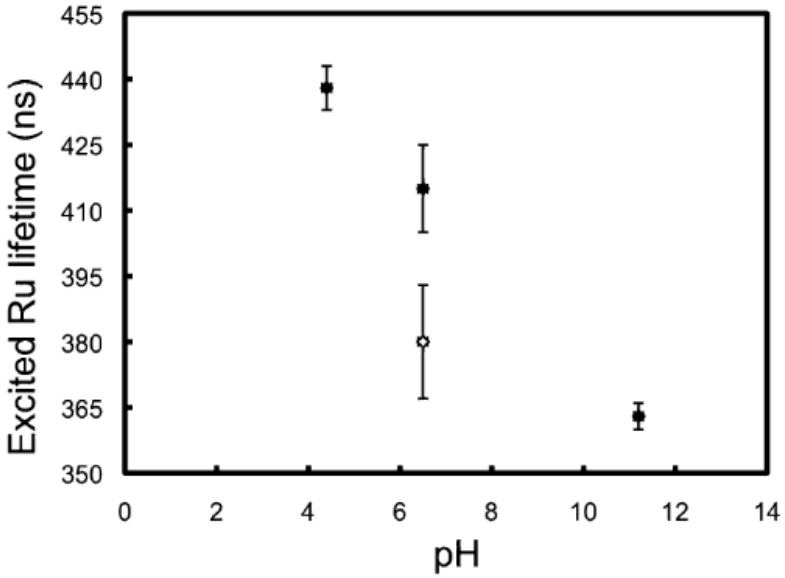


Figure 1. *Variation in the excited Ru^{II} lifetime in the system. Ru^{II} (10^{-5} M) and MV^{2+} (10^{-3} M) at different pH values with EDTA ($2x10^{-3}$ M; black circles) and EDTA ($2x10^{-3}$ M)+phosphate buffer (10^{-2} M; white square).*

In photoinduced electron transfer, it is well established that the formal charge of the donor/acceptor components, their solvation, the ionic force of the medium, and the pH can have dramatic effects on the rate and efficiency of electronic transfer.[15] Thus, in this study, the influence of both the presence and the absence of phosphate buffer was first addressed by measuring the lifetime of a model system by using $[RuII\text{-}(bipy)_3]^{2+}$ (bipy=2,2'-bipyridyl) as PS and methyl viologen (MV^{2+}) as the electron acceptor (**Figure 1**).

Figure 1 shows that the pH is not the sole parameter that controls the electronic exchange processes. Indeed, at pH 6.6 the addition of phosphate buffer leads to a Ru lifetime value that almost matches the lifetime measured under basic conditions. The logical questioning concerns the occurrence of a buffer effect and if the nature of the buffer influences the formation of dihydrogen. Thus, a very simple combination that involves EDTA–TiO_2/Pt and PB–EDTA–TiO_2/Pt was investigated. In both cases, EDTA was used as the electron donor, whereas

TiO2 played the role of the photosensitizer. **Table 2** displays the results obtained under natural daylight irradiation. The samples were exposed for 4 days, to successive daily irradiations of 141, 746, 509, and 532 J cm^{-2}.

	% H_2	H_2 [mmol L^{-1}]
EDTA buffer (0.1 M)	8.4	3.5
EDTA buffer (0.1 M) + phosphate buffer (1 M)	0	0

Table 2. *H_2 generation under natural daylight conditions. The volume of the solution is 2 mL, the TiO_2/Pt mass is equal to 1 mg ($m_{Pt} \approx 0.02$ mg), the free gas volume is 2 mL, and the sample pH is 6.6.*

Two major pieces of information should be highlighted. First, these simple experiments showed a drastic decrease in H_2 generation when the aqueous solution contains phosphate buffer. In contrast, the absence of phosphate buffer allowed substantial dihydrogen generation merely under daylight. Second, in the absence of another photosensitizer, the generation of H_2 using EDTA/TiO_2/Pt shows that the daylight UV illumination is sufficient to generate H_2 in significant amounts. Although comparative studies of multicomponent and multiparameter photocatalytic systems is a very difficult and complicated task,[16] the performance of this simple system can be subsequently estimated in light of reported efficient systems.[17, 18] To investigate this efficiency in the UV range under reproducible conditions, a solar-light simulator (spectrum AM 1.5 G) was used to probe several systems: 1) EDTA buffer (pH 6.6), 2) EDTA buffer with phosphate buffer (pH 6.6), 3) acid EDTA (pH 4.4), 4) TEOA buffer

pH 6.8), and 5) TEOA with phosphate buffer (pH 6.8). In the present study, the time of irradiation did not exceed 24 hours (**Figure 2**).

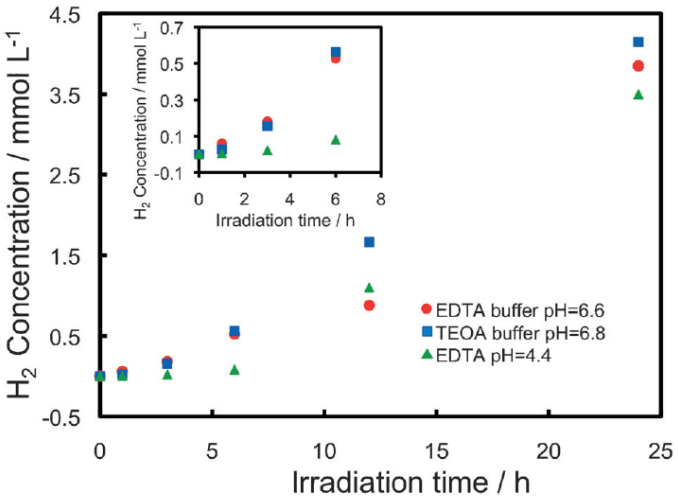


Figure 2. *H_2 generation under AM 1.5 G for 0.1 M H_2Y^{2-} at pH 4.4 (green triangles), 0.1 M EDTA buffer at pH 6.6 (red circles), and 0.1 M TEOA acidified by HCl at pH 6.8 (blue squares). For purposes of clarity, the null values obtained for all irradiation times in the presence of 1m phosphate buffer (both with EDTA or TEOA) are omitted. Inset: magnification of H_2 evolution during the first six hours of illumination. The experimental conditions are those listed in Table 2 except for the use of a solar simulator.*

When phosphate buffer was present, no production of H_2 was detected, regardless of the nature of the electron donor (TEOA or EDTA). This observation points out that the counterproductive phosphate buffer effect is not specific to EDTA. Interestingly, in the absence of phosphate buffer, H_2 was detected after only one hour of irradiation. Moreover, the gas production greatly increased with illumination time (see **Figure 2**). These results highlight the efficiency of the experimental conditions for the production of H_2. However, for longer illumination times, the results shown in **Figure 2** must be considered carefully owing to the pH variation during the irradiation process. The indicative pH values after irradiations are listed in **Table 3**.

	t_{irr} [h]					
	1	2	3	6	12	24
EDTA buffer	6.6	6.6	6.6	6.6	6.7	6.8
EDTA acid	4.4	4.5	4.6	4.7	5.1	5.3
TEOA	6.8	6.5	6.4	6.2	5.8	5.3

Table 3. *pH values measured after different irradiation times (t_{irr}).*

The variations in H_2 generation with time might be related to the chemical stability of EDTA (or TEOA), since these electron donors are known to degrade after electron donation.[3, 19] Thus, the associated pH changes and byproducts might perturb the generation of dihydrogen. Considering the kinetics of degradation (e.g., for EDTA[19]) and the data in **Table 3**, it is reasonable to assume that during the first six hours, the aqueous medium remains free of dominating contamination by decomposition products. Nevertheless, the evolution of the pH in the TEOA experiment can denote either the weakness of the buffer and/or fast degradation kinetics. For this reason, the rest of the present study mainly focuses on EDTA and the control of pH by self-buffering with the sacrificial electron donor. Prior to a discussion on EDTA/TiO_2 interfacial processes, it should be noted that production of H_2 was lower at the acidic pH value of 4.4 relative to the nearly neutral pH value of 6.6 despite an expected lower-band bending in acidic media.[20] This observation is consistent with previous results that involve EDTA.[21, 22]

To investigate processes that take place on the surface of TiO_2, electron paramagnetic resonance (EPR) measurements were performed by using the spin-trapping technique. Paramagnetic 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) molecules (EPR-active) were used to trap reactive species, such as the hydroxyl radical ($OH^{\bullet}$) or protons ($H^{\bullet}$), which are produced under irradiation on the surface of TiO_2 and lead to stable diamagnetic products. The decay of the EPR signal of TEMPOL was thus used to probe the efficiency of thehotogeneration of radicals.[23] **Figure 3 a,b** show the results for EDTA and TEOA in the presence and absence of phosphate buffer, respectively.

These data corroborate very well the effect of the phosphate buffer observed for the H_2 production experiments. The almost complete disappearance of the paramagnetic probe occurred within 35 to 40 minutes when phosphate buffer was present, whereas in the absence of phosphate buffer, less than 6 and 15 minutes were sufficient in the presence of EDTA and TEOA, respectively. A possible explanation for this peculiar behavior might be related to the adsorption of phosphate on TiO_2,[24] which would drastically preclude the electron transfer between EDTA (or TEOA) and TiO_2, thereby causing insufficient electron density in the conduction band of TiO_2. The difference in H_2 production between pH values of 4.4 and 6.6 still remained puzzling. **Figure 3 c,d** show the respective EPR measurements that correspond to these two pH values. Within a similar overall trend, a slight discrepancy can be seen: the TEMPOL decay is slower under acidic conditions.

These results suggest a reasonable explanation for the buffer effect on the performance of a catalytic system as simple as a self-buffered donor and a colloidal TiO_2/Pt photocatalyst. On the one hand, the phosphate buffer seems to limit the electron transfer between the donor and the semiconductor considerably, thereby decreasing the production of proton radicals. On the other hand, water can therefore act as an electron donor by filling the holes and producing $OH^{\bullet}$ radicals.[25] Therefore, the slow disappearance of TEMPOL (see **Figure 3a**) arises from the low generation of reactive $H^{\bullet}$ and $OH^{\bullet}$ species on the TiO_2 surface.

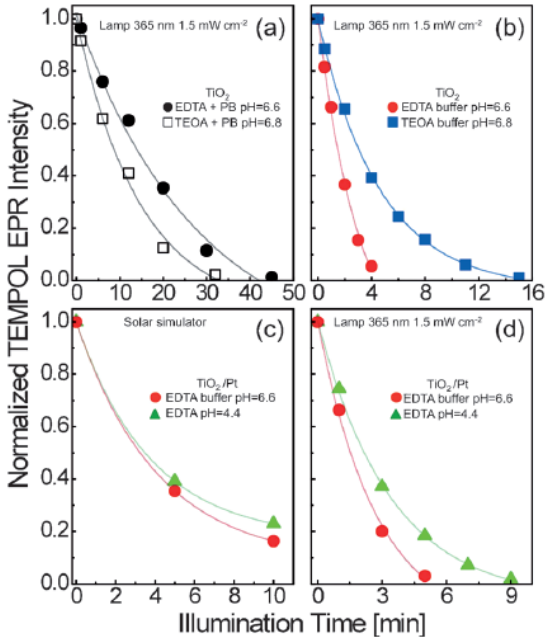
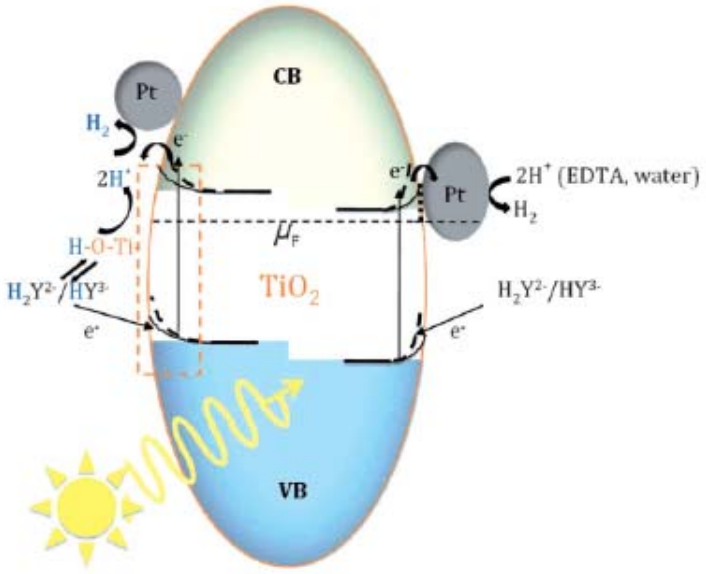


Figure 3. *Top: Photocatalytic degradation of TEMPOL (200 µM) in the presence of a TiO_2 suspension (0.1 gL^{-1}) with (a) 1M phosphate buffer (pH 6.6)+0.1 M EDTA buffer at pH 6.6 (black circles) and 1 M phosphate buffer (pH 6.8)+0.1 M TEOA at pH 6.8 (white squares); and (b) 0.1 M EDTA buffer at pH 6.6 (red circles) and 0.1 M TEOA at pH 6.8 (blue squares). The excitation source is a monochromatic lamp (λ=365 nm) providing 1.5 $mWcm^{-2}$. Bottom: Photocatalytic degradation of TEMPOL (200 µM) in the presence of a 0.1 g L^{-1} TiO_2/Pt suspension with (c) 0.1 M EDTA buffer at pH 6.6 (red circles) and 0.1 M EDTA at pH 4.4 (green triangles) using solar light simulator AM 1.5 G and (d) the same with a UV lamp (365 nm,1.5 $mWcm^{-2}$). All solutions were bubbled with Ar for at least 10 minutes prior to experiments, and all decays were fitted with a single exponential.*

From the point of view of hydrogen production, it can be assumed that on the platinum surface, two proton radicals must be close to one another to form H_2. The presence of phosphate buffer slows down the radical production and limits the possibility of being in this optimum state. The proton radical is very unstable; therefore it will react rapidly with species

in solution and will not be available to produce dihydrogen. Additionally, steric hindrance might force TEMPOL to react with small radical species such as $H^{\bullet}$ or $OH^{\bullet}$.[23] The EPR measurements clearly show that in the absence of phosphate buffer, the probe is consumed at a much faster rate, which is significant for a higher production of radicals.

Because an electron donor is present in solution and the oxygen content is lowered by either bubbling or freeze pumping, the presence of a small amount of hydroxyl radical and superoxide can be assumed while the main remaining species is $H^{\bullet}$. As shown in **Figure 3 b,d**, the noticeable disappearance of the probe does not significantly depend on the presence of Pt on TiO_2. This observation points to the core of the mechanism responsible for H_2 production for which the Schottky barrier is usually involved in electron trapping on platinum for watersplitting process. Our observations suggest that $H^{\bullet}$ production also takes place on the TiO_2 surface (see **Scheme 1**). This hypothesis is consistent with the high surface-to-volume ratio, which is an influential parameter in this type of mechanism.[26] This process might be combined with the trapping of $H^{\bullet}$ on Pt particles upon diffusion to form H_2. A blank test performed without platinum allowed the detection of H_2 traces. This hypothesis is further supported by considering the acid–base properties of the TiO_2 surface for which two acid–base equilibria are known [**Eqs. (1)** and **(2)**]:[27]



Scheme 1. *Proposed mechanism for H_2 production under the neutral experimental conditions (pH range = 6.5–7), the surface states, and the Schottky barrier. VB, CB, and μ_F correspond to the valence band, conduction band, and Fermi level, respectively.*

$Ti\text{-}OH_2^+ = Ti\text{-}OH + H^+$ $pK_{a1} \approx 5$ (1)

$Ti\text{-}OH = Ti\text{-}O^- + H^+$ $pK_{a2} \approx 8$ (2)

These pK_a values are for TiO_2 itself and should be slightly lower in the presence of platinum particles.[28, 29] Thus, the behavior of surface states seems critical in the peculiar buffer effect and is expected to account for the difference in activities at various pH values. At pH 4.4, the TiO_2 surface groups are of the $Ti\text{-}OH_2^+$ type, and EDTA is known to be adsorbed.[14] At this pH, an electron promoted to the conduction band can be trapped to generate H_2O on the TiO_2 surface and thus will not react with TEMPOL. This process competes with H_2 production. Other additional parameters might also affect the surface states. For example, it has been shown in the case of titanium oxides that when the pH decreases, the photoproduction of $OH^\bullet$ increases.[16] Thus, further combination of $OH^\bullet$ and $H^\bullet$ radicals might also lead to water formation and will increase competition with the production of hydrogen. At pH 6.6, TiO_2 surface groups are mainly Ti-OH. Owing to the pK_a value of EDTA, proton exchange easily takes place with the Ti-OH groups on the surface, thus enhancing the production of $H^\bullet$ radicals.

In conclusion, a very simple combination of an EDTA electron donor with colloidal TiO_2-supported Pt in EDTA self-buffered neutral aqueous media allows the production of hydrogen on the millimolar scale under daylight illumination. These results also demonstrate the counterproductive effect of phosphate buffer. Although the experimental conditions of this study might not be optimum for real-life applications,[29, 30] the effects of self-buffering definitively show that the optimization of the electron donor, the properties of the buffer, and the (ED, buffer)/TiO_2 interface might create new prospects in the field of fossil energy substitution. Finally, the analysis of such a simple system highlights critical parameters that influence H_2 photogeneration.

Acknowledgements

This study was supported by the C.N.R.S. (Centre National de la Recherche Scientifique) and Universit_ de Strasbourg. We thank the French Ministry of Research. We also gratefully acknowledge Martine Heinrich, Suzanne Libs, Rémy Louis, Paul Marie Marquaire, Hoan Nguyen Cong, Christelle Perrin, Romain Ruppert, and Jennifer Wytko for their help and advice.

Keywords

EPR spectroscopy, hydrogen, interfaces, platinum, titanium

References

[1] A. Fujishima, K. Honda, *Nature* **1972**, 238, 37–38.
[2] J. M. Lehn, J.-P. Sauvage, *Nouv. J. Chim.* **1977**, 1, 449 –451.
[3] K. Kalyanasundaram, J. Kiwi, M. Grätzel, *Helv. Chim. Acta* **1978**, 61, 2720 –2730.
[4] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, 110, 6595 –6663.
[5] J. Yu, J. Ran, *Energy Environ. Sci.* **2011**, 4, 1364 –1371.
[6] J. Yu, Y. Hai, B. Cheng, *J. Phys. Chem. C* **2011**, 115, 4953 –4958.
[7] Q. Xiang, J. Yu, *J. Phys. Chem. Lett.* **2013**, 4, 753– 759.
[8] Y. Qu, X. Duan, *Chem. Soc. Rev.* **2013**, 42, 2568 – 2580.
[9] H. M. Chen, C. K. Chen, R.-S. Liu, L. Zhang, J. Zhang, D. P. Wilkinson, *Chem. Soc. Rev.* **2012**, 41, 5654– 5671.
[10] F. E. Osterloh, *Chem. Mater.* **2008**, 20, 35–54.
[11] Y. Li, G. Lu, S. Li, *Appl. Catal. A Gen.* **2001**, 214, 179– 185.
[12] F. Lakadamyalis, E. Reisner, *Chem. Commun.* **2011**, 47, 1695 –1697.
[13] M. R. Simond, K. Ballerat-Busserolles, Y. Coulier, L. Rodier, J.-Y. Coxam, *J. Solution Chem.* **2012**, 41, 130 –142.
[14] A. P. Davis, D. L. Green, *Environ. Sci. Technol.* **1999**, 33, 609 –617.
[15] M.-C. Richoux, A. Harriman, *J. Chem. Soc. Faraday Trans. 1* **1982**, 78, 1873 –1885.
[16] Q. Xiang, J. Yu, P. K. Wong, *J. Colloid Interface Sci.* **2011**, 357, 163 –167.
[17] C. Liu, J. Tang, H. M. Chen, B. Liu, P. Yang, *Nano Lett.* **2013**, 13, 2989 –2992.
[18] K. Zhang, Q. Liu, H. Wang, R. Zhang, C. Wu, J. R. Gong, *Small* **2013**, 9, 2452 –2459.
[19] T. H. Madden, A. K. Datye, M. Fulton, *Environ. Sci. Technol.* **1997**, 31, 3475 –3481.
[20] R. Witzleben, M. Lorenz, G. Israel, *J. Mater. Sci.* **1994**, 29, 389– 393.
[21] K. Hirano, E. Suzuki, A. Ishikawa, T. Moroi, H. Shiroishi, M. Kaneko, *J. Photochem. Photobiol., A* **2000**, 136, 157–161.
[22] C. Gomez Silva, R. Ju_rez, T. Marino, R. Molinari, H. Garcia, *J. Am. Chem. Soc.* **2011**, 133, 595 –602.
[23] K. Pierzchała, M. Lekka, A. Magrez, A. J. Kulik, L. Forr_, A. Sienkiewicz, *Nanotoxicology* **2012**, 6, 813 –824.
[24] P. A. Connor, A. J. McQuillan, *Langmuir* **1999**, 15, 2916 – 2921.
[25] T. Hirakawa, H. Kominami, B. Ohtani, Y. Nosaka, *J. Phys. Chem. B* **2001**, 105, 6993– 6999.
[26] L. Kronik, Y. Shapira, *Surf. Interface Anal.* **2001**, 31, 954 –965.
[27] B. Ohtani, Y. Okugawa, S. Nishimoto, T. Kagiya, *J. Phys. Chem.* **1987**, 91, 3550 –3555.
[28] P. Pichat, *New J. Chem.* **1987**, 11, 135 –140.
[29] A. L. Linsebigler, G. Lu, J. T. Yates, Jr., *Chem. Rev.* **1995**, 95, 735 –758.
[30] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **2010**, 110, 6446– 6473.