

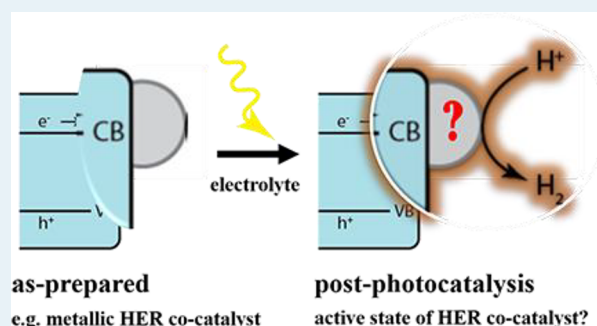
# Driving Surface Redox Reactions in Heterogeneous Photocatalysis: The Active State of Illuminated Semiconductor-Supported Nanoparticles during Overall Water-Splitting

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**ABSTRACT:** Materials used for photocatalytic overall water splitting (POWS) are typically composed of light-absorbing semiconductor crystals, functionalized with so-called cocatalytic nanoparticles to improve the kinetics of the hydrogen and/or oxygen evolution reactions. While function, quantity, and protection of such metal(oxide) nanoparticles have been addressed in the literature of photocatalysis, the stability and transients in the active oxidation-state upon illumination have received relatively little attention. In this Perspective, the latest insights in the active state of frequently applied cocatalysts systems, including Pt, Rh/Cr<sub>2</sub>O<sub>3</sub>, or Ni/NiO<sub>x</sub>, will be presented. While the initial morphology and oxidation state of such nanoparticles is a strong function of the applied preparation procedure, significant changes in these properties can occur during water splitting. We discuss these changes in relation to the nature of the cocatalyst/semiconductor interface. We also show how know-how of other disciplines such as heterogeneous catalysis or electro-catalysis and recent advances in analytical methodology can help to determine the active state of cocatalytic nanoparticles in photocatalytic applications.

**KEYWORDS:** photocatalysis, cocatalysts, deactivation, interfaces, water splitting



Photocatalytic conversion of solar energy is considered an ideal route to produce chemical fuels from abundant feedstocks like water.<sup>1–4</sup>

Photocatalytic overall water splitting (POWS) is a thermodynamically unfavorable uphill reaction ( $\Delta G > 0$ ), and to achieve a techno-economically competitive hydrogen production process, it is critical to develop a photocatalytic water splitting system with high solar-to-hydrogen (STH) efficiencies (>10%) and long-term stability.<sup>5,6</sup> In photocatalysis, efficiencies are determined by (i) the optical properties of the applied semiconductor, that is, band gap or light absorption efficiency ( $\eta_{\text{abs}}$ ), and (ii) the charge separation efficiency ( $\eta_{\text{sep}}$ ). Significant progress has been made in the last decades in the development of new semiconductor materials, yet relatively low overall conversion efficiencies of the available (composite) materials have prevented the practical implementation of solar fuel production by (heterogeneous) photocatalysis.<sup>6</sup>

Based on the common perception that optimum performance requires optimized optical and electrical properties (i.e., a bulk band structure that enables absorption of larger fractions of visible light ( $\leq 600$  nm) and efficient separation of generated charge carriers with little loss by recombination), the development of novel semiconductor materials is dominating the research efforts of the community.

In heterogeneous photocatalysis, liquid (aqueous electrolyte)–solid (semiconductor) interfaces are formed. Usually n-

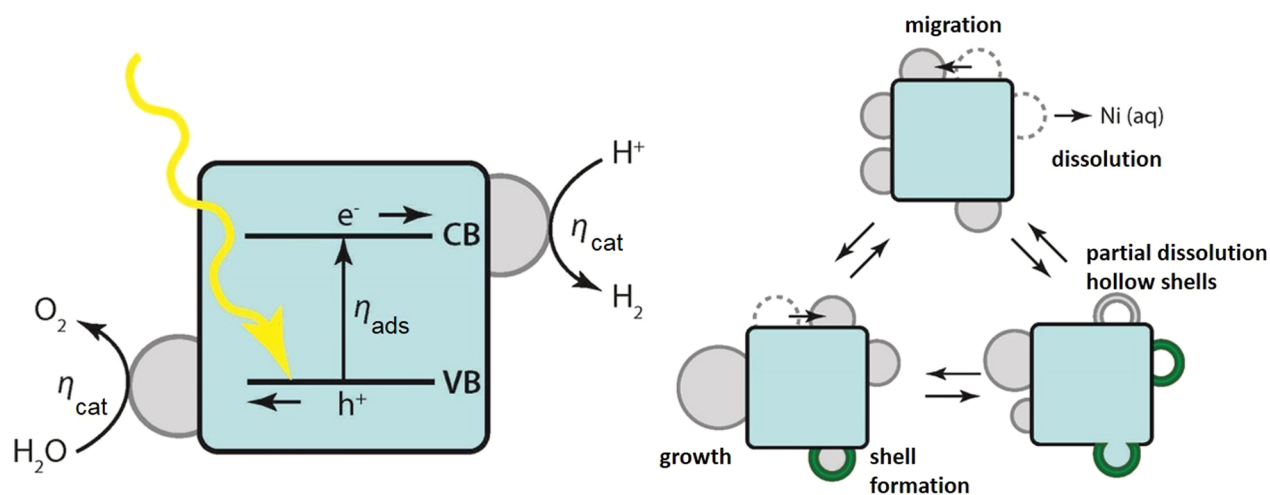
type semiconductors are employed, and interfacial charge separation is achieved by an upward band bending caused by the adjustment of the Fermi levels of the semiconductor and the electrolyte (establishing thermodynamic equilibrium).<sup>7</sup> Upon illumination (using illumination intensities insufficient to establish flat band potentials, e.g. by fully reversing band bending) positive charges generated in the depletion regime will be effectively transferred to the semiconductor/electrolyte interface, whereas electrons are transferred to the bulk. Nevertheless, transfer of the majority carriers (electrons) to the surface is essential to drive the reduction of protons. Therefore, metal nanoparticles are usually employed, which facilitate electron accumulation at the surface (for further information about charge separation, band bending, etc., the readers are referred to existing textbooks and reviews<sup>7–9</sup>).

Another important function of the metal(oxide) nanoparticles is to achieve effective POWS by promoting surface reactions ( $\eta_{\text{cat}}$ ),<sup>10,11</sup> and in fact, a proper alignment of bulk properties and surface catalysis is required to fully utilize the intrinsic properties of a semiconductor for overall water splitting (Figure 1). Usually  $\eta_{\text{cat}}$  of semiconductor surfaces is low (high overpotentials and slow kinetics for the catalytic H<sub>2</sub> and O<sub>2</sub> evolution or CO<sub>2</sub> reduction) causing severe surface

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**Figure 1.** (Left) Schematic representation of photocatalysis. Illumination of a semiconductor with the efficiency,  $\eta_{\text{ads}}$ , is followed by charge carrier separation  $\eta_{\text{sep}}$  and the surface redox reaction occurring at the surface of the cocatalyst particles,  $\eta_{\text{cat}}$ . Here, dual cocatalyst functionalizations (e.g. hydrogen and oxygen evolution) are driven by different cocatalysts. (Right) Co-catalysts can be dynamic in nature, and a few examples of feasible changes of the cocatalyst are sketched.

recombination of charge carriers. It is important to emphasize that in comparison to heterogeneous catalysis, in photocatalysis the cocatalytic nanoparticles are not thermally activated but rather by the light-driven generation of charges in the semiconductor, followed by charge transfer across the interface of the applied semiconductor and the metal(oxide) nanoparticles. After successful transfer of charges (electrons to drive HER), the cocatalysts (electrocatalyst) allow redox reactions by lowering the overpotential of electron transfer reactions, similar to electrocatalysis.<sup>8,9,12</sup>

Suitable materials for a specific reaction can thus be chosen following the guidelines established by electrochemists. For instance, noble and non-noble metals (Pt, Rh, Ru, Au, or Ni),<sup>13–16</sup> metal sulfides (e.g., MoS<sub>2</sub> or NiS),<sup>17,18</sup> or metal phosphides (e.g., NiP or FeP)<sup>19</sup> are well-known constituents of electrodes used in water or carbon dioxide reduction. The community studying electrochemistry is also well aware of the fact that metal oxides (IrO<sub>x</sub>, MnO<sub>x</sub>, and CoO<sub>x</sub>)<sup>20–22</sup> and metal oxyhydroxides (NiOOH, or FeOOH)<sup>23,24</sup> promote water oxidation. Several of these materials (Rh, Ni, Pt for reductive hydrogen evolution) are commonly applied as cocatalysts in heterogeneous photocatalysis. It should be mentioned that in photocatalytic overall water splitting, activity is the primary criterion for selection of the composition of the cocatalytic nanoparticles, while electrochemical selectivity receives little attention.<sup>25</sup> An exception is the consideration of the back reaction in water splitting (i.e., the recombination of hydrogen and oxygen to water) because these products are formed in close proximity. Conversion of oxygen and hydrogen to form water can be triggered (i) electrochemically by reduction of oxygen (the oxygen reduction reaction (ORR)) or the oxidation of hydrogen (the hydrogen oxidation reaction, (HOR)) on the hydrogen and oxygen evolution sites of the cocatalysts, or (ii) thermally by catalytic activation of hydrogen or oxygen.<sup>6</sup> While electrochemically induced hydrogen or oxygen activation is only feasible under illumination (initiating the required electrochemistry), thermal activation is feasible in the dark, albeit this is likely enhanced during illumination by the possible presence of local hotspots.

To achieve electrochemical selectivity for the “forward” hydrogen and oxygen evolution from water, in earlier studies,

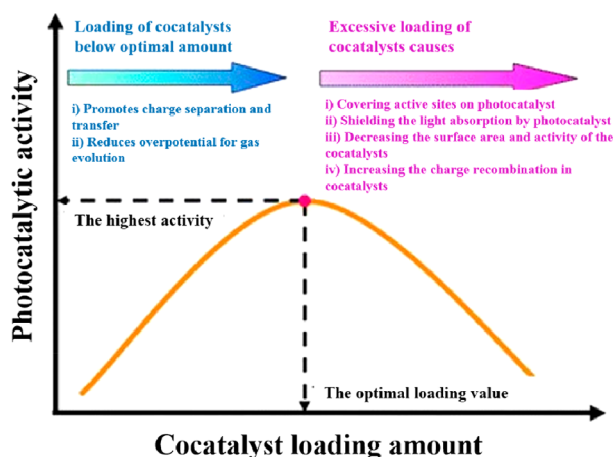
solution additives (carbonate salts)<sup>26</sup> and sodium hydroxide coatings<sup>27</sup> were suggested, whereas in recent literature, primarily core–shell structures are used.<sup>6,25</sup> Frequently applied core–shell structures are chromium oxide (e.g., Rh/Cr<sub>2</sub>O<sub>3</sub>) or nickel oxide (Ni/NiO<sub>x</sub>).<sup>6</sup> Titanium dioxide and lanthanide oxides were also reported as applicable shell material.<sup>28</sup> Here, it is interesting to note that the same principles have already been applied for decades in the chlorate industry, showcasing the successful adaptation in heterogeneous photocatalysis. In the chlorate industry deposition of a CrO<sub>x</sub> film on the cathode is essential to facilitate selective hydrogen formation and to prevent reduction of oxychlorides. Despite its frequent use, the exact structure, working mechanism, and location of the electrocatalytic hydrogen evolution reaction are not yet exactly known, and consequently, the purpose of these oxides in heterogeneous photocatalysis might also be diverse.<sup>29,30</sup>

Apart from the benefits of lower overpotentials and favorable kinetics, functionalization of semiconductor surfaces by metallic, metal oxide, or even core–shell structured cocatalysts adds additional complexity to the development and understanding of photocatalytic materials.<sup>6</sup> Different time scales of photoexcitation and catalytic events are still inevitable, and positive or negative charging of cocatalysts particles by trapping of charge carriers (in turn potentially increasing  $\eta_{\text{sep}}$ ) will occur during prolonged illumination.<sup>11</sup> Furthermore, the location of the respective cocatalysts driving reductive (H<sub>2</sub> evolution, CO<sub>2</sub> reduction) or oxidative (O<sub>2</sub> evolution) reactions and the interface between the semiconductor surface and the cocatalyst are of importance. The interface has to be carefully designed to generate drift currents by an effective and adequate potential gradient as recently pointed out by Takanae et al.,<sup>11</sup> and it is important to realize that these gradients might not be achieved by random arrangement of cocatalyst particles of various sizes. For very small-sized particles, the electronic structure of cocatalyst (or of a semiconductor) will even be defined by quantum size effects.

In contrast to photoelectrocatalytic processes, where materials for reductive and oxidative processes can be optimized independently, for particulate semiconductor materials favorable interfaces and depositing cocatalysts at preferred locations must be realized on a (single) semi-

conductor particle, underlining the fact that photocatalysis must be considered as a multidisciplinary field of research. Among others, expertise in semiconductor physics, (in)organic materials chemistry, and (electro-)catalysis is required to develop efficient systems and fully understand individual functions of multicomponent photocatalysts.<sup>32–34</sup>

The cocatalyst loading is commonly of primary concern and a typical relationship between loading and activity of photocatalysts is depicted in Figure 2. This simple relationship



**Figure 2.** Relationship between the amount of a cocatalyst and the photocatalytic activity of heterogeneous photocatalyst. Reproduced with permission from ref 31. Copyright 2014 Royal Society of Chemistry.

does not account for differences in the active state of a cocatalyst as a function of loading, nor for the effectiveness of interfaces of semiconductor/cocatalysts (potential shifts) and likely overestimates the required loading of cocatalysts. Another common mistake is that the same cocatalyst loading (and cocatalyst material) is applied to measure the activity of different semiconductor materials (or the same semiconductor material with different morphology and/or particle sizes causing changes in the density of state and different/incomplete band bending due to quantum size effects). However, optimization of loading and accompanied dispersion of nanoparticles, might be dependent on the applied semiconductor. Moreover, the semiconductor/cocatalyst interface might be different, and these factors determining photocatalytic properties are typically not addressed.<sup>35</sup>

Heterogeneous photocatalysts are usually tested in recirculating batch reactor systems and their activity is defined by the amount of accumulated gas species detected by methods such as gas chromatography. Due to detection limits and the generally slow data acquisition first data points are only obtained after prolonged illumination of about 1 h. This realistic and potentially scalable approach (batch-type bags<sup>5,36</sup>) circumvents that changes in the photocatalytic properties during the “start-up phase” can be revealed. Changes during start-up are known from heterogeneous catalysis, and recently we have shown that dramatic changes in the photocatalytic performance of heterogeneous photocatalysts occur during initial illumination: steady-state activity is only obtained after several minutes/hours.<sup>37,38</sup> We were able to assign changes in the photocatalytic behavior to changes of the cocatalyst using differential reactor operation and fast product detection.<sup>36,39</sup>

In summary, it is widely recognized that the use of one or more cocatalyst compositions on the surface of a semiconductor is indispensable to achieve high efficiencies.<sup>40</sup> However, there is still little experimental proof for the operating mechanism and active morphology and oxidation state during photocatalytic operation.<sup>8,9</sup> Here, we will focus specifically on transients in the composition of cocatalysts upon illumination, and highlight the need to use advanced in situ or operando characterization methods to determine the “real” active state of cocatalysts. Furthermore, determining dissolved ions after testing and postcatalytic transformations of the cocatalysts (e.g., particle growth) should be revealed. This appears to be especially important for complex core–shell systems. Defining the active state is also mandatory to fully describe the properties of the different interfaces (semiconductor/cocatalyst, semiconductor/electrolyte).

### ■ TRANSIENT BEHAVIOR OF Pt AND Ni/NiO COCATALYSTS: EXAMPLES OF COCATALYST REARRANGEMENT

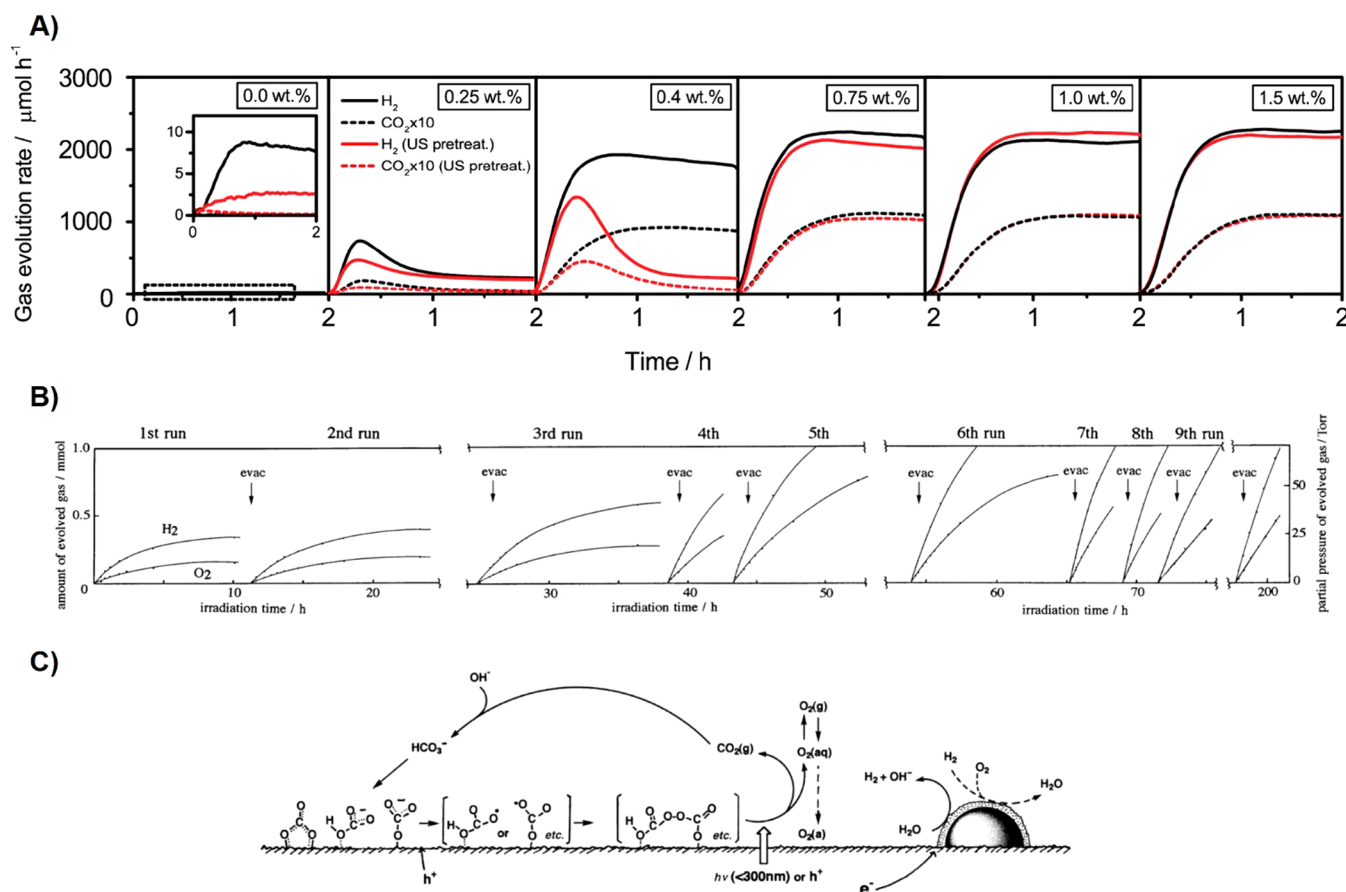
As previously indicated, it is known that a volcano-like shape describes the relationship of cocatalyst loading and photocatalytic activity (Figure 2).<sup>41</sup> This simplified dependence ignores size-dependent electronic structures and activities, transients in composition, and deactivation of deposited nanoparticles.

The deactivation of a cocatalyst/semiconductor composite might occur because of

- (1) changes of the light absorbing semiconductor material (e.g., by corrosion);
- (2) changes/rearrangement of the applied cocatalysts, in particular modification of the physicochemical properties of a cocatalyst, such as oxidation state, phase composition, particle size and atomic structure.

As the stability of photocatalytic composite materials is usually revealed by repetitive testing in batch reactors and subsequent standard (bulk) characterization methods such as X-ray diffraction or UV–vis spectroscopy, deactivation of the semiconductor can be easily recognized (e.g., for sulfide-based materials, corrosion is a prominent pathway for deactivation).<sup>42</sup> These routines might be feasible to predict stability of composite photocatalysts in steady-state conditions, however, deactivation during the initial stages of catalytic testing are not resolved. Furthermore, structural/electronic changes of the cocatalyst present in low quantities on the semiconductor surface are not accessible by standard bulk characterization.

For Pt-modified SrTiO<sub>3</sub>,<sup>37</sup> prepared by photodeposition in the absence of sacrificial agents, transients in oxygen evolution were observed and steady-state conditions were only achieved after extended illumination. Surface characterization with particular emphasis on Pt characterization was performed. XPS revealed that the excess of formed oxygen was well-correlated with a reduction of the as-prepared PtO<sub>x</sub> to metallic Pt. While the formation of metallic Pt during illumination on an n-type material might not be surprising, these measurements nicely demonstrate that photodeposition of Pt in the absence of sacrificial agents is a slow process, and full reduction might only be achieved during photocatalytic testing. Moreover, in the same study Pt-modified Rh:SrTiO<sub>3</sub> was prepared and characterized using the same approach. Interestingly, for prereduced metallic Pt on Rh:SrTiO<sub>3</sub> oxidation occurred during the testing, and the “active” Pt-species in steady-state



**Figure 3.** (A) Gas evolution rates during photocatalytic hydrogen evolution for a series of P25 catalysts loaded with different amounts of Pt. Deactivation is observed at low Pt loadings independent of the pretreatment with ultrasound (US) (e.g., 0.25 wt %) but not at high Pt loadings ( $\geq 0.75$  wt %). Reproduced with permission from ref 43. Copyright 2017 American Chemical Society. (B) Time course of hydrogen and oxygen during illumination of a Pt(0.3 wt %)/TiO<sub>2</sub> photocatalyst in the presence of 0.3 g of Na<sub>2</sub>CO<sub>3</sub>. The severe changes in evolved H<sub>2</sub> and O<sub>2</sub> clearly point to rearrangements of the heterogeneous photocatalyst; and (C) proposed mechanism of the overall photocatalytic water splitting over Pt-TiO<sub>2</sub> systems in the presence of carbonate salts in aqueous solution. B and C are reproduced with permission from ref 26. Copyright 1997 Royal Society of Chemistry.

conditions resembled PtO<sub>x</sub> rather than metallic Pt. Clearly the presence of a dopant not only influences the optical properties of the semiconductor but also changes the interfacial charge transfer phenomena and, consequently, the oxidation state of the cocatalyst (Pt).

In electrochemistry, the oxidation state of active Pt anodes has also been discussed, and generally oxidation of the surface occurs before oxygen is evolved. The chemical potential of the photogenerated holes in the semiconductor are likely sufficient to drive the partial oxidation of Pt to PtO<sub>x</sub> in particular on p-type semiconductors. It has been proposed that Rh:SrTiO<sub>3</sub> is in fact a p-type semiconductor.<sup>38</sup> Apart from the electrochemically driven oxide formation, thermal growth of surface oxides must be considered because of the presence of local hot spots governed by intensive illumination. This certainly highlights that *post-catalysis* characterization is required to fully describe the composition of a working photocatalyst.

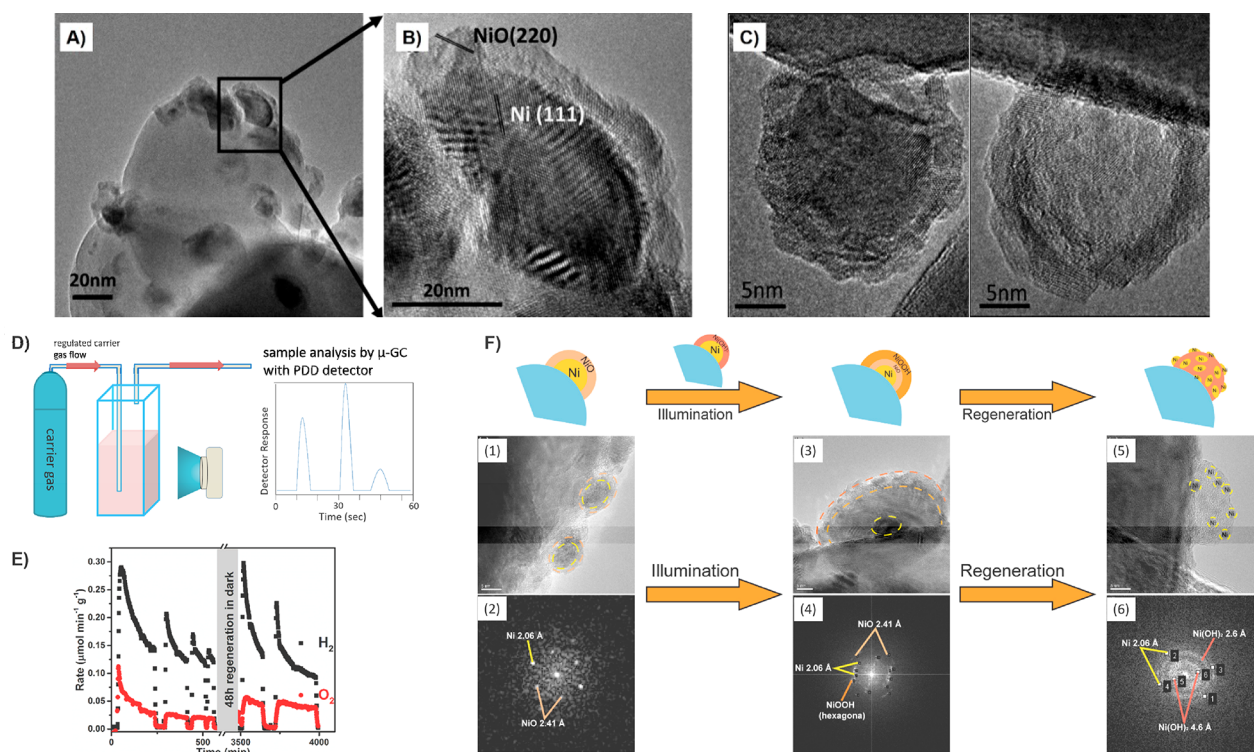
Haselmann et al.<sup>43</sup> recently reported for Pt-loaded TiO<sub>2</sub> an early stage deactivation after ultrasound pretreatment. The fast deactivation (within approximately 1 h of illumination) was primarily observed for composites with low Pt-loading (Figure 3A). The authors related the observed deactivation to a “dynamic” interaction of Pt clusters and/or particles with surface oxygen vacancies. In fact, the authors observed a

change in reaction mechanism as well as encapsulation of Pt particles presumably by thin TiO<sub>2</sub> shells. Such strong metal–support interactions (SMSI) are frequently reported in heterogeneous catalysis; however, for heterogeneous photocatalysis, the phenomenon is hardly discussed.<sup>43,44</sup> Finally, it is worth noting that Haselmann et al.<sup>43</sup> compared low (= deactivating) and high (= nondeactivating) Pt loading using similar Pt particle size distributions, and Pt leaching or particle migration and growth were excluded as causes of deactivation.

Along these lines, in an earlier study by Arakawa et al.,<sup>26</sup> the authors report that during illumination of Pt/TiO<sub>2</sub> photocatalysts, the Pt was covered with some titanium hydroxide compounds and speculated that the rate of the back reaction was efficiently suppressed. As depicted in Figure 3B, the full development of the active photocatalyst required prolonged illumination, and therefore, it was easily revealed by standard gas chromatography. For the appearance of the SMSI effect-related shell, the authors concluded that carbonate addition to the reaction solution is essential. They also concluded that carbonates might be actively involved in the formation of oxygen.

Finally, Li et al.<sup>45</sup> presented an interesting approach using Pt or PtO<sub>x</sub> clusters (approximately 1 nm) loaded on TiO<sub>2</sub> nanosheets to facilitate overall water splitting. Even though





**Figure 4.** (A,B) structure of 1 wt % Ni@NiO core/shell particles on TiO<sub>2</sub> after preparation. (C) Partial void/shell structures show cleavages in between TiO<sub>2</sub> and Ni metal, and void/shell structures after deactivation of the composite photocatalysts. (A–C) Reproduced with permission from ref 46. Copyright 2015 American Chemical Society. (D) Schematic design of a differentially operated photoreactor. (E) Measured transients in H<sub>2</sub> and O<sub>2</sub> evolution for Ni@NiO<sub>x</sub> SrTiO<sub>3</sub> and (F) corresponding HRTEM images and corresponding FFT results of the (1,2) as-prepared, (3,4) illuminated, and (5,6) regenerated Ni@NiO<sub>x</sub> SrTiO<sub>3</sub> composite material. The observed changes in morphology and composition of the Ni@NiO<sub>x</sub> cocatalysts during overall water splitting are also schematically indicated. (E,F) Reproduced with permission from ref 38. Copyright 2017 American Chemical Society.

some arguments regarding favorable electrochemical selectivity of the PtO<sub>x</sub> cocatalyst are questionable, the surface characterization of the materials prior to and after photocatalytic experiments are quite interesting and suggest structural rearrangement of the cocatalysts. While the authors argued using prolonged testing, density functional theory, and various characterization techniques that the applied PtO<sub>x</sub> cocatalyst is stable, distinct differences in the provided characterization data between as-prepared and tested materials are visible, such as particle growth (by TEM) and (slight) changes in the electronic structure of the PtO<sub>x</sub> particles. For the Pt modified TiO<sub>2</sub> sheets, observed changes are more severe, and XPS clearly indicates the formation of PtO<sub>x</sub> species after catalysis. As indicated above, the formation of surface oxides is feasible by electrochemical or thermal oxidation. While the data provided by Li et al.,<sup>45</sup> did not show transients in gas evolution, the provided characterization data suggest “dynamic” changes of the material during illumination, again highlighting the importance of detailed *post*-catalysis characterization of the cocatalyst.

Due to its stability (e.g., Pourbaix diagram<sup>47</sup>) and the well-known performance in HER reaction, Pt is one of the most frequently applied cocatalyst. Another promising candidate is composed of Ni and NiO<sub>x</sub> arranged in a core–shell like structure. Core–shell systems are preferred over pure Ni, pure NiO<sub>x</sub>, and physical mixtures of Ni and NiO<sub>x</sub>; in the early work by Domen et al.,<sup>48,49</sup> it was suggested that Ni/NiO<sub>x</sub> core–shell particles deposited on SrTiO<sub>3</sub> provide the catalytic sites for hydrogen evolution (Figure 4). However, because of the

complexity of the cocatalyst system and the properties of Ni (several feasible oxidation states and feasibility of corrosion), sufficient evidence of the working state of Ni/NiO<sub>x</sub> core–shell particles is still missing. Osterloh et al.<sup>50</sup> suggested that a core–shell model is not representative of the active phase(s). Using surface voltage spectroscopy, they demonstrated that the metallic Ni cores function as electron trapping sites and NiO<sub>x</sub> shells served as hole trapping sites.<sup>50</sup> Thus, Ni and NiO<sub>x</sub> promote formation of hydrogen and oxygen, respectively, making it a dual function cocatalyst. This assignment of functionalities is in agreement with active states known from electrochemical water splitting and leads to an appealing concept in which coloaded of water reduction and oxidation catalyst on the surface of photocatalysts might improve the overall water splitting efficiency.<sup>6,40</sup>

More recently, we investigated the same system, namely, Ni/NiO<sub>x</sub>-modified SrTiO<sub>3</sub> using a differentially operated slurry reactor (Figure 4D) and the fast detection mode of a micro-GC equipped with a pulsed discharge detector (PDD) to investigate the transients in H<sub>2</sub> and O<sub>2</sub> evolution in the initial stage of illumination.<sup>38</sup> The PDD detector offers significant advantages in sensitivity over conventional TCD detectors (for further information, see ref 51). Combined with the efficient product separation in μ-GC, detection of changes in the product evolution rates on the minute time-scale can be easily achieved. For Ni/NiO<sub>x</sub>-modified SrTiO<sub>3</sub> significant transient in hydrogen evolution accompanied by a substoichiometric H<sub>2</sub>:O<sub>2</sub> ratio (>2) was observed. Characterization by XPS and high-resolution transmission electron microscopy (HRTEM)

suggested that  $\text{Ni}(\text{OH})_2$  was oxidized to  $\text{NiOOH}$ .  $\text{NiOOH}$  is a well-known OER catalyst, suggesting a promoting effect of oxygen evolution by  $\text{NiOOH}$  (Figure 4). Only after stirring in the dark the required stoichiometric  $\text{H}_2:\text{O}_2$  ratio was obtained, and ex-situ characterization suggested that severe reorganization of the system occurred, as metallic Ni was embedded in a  $\text{NiO}_x$  matrix. Finally, Crozier et al.<sup>46,52</sup> provided evidence by HRTEM that deactivation of their composite system was governed by leaching of metallic Ni resulting in hollow  $\text{NiO}_x$  shells or oxidation of Ni resulting in the formation of  $\text{NiO}_x$  particles (Figure 4). Evidently, in this system Ni serves as sacrificial reagent triggering the formation of hydrogen during illumination. In summary, it is evident that the simple model of static cocatalysts cannot describe the behavior, either under illumination or in the dark.

Logically, also for other cocatalyst systems and especially complex materials like the common  $\text{Rh}/\text{Cr}_2\text{O}_3$  core-shell cocatalysts, dynamic rearrangement during initial testing or prolonged illumination might occur. In fact, chromium oxide/oxyhydroxide films used in the chlorate process are usually considered as being dynamic in nature. Here, it is also interesting to note the following: (1) mixed metal (oxide) cocatalysts show comparable or even higher photocatalytic performances;<sup>4,53,54</sup> (2)  $\text{Cr}_2\text{O}_3$  shells are less effective in suppressing the back reaction of  $\text{H}_2$  and  $\text{O}_2$  when applied on Pt metal particles, suggesting that a simple description of  $\text{CrO}_x$  shells on metallic particles is not sufficient to describe the cocatalyst material.<sup>53,55</sup>

## ■ LEARNING FROM OTHER DISCIPLINES

Concerning the purpose of a cocatalyst, e.g. facilitating redox reactions at the semiconductor surface, guidelines to the design, stability, and understanding of active sites can be found in electrocatalysis (ignoring the semiconductor/electrocatalysts interface). Typically, in electrocatalysis, activities, and stabilities of an electrocatalyst are addressed by voltammetry and chronoamperometric/-potentiometric measurements. Subsequent or even in situ surface characterization is used to obtain structure-activity relations. Leaching and corrosion are investigated by determining metal contents in the used electrolyte. The number of active sites is precisely estimated by the materials weight, or the number of electrochemically active surface sites. In fact, certain protocols are established to ensure a practical description of materials and the reproducibility of the obtained results.<sup>56-58</sup> Similar protocols might be required in photocatalysis. For example, in electrocatalysis, and especially for oxygen evolution, it is known that pseudostability during long-term testing can be achieved by providing a sufficient amount of electrocatalytically active material.<sup>57</sup> In these cases, corrosion currents might be significantly smaller than currents generated due to the gas evolving reaction, and monitoring mass losses or detecting dissolved material in the electrolyte is a necessity.<sup>57</sup> It is also known that corrosion of noble metals such as Pt or Ir occurs during potential cycling, by successive oxidation and reduction of the surface.<sup>59-61</sup> Time scales of corrosion might be different between electro- and photocatalysis due to different proton/hydroxyl concentrations of the electrolyte, but a local pH gradient might still facilitate corrosion. A first indication of materials properties in different electrolyte conditions can be obtained using Pourbaix diagrams.

Just recently, along with the development of appropriate in situ techniques, such as high-pressure XPS, changes in the

oxidation state of  $\text{NiO}_x$  and  $\text{IrO}_2$  OER catalysts were revealed during electrochemical oxygen evolution.<sup>62-65</sup> For example, for Ir-based OER materials, it is commonly observed that amorphous phases possess higher activities than their crystalline counterparts: the reasoning behind this observation is still a matter of speculation. Studying the oxidation state of Ir during OER using X-ray photoemission and absorption spectroscopy, Schloegel et al. were able to determine that (1) metallic Ir converts into a mixed-valence, conductive iridium oxide matrix, and (2) active sites in amorphous iridium oxide are likely composed of a weakly bound oxygen, susceptible to nucleophilic attack. Furthermore, the authors point out that a dynamic framework is required to allow flexibility in the oxidation state of Ir, which is required for the formation of oxygen.<sup>62,63</sup>

Another interesting material known to change oxidation states during catalysis is  $\text{NiO}_x$ . The exact nature of the active site is still under debate. An interesting observation that needs to be highlighted is that incooperation of Fe-traces into the NiO-matrix results in dramatically improved OER capabilities.<sup>66,67</sup> Similar observations were also reported for Co- and Mn-based materials, highlighting the importance of contaminants in applied electrolytes. For photocatalytic systems, a proper understanding of the effect of metal-traces in electrolytes is even more important as, in contrast to electrochemical applications, cocatalyst quantities are typically small, and functional changes by contaminant incorporation will be expressed more dramatically.

Peculiar observations that might be of interest can also be found in electrochemical literature discussing effects of Cr-oxide films used to obtain electrochemical selectivity.<sup>29,30</sup> Generally, Cr-oxide films are reported to increase the electrochemical selectivity of the hydrogen evolution reaction. Interestingly, Cr-oxide films are also reported to influence the activity of hydrogen evolution catalysts. For example, for  $\text{Pt}@\text{CrO}_x$  materials slightly higher overpotentials are measured for hydrogen evolution as compared to unprotected Pt. For Au-based materials, however, Cr-oxide films appear to positively influence the HER performance, suggesting different functions of the Cr-oxide film depending on the metal substrate. The effect of Cr-oxide is not yet fully understood in electrochemical systems; similarly, the basic model of a core covered by a Cr-shell where the shell solely inhibits the backreaction might underestimate the role of Cr-oxide in photocatalysis.

As in the field of photocatalysis, major attention has been paid to the development of suitable semiconductor materials in photoelectrochemistry. Indeed, significant progress has been made in understanding and engineering semiconductor/cocatalyst interfaces.<sup>68</sup> For example, selective charge carrier contacts deposited between semiconductor and electrocatalyst were shown to dramatically improve the separation efficiencies and stabilities of PEC photoelectrodes.<sup>68,69</sup> A feasible hole storage/extraction layer reported by Li's group is  $\text{MoO}_x$ .<sup>69</sup> Given that  $\text{MoO}_x$  and  $\text{CrO}_x$  films possess similar charge carrier transport properties,  $\text{MoO}_x$  and  $\text{CrO}_x$  might serve similar purposes in composite photocatalysts.<sup>70,71</sup> However, it will be a major challenge to use selective contacts on the nanoscale and only locally on semiconductor particles. Nevertheless, the results obtained in PEC are encouraging and similar approaches should be followed in heterogeneous photocatalysis.

Another interesting concept toward improved understanding of semiconductor/cocatalysts interfaces was presented by

Boettcher et al.<sup>72</sup> They showed that ion-permeable catalysts such as Co-Pi and NiOOH, form adaptive Schottky-junctions with the semiconductor surface. Adaptive junctions change in situ with the oxidation level of the cocatalysts, leading to improved performances compared with dense cocatalysts. Given the porous nature of NiO<sub>x</sub> or chromium oxide films, for example, the adaptive junction concept will also be applicable in photocatalysis.

Finally, knowledge developed in heterogeneous catalysis should be considered for design of composite catalysts. Heterogeneous catalysts are composed of a support (e.g., an oxide such as silica or alumina) on which well-dispersed metallic nanoparticles with (ideally) a narrow size-distribution are deposited. In photocatalysis, however, size distributions receive relatively little attention, and loading is solely optimized according to the relationship depicted in Figure 2. Co-catalysts of different sizes will develop different semiconductor/cocatalyst interfaces, as recently shown by Takanabe et al.<sup>9</sup> Accordingly, the effectiveness of electron-transfer to the cocatalyst and the shift of the chemical potential (i.e., the potential required to drive the redox-reaction) will depend on particle size. For very small particles, quantum size effects must be considered. Furthermore, stability issues and transition in oxidation states are likely particle-size-dependent and are difficult to investigate using a random arrangement of cocatalyst particles on the surface. One example indicating the feasibility of creation of particles in a narrow size range was recently reported by Li et al.<sup>73</sup> Well-dispersed Pd nanoparticles were deposited on solid solutions of GaN:ZnO using atomic layer deposition (ALD). Remarkably, only 0.13 wt % Pd was required to obtain optimized functionality of the semiconductor.

Charge transfer and the subsequent shift of the chemical potential can be followed using Infrared spectroscopy and carbon monoxide probe molecules, as recently shown by Domen et al.<sup>12</sup> The potential shift is clearly averaged over all metallic particles deposited, and differences between particles might exist. Still these results evidence that a better understanding of cocatalysts can be developed using suitable characterization techniques.

Multicomponent catalysts are also frequently applied in industrial heterogeneous catalysis: the different functions of the individual components cause improved performance and stability, and as depicted above for photocatalytic water splitting especially, the stability (see leaching of Ni in the case of Ni/NiO) might be important. In this respect, it should be mentioned that recently a quaternary system consisting of Cr- and Mo-oxide together with either Rh or CuO<sub>x</sub> were applied for POWS showing improved water splitting behavior and stabilities.<sup>71,74</sup>

In heterogeneous catalysis, it is known that as-prepared materials are converted to the actual active catalyst primarily during the initial stages of catalytic testing. For example, changes that might occur are particle sintering and Ostwald ripening,<sup>75–77</sup> or even encapsulation of metallic particles by thin substoichiometric oxides.<sup>56</sup> An important parameter in heterogeneous catalysis is the turnover frequency (TOF), defining the reactivity per exposed surface site per unit of time. While it is important to note that the concept of TOF is not applicable to compare different heterogeneous photocatalysts and a high TOF is *not* a requirement for high photocatalytic efficiency, comparing TOFs calculated for fresh and used photocatalysts will underline changes occurring during reaction

(e.g., by dissolution of the cocatalyst or changes in the interfacial properties between the cocatalyst and the semiconductor). In electrocatalysis, TOFs are potential-dependent, and because of the requirements of photocatalysis, TOF numbers will provide indications of the generated potentials within the semiconductor and the quality of the (averaged) semiconductor/cocatalyst interface (considering a similar dispersion of the cocatalyst). Though the number of surface active sites on the semiconductor photocatalyst is difficult to define, advanced characterization methods, such as high-resolution X-ray photoelectron spectroscopy or low-energy ion scattering, allow for a good estimate (e.g. of the number of available metallic sites for HER). Thus, TOF numbers (and the required materials characterization) might add additional fundamental understanding to describe the behavior of heterogeneous photocatalysts.<sup>78,79</sup> Still it is important to report STH or quantum efficiencies (QE) for comparison of different heterogeneous photocatalysts. These values should be reported for the individually optimized system (i.e., optimized photocatalyst amount as well as optimized cocatalyst loading). For further information about the definition of these values, the reader is referred to IUPAC conventions and existing literature.<sup>6,80</sup>

As depicted by the examples mentioned above from electrochemistry and heterogeneous catalysis, using existing knowledge of other disciplines is beneficial for the development of heterogeneous photocatalyst systems.

## ■ POINTS FOR IMPROVEMENT IN COCATALYST DEVELOPMENT

A fair comparison of photocatalytic activities obtained in different laboratory's is complicated by differences in reactor type and irradiance (light intensities and lamps). Changes in pH and/or temperature will also significantly influence activities.<sup>80</sup> These issues have already been recognized, and reporting of photocatalytic activities should always include a precise description of the process parameters and conditions, such as changes in pH during reaction.

Still it appears to be difficult to reproduce photocatalytic data mainly due to the complexity of materials. Common semiconductor materials are well-characterized, but significant progress is required in the description and characterization of cocatalysts. Modification of semiconductor surfaces is non-trivial, and yet it is not known whether conventional methods such as impregnation or other techniques, such as photo-deposition,<sup>81</sup> are preferable. Independent of the preparation techniques, it is important to realize that cocatalysts will likely *be in a dynamic state during reaction, and analyzing active sites during reaction is essential*. These dynamics should be revealed by advanced characterization techniques, preferably in operando conditions.

Furthermore, it should be considered that semiconductor particles have a heterogeneous surface structure, resulting in various exposed facets and surface defects. Defects and interfacial energy levels are regularly discussed in terms of recombination losses occurring during charge separation and transport; however, the surface heterogeneity will also result in different semiconductor cocatalyst interfaces, which will likely cause different (dynamic) states or even result in nonactive "spectators". Such spectators on the surface can even be detrimental and decrease the efficiency of light absorption by the semiconductor. Besides a few studies, cocatalyst loadings used in photocatalytic research are relatively large,<sup>82,83</sup> and it is



arguable that these loadings can be reduced when positioned at appropriated places/facets on the semiconductor surface.

The required cocatalyst loading is even more important when water reduction and water oxidation electrocatalysts are simultaneously applied (co-loading) on a single semiconductor surface.<sup>84</sup> While co-loading might improve charge separation efficiencies and surface catalysis, the complexity of the system increases dramatically. Here, it is also of interest to develop suitable strategies to achieve selective contacts and facilitate the required electron and hole transfer processes toward the respective cocatalysts.

Non-noble metal-based materials are interesting, alternative cocatalysts. Generally, non-noble metal materials possess good activities for the forward H<sub>2</sub> evolution reaction, and good electrochemical selectivity is expected as non-noble metals are usually poor catalysts to drive thermal recombination of hydrogen and oxygen, or the electrochemical reduction of oxygen. In these cases the use of complex core-shell structured materials will be redundant.<sup>70,85–87</sup> From PEC studies, it is even known that catalysts such as Mo<sub>2</sub>C,<sup>88</sup> MoS<sub>2</sub>,<sup>88,89</sup> and other transition metal oxides<sup>90</sup> are suitable to achieve stable PEC performances. Most of these non-noble materials possess semiconducting properties,<sup>91</sup> which will change the description of the semiconductor/cocatalyst interface. Unfortunately, from electrocatalysis, it is also known that non-noble materials usually require higher overpotentials, which increases the necessary chemical potential of electrons to drive the redox reaction. Also, higher mass-loadings might be mandatory,<sup>19</sup> which in-turn are detrimental in photocatalytic applications.

The above-mentioned phenomena showcasing the transformation of applied cocatalysts are not yet fully understood, and it is worth emphasizing that additional efforts to develop new cocatalysts and better understand the behavior of currently applied cocatalysts systems are required. Understanding is particularly important and crucial to design of composite heterogeneous photocatalysts that are able to drive solar-fuel-generating reactions. It appears to be important to include descriptors and knowledge developed in electrocatalysis, photoelectrocatalysis, and heterogeneous catalysis including the various advanced (in situ/operando) characterization techniques that are nowadays applicable for characterization of developed materials.<sup>11,79,86</sup> In this respect, a very recent study using in situ X-ray absorption spectroscopy indicates that the physicochemical state of cocatalysts is significantly affected by light and surrounding electrolyte, leading to substantial differences in photocatalytic activity.<sup>92</sup>

Specifically, it is suggested to consider the following when using cocatalysts.

First, cocatalyst development should be guided by a rational approach focusing on an effective charge transfer from the semiconductor to the cocatalyst to facilitate chemical potential shifts. Clearly, random deposition of cocatalysts should be avoided, and photodeposition could be a means to selectively deposit metal nanoparticles on the desired surface locations. Understanding the interfacial phenomena during photodeposition is also necessary.

Second, optimization of particle sizes, dispersion, and loading must be performed individually for every semiconductor composition. We suggest the optimized cocatalyst system is strongly dependent on the applied semiconductor.

Third, understanding cocatalyst functionality requires detailed characterization. Characterization should be performed

before and after catalytic testing and preferably in situ (see, for example, recent efforts in electrocatalysis). Detection of ions dissolved in solution after catalytic testing is indicative of cocatalyst instability.

Fourth, an approach to facilitate better understanding might be the use of differentially operated reactor systems, in addition to the conventional recirculating batch reactors. These systems will allow reliable probing of the stability and activity of photocatalyst composite materials. Essential information, applicable to the development of heterogeneous photocatalysts, might be obtained during initial stages of testing.

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### Notes

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