

The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset?

Stephanie K. Loeb,^{†,‡} Pedro J. J. Alvarez,^{†,§} Jonathon A. Brame,^{||} Ezra L. Cates,[⊥] Wonyong Choi,[#] John Crittenden,[¶] Dionysios D. Dionysiou,[□] Qilin Li,^{†,§} Gianluca Li-Puma,[■] Xie Quan,[○] David L. Sedlak,[●] T. David Waite,[△] Paul Westerhoff,^{†,▽} and Jae-Hong Kim^{*,†,‡}

[†]Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment (NEWT) 6100 Main Street, MS 6398, Houston, Texas 77005, United States

[‡]Department of Chemical and Environmental Engineering and, Yale University, 17 Hillhouse Avenue, New Haven, Connecticut 06511, United States

[§]Department of Civil and Environmental Engineering, Rice University, 6100 Main Street, Houston, Texas 77005, United States

^{||}US Army Engineer Research and Development Center (ERDC), 3909 Halls Ferry Road, Vicksburg, Mississippi 39180, United States

[⊥]Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, South Carolina 29625, United States

[#]Division of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang 37673, Korea

[¶]Brook Byers Institute for Sustainable Systems, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[□]Environmental Engineering and Science Program, Department of Chemical and Environmental Engineering, 705 Engineering Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0012, United States

[■]Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU, United Kingdom

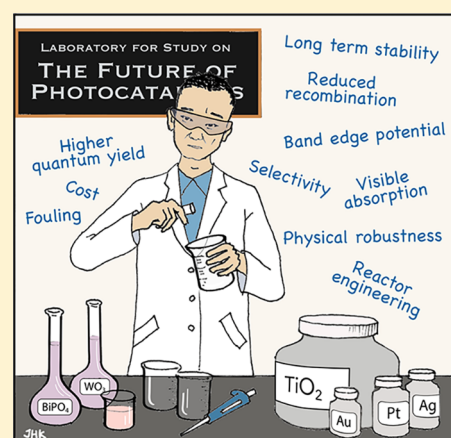
[○]Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

[●]Department of Civil & Environmental Engineering and Engineering Research Center for Reinventing the Nation's Urban Water Infrastructure (ReNUWIt), University of California, Berkeley, California 94720, United States

[△]School of Civil and Environmental Engineering, University of New South Wales, Sydney New South Wales 2052, Australia

[▽]School of Sustainable Engineering and The Built Environment, Arizona State University, Box 3005, Tempe, Arizona 85287, United States

ABSTRACT: Advanced oxidation processes via semiconductor photocatalysis for water treatment have been the subject of extensive research over the past three decades, producing many scientific reports focused on elucidating mechanisms and enhancing kinetics for the treatment of contaminants in water. Many of these reports imply that the ultimate goal of the research is to apply photocatalysis in municipal water treatment operations. However, this ignores immense technology transfer problems, perpetuating a widening gap between academic advocacy and industrial application. In this Feature, we undertake a critical examination of the trajectory of photocatalytic water treatment research, assessing the viability of proposed applications and identifying those with the most promising future. Several strategies are proposed for scientists and engineers who aim to support research efforts to bring industrially relevant photocatalytic water treatment processes to fruition. Although the reassessed potential may not live up to initial academic hype, an unfavorable assessment in some areas does not preclude the transfer of photocatalysis for water treatment to other niche applications as the technology retains substantive and unique benefits.



Published: December 21, 2018

INTRODUCTION

Imagine a still image of the sun hanging low in the horizon—is it rising or setting? Only by examining subsequent time lapse images can we predict its future direction. The development of a new technology follows a similar path but of unknown length, rising from its initial conception to reach a zenith of popularity before arcing back toward the horizon. Photocatalytic advanced oxidation processes (AOPs) for water treatment have traveled a long path of technological development, having been the subject of extensive research over the past 35 years. Conventional AOPs employ precursor chemical oxidants, such as O_3 and H_2O_2 , in combination or with an input of energy (e.g., ultraviolet (UV) irradiation), to produce reactive oxygen species (ROS) for the oxidative destruction of contaminants in water. Heterogeneous semiconductor photocatalysis enables advanced oxidation via a fundamentally different mechanism: photons with energy equal to or greater than the material's band gap are absorbed by a particulate catalyst resulting in the formation of a conduction band electron (e_{cb}^-) and valence band hole (h_{vb}^+) pair. Although both e_{cb}^- and h_{vb}^+ can participate in a suite of redox reactions relevant to water treatment, hydroxyl radicals ($\cdot OH$), both surface-bound and in bulk phase, are considered the dominant oxidant.¹ Historically adapted from the discovery of photoelectrochemical water-splitting at the surface of a TiO_2 electrode,² photocatalysis was quickly recognized for its potential in water treatment.^{3,4}

The advantages of photocatalytic water treatment over homogeneous-phase AOPs are well documented. The benchmark commercial semiconductor material, TiO_2 , is inexpensive ($\sim \$1/kg$),⁵ physically robust, and relatively nontoxic. It requires low-energy ultraviolet light (UV-A) for excitation, allowing for potential solar applications. As a heterogeneous catalytic process, it obviates the need to continuously supply precursor chemicals, which is a striking benefit for some applications particularly those in remote or resource-limited locations. A recent surge in scientific literature—over 8000 articles since 2000—on the topic of photocatalytic water treatment reflects this optimism (Figure 1). Despite substantial research over the past few decades, the application of photocatalysis in practical water treatment systems has been very limited compared to conventional AOPs. Considering these trends, how should the research community view the technology horizon of photocatalytic water treatment? In this Feature, we examine the current status of heterogeneous semiconductor photocatalytic water treatment, emphasizing barriers to technology transfer, examining the feasibility of practical applications, and identifying key research needs for overcoming obstacles, in search of answers to this question.

FUNDAMENTAL ROADBLOCKS PREVENTING TRANSFER OF RESEARCH TO PRACTICE

The difficulties impeding commercial success of photocatalytic AOPs are evidenced by the small number of systems currently being used in water treatment practice. This is at odds with an abundance of literature reporting the use of photocatalysis for the treatment of common surface and groundwater pollutants. Typically performed at bench-scale, these studies tend to over-represent the opportunities and under-represent the limitations demonstrated by the technology when applied in the field. An overemphasis on material design and mechanistic evaluations has led to some hubris in the academic literature regarding the practicality of photocatalysis, perpetuating the gap between

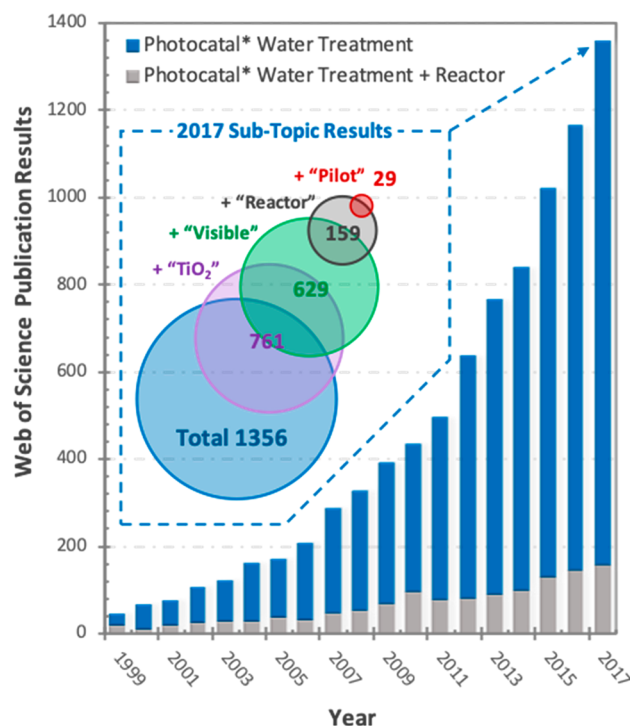


Figure 1. Publications trends in photocatalytic water treatment research. Web of Science results for the number of yearly publications on photocatalytic water treatment from 1999 to 2017. Inset shows detailed results from the most recent complete reporting year (2017), with each search keyword (i.e., “ TiO_2 ”, “visible”, “reactor”, and “pilot”) modifier added to “photocatal* water treatment” individually. Results indicate that only a small fraction of publications consider reactor design or pilot scale investigations.

(booming) academic research and (modest) industrial application. Consequently, skepticism has grown, leading some to question whether photocatalysis will become a mainstream water treatment technology within the next two decades.

Among the foremost roadblocks identified, low photo-conversion efficiency remains a major challenge. Each step of the photoconversion process has an associated loss of efficiency, as detailed in Figure 2. Consistently, quantum yields (Φ) reported in the literature, while varying widely depending on the photocatalysts and experimental conditions, are a few percent at most, even when measured using a probe substrate with monochromatic irradiation near the band gap (Table 1 inset in Figure 2). Compared to other AOPs, such low Φ for $\cdot OH$ production is considered the most critical drawback in photocatalytic water treatment. Taking UV/ H_2O_2 AOPs as an example, the photolytic decomposition of H_2O_2 in organic-free water at 254 nm has a reported Φ of 50%, and a resulting $\cdot OH$ production yield near 100%,^{17,18} making it very challenging for photocatalysis to compete in terms of energy efficiency. However, it should be noted that TiO_2 can absorb photons in the less energetic UV-A range, permitting the use of sunlight, and it does not require H_2O_2 addition, which is a major cost in conventional AOPs.

As an additional limitation inherent to all AOPs, only a small fraction of generated ROS contributes to the eventual destruction of target pollutants. The high reactivity ($\sim 10^9 M^{-1} s^{-1}$ for many organic contaminants)¹⁹ and nonspecificity of $\cdot OH$ is generally considered an advantage of AOPs over

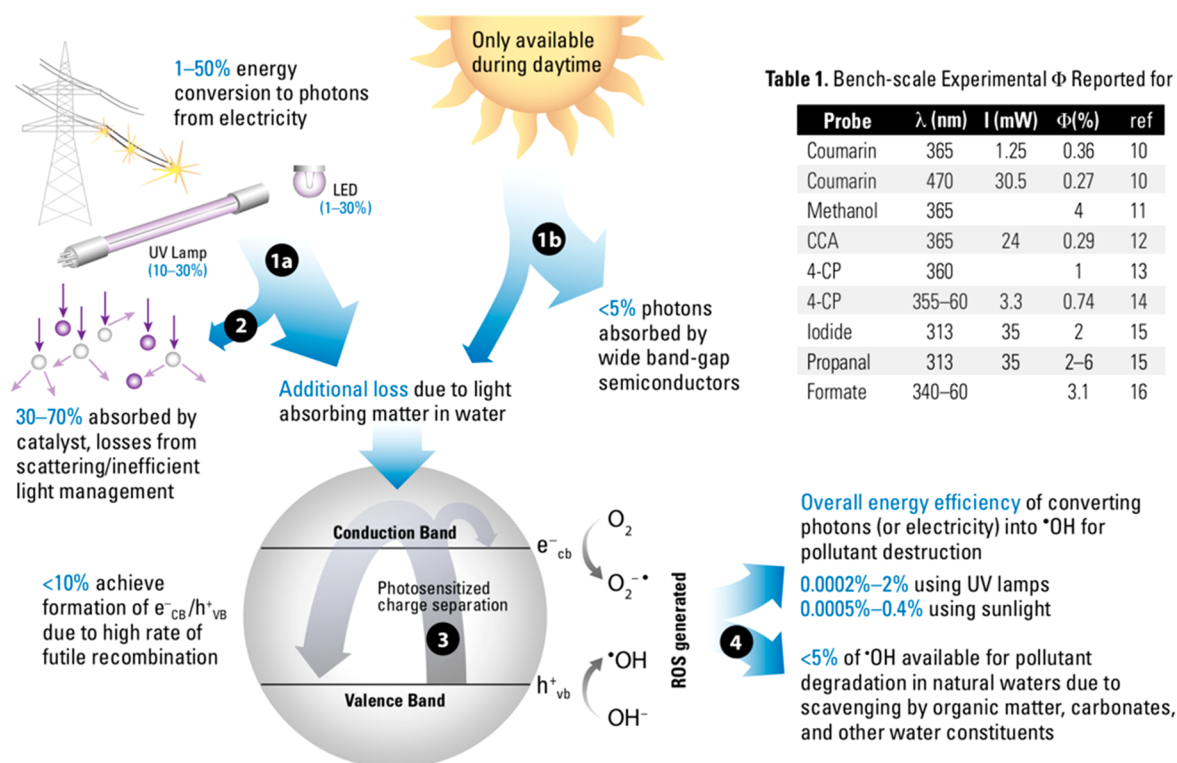


Figure 2. Detailing the low-energy conversion efficiencies in typical TiO_2 photocatalytic water treatment processes. Photons are generated either by electrical conversion or directly harnessing solar energy. (1a) Although low-pressure mercury lamps are typical, blue/UVA LEDs are being increasingly studied, with wall plug efficiencies nearing 30%.⁶ (1b) Electrical conversion losses are obviated when harnessing solar energy; however, < 5% of solar photons are absorbed as the wide band gap ($E_g = 3.0\text{--}3.2$ eV; 390–410 nm) of TiO_2 is poorly matched to the solar spectrum.⁷ (2) Photons entering the reactor can be lost through intrinsic scattering by the particulate and inefficient light management leading to catalytic absorption of 30–70% of the photons emitted into a typical slurry reactor.⁸ (3) Photons absorbed by the catalyst can then produce e_{cb}^- and h_{vb}^+ , which further perform redox reactions at the catalyst surface to generate ROS. Regardless of the source of light, a majority (>90%) of photogenerated e_{cb}^-/h_{vb}^+ pairs recombine rapidly (within sub μs),^{4,9} leading to quantum yields (Φ) of less than 10% for most materials. The inset table shows a list of experimentally reported bench-scale material Φ for $\cdot\text{OH}$ production from various TiO_2 photocatalysts.^{10–16} (4) The availability of generated ROS for pollutant destruction is greatly decreased through scavenging. As an illustration, a representative estimate of natural water containing 3 mg-C/L ($k(\cdot\text{OH}) = 10^8$ L/mol-C·s) and 50 mg/L of bicarbonate alkalinity as CaCO_3 ($k(\cdot\text{OH}\cdot\text{HCO}_3^-) = 8.5 \times 10^7$ /M·s) suggests that <5% of $\cdot\text{OH}$ would be available compared to distilled water (i.e., in the absence of scavengers) at the same pH.

other treatment systems. However, the presence of natural organic matter (NOM), carbonate species, and other background constituents can greatly limit the effectiveness of photocatalytic processes by scavenging ROS and absorbing light (Figure 2).^{20,21} Studies conducted at pilot and full-scale have indeed observed these effects to be exacerbated by the presence of multiple interfering compounds coexisting at variable concentrations.²² Although engineering and materials science are poised to make significant efficiency improvements, inherent constraints of the technology cannot be neglected when translating new research advances to industrial applications.

EFFORTS TO ADVANCE PHOTOCATALYTIC MATERIALS

Limited industry adoption has done little to suppress the steady flow of studies focused on the development of new photocatalytic materials. Inspired by advances in materials science and nanotechnology, an increasingly larger portion of research has sought to develop improved catalyst materials. Early efforts began with modifications to anatase TiO_2 . For example, flame pyrolysis synthesis of the well-known P25 TiO_2 powder is not only economical at industrial scale, but has been found to result in a minority rutile phase fraction, improving

photocatalytic activity.²³ Indeed, TiO_2 has retained a central locus in photocatalytic materials science research, which continues to concentrate on two major limitations of TiO_2 as avenues for improving catalyst performance: limited absorption and the high recombination rate of photogenerated primary species e_{cb}^- and h_{vb}^+ .

Many notable augmentations to TiO_2 have been achieved. Extending the photoactivity to lower energy wavelengths was first realized by the incorporation of transition metals (e.g., Fe, Cr, and V),^{24,25} and later by introducing nonmetal dopants (e.g., N, C, F, and S)²⁶ to create oxygen vacancies or low lying interband states at the localized energy levels of the dopant. In a recent leap-ahead application of this approach, surface hydrogenation was employed to create many disorder-induced midgap states, upshifting the valence band-edge, resulting in black/blue-colored TiO_2 crystals with absorption near the infrared region.²⁷ Though effective at improving absorption of visible light, too many midgap states can lead to excessive recombination and an overly narrowed band structure, reducing the redox potential of the e_{cb}^-/h_{vb}^+ pair and impacting the type of ROS produced.²⁸ The formation of heterojunctions with smaller band gap semiconductors²⁹ or sensitization with organic chromophores³⁰ can also widen the absorption toward visible light. Similarly, visible light-absorbing noble metal

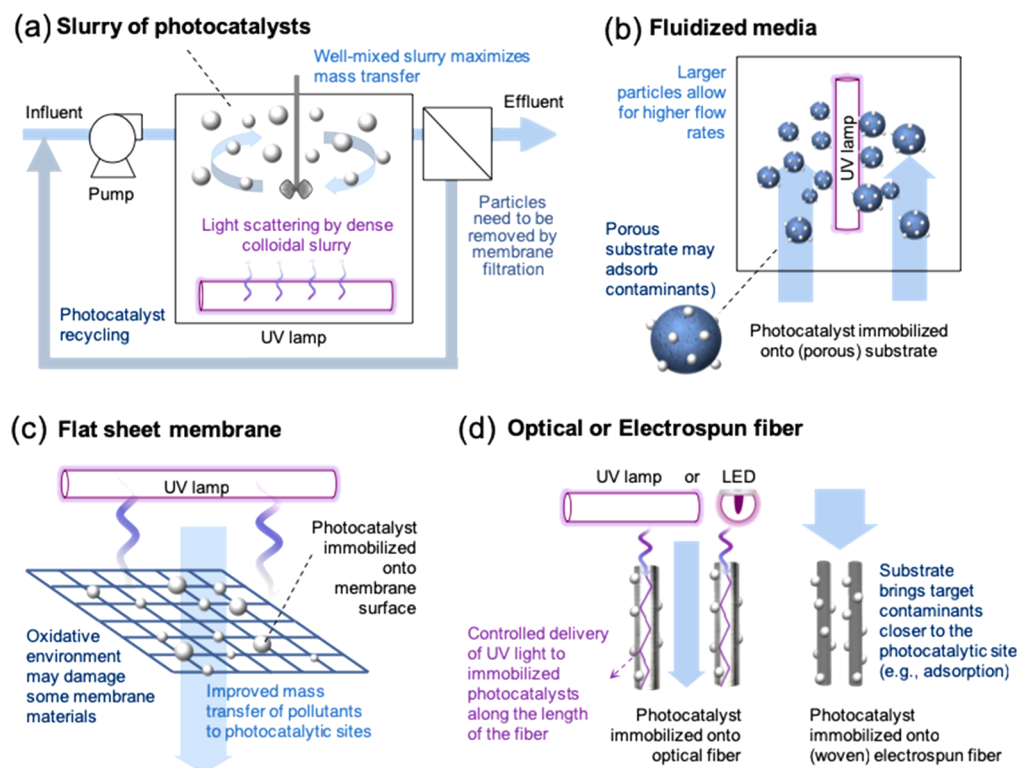


Figure 3. Select reactor designs for semiconductor photocatalytic water treatment: (a) A typical slurry reactor system consisting of a reactor containing suspended TiO_2 photocatalysts with a quartz encased LP Hg UV light source and membrane filtration for catalyst recovery. (b–d) More recently developed reactor designs incorporating immobilized catalyst particles obviating the need for post-treatment membrane separation.

nanoparticles can inject electrons into the photocatalyst conduction band.³¹

Junctions with metals have also been extensively employed to reduce recombination, acting as electron withdrawing centers through the formation of a rectifying Schottky barrier.³² However, high loadings of cocatalysts can limit the surface area, complicate the synthesis procedure, and result in a physically fragile composite material. This same composite architecture can be achieved by replacing metals with semimetallic carbonaceous materials such as graphene,³³ but the intrinsic instability of these materials in an oxidative environment remains an unresolved challenge. Nanoscale control over structural hierarchy and porosity present additional opportunities to improve the efficiency of TiO_2 by promoting charge migration and increasing surface area.^{34–36} Many researchers continue to focus on improving the performance and stability of these augmented TiO_2 materials.

Beyond modifications to TiO_2 , other semiconductor materials have been investigated as substitutes for TiO_2 . CdS and WO_3 are relatively effective visible light photocatalysts, but toxic components such as Cd are clearly incongruent with safe and sustainable water treatment practices. Graphitic carbon nitride (C_3N_4) is a metal-free visible light photocatalyst with a tunable electronic structure,^{37,38} though it exhibits poor chemical stability. Hybrid organic–inorganic perovskite materials offer a structural platform for highly tailored absorption/charge transport properties using low cost, earth-abundant materials.³⁹ Increasingly popular in the solar cell literature, a major limitation of perovskites in environmental applications has been instability in wet conditions—clearly a drawback for water treatment. Some materials have emerged as viable alternatives to TiO_2 : platinumized tungsten oxide (Pt/

WO_3) is able to produce $\cdot\text{OH}$ under visible light through multielectron reduction by the in situ generation and subsequent decomposition of H_2O_2 .⁴⁰ A newly emerging alternative, BiPO_4 has a more positive valence band maximum potential than TiO_2 resulting in increased oxidation power, higher photoactivity, and greater efficiency of mineralization at the expense of requiring higher energy UV excitation.⁴¹ Creative and yet-to-be-devised solutions are required to translate these promising materials into practical water treatment applications. These fundamental research efforts, which have been further detailed in a number of comprehensive reviews,^{42–44} continue to result in better materials while deepening our knowledge of semiconductor photocatalytic treatment.

Considering the depth of high-quality research conducted to advance photocatalysis materials science, it is prudent to scrutinize why TiO_2 has yet to be superseded by a next-generation material. A primary challenge in the field is identifying a threshold requirement for replacement; what determines whether a breakthrough material is “better” than TiO_2 ? Beyond bench-scale evaluation, many practical challenges have been overlooked in research that focuses on novel materials development. Our review of the literature reveals a proliferation of scientifically interesting, yet impractical materials that are fragile, chemically unstable, or have expensive, rare, or inherently toxic components. Evaluation conditions that more completely reflect industrial application by expanding performance criteria beyond absorption (i.e., greater spectral match and less scattering) and quantum yield (i.e., reduced recombination) to include cost of production, long-term stability, robustness, ease of

separation, and other application specific conditions, would aid in technology transfer.

■ PHOTOCATALYTIC REACTOR DESIGN AND SYSTEM EVALUATION

The focus of academic research on materials development rather than reactor or systems engineering arguably overlooks opportunities to improve the performance of photocatalytic water treatment systems through innovative reactor design. Despite numerous studies in this area,⁴⁵ the sparse configurations in practice have largely been restricted to reactor systems with light emitted into a slurry of well-mixed TiO₂ particles to maximize photon absorption and mass transfer of redox species,⁴⁶ as shown in Figure 3a. These systems may be competitive with other AOPs in selected niche applications discussed below; however, they remain unoptimized and suffer from limitations including low energy efficiency, slow reaction kinetics, and in selected cases, catalyst fouling or photoaggregation.^{22,47} Alternatively, photocatalysts can be immobilized onto support substrates, eliminating the need for ultrafiltration separation and reducing shear stress on catalyst particles. The efficiency of immobilized systems, however, can be further limited by obscured catalyst surface area, reduced illuminated catalyst surface area per volumetric water treated, and higher rates of photon scattering. Immobilization substrates explored (Figure 3b–d) include optical fibers for improved light management⁴⁸ and fluidized media,⁴⁹ foam porous supports,⁵⁰ membranes,⁵¹ and electro-spun fibers,⁵² which have each been engineered to improve pollutant destruction while minimizing ROS scavenging. The majority of these immobilized reactor designs remain at bench scale or in conceptual phase. Recent rapid advances in light emitting diode (LED) technology are poised to inspire a new generation of innovative reactor designs due to their advantageous over gas discharge lamps including less fragile casings, lack of toxic components, small size, and rapid warm-up time.^{53,54}

The relatively slow translation of these studies to industrial practice is likely related to the complexity of large-scale system design, something often overlooked at bench scale. Such barriers, however, have not limited increasingly widespread, full-scale adoption of UV and UV/H₂O₂ water purification applications,⁵⁵ which likewise require radiation field determination. Radiation scattering by the catalyst makes it cumbersome to assess the local volumetric rate of photon absorption (LVRPA) at each point within a photocatalytic reactor by analytically or numerically solving the radiation transfer equation (RTE). In a simplified approach, the six-flux-model (i.e., following scattered photons routed through the six directions of the Cartesian coordinates) has been successful in calculating LVRPA at accuracies close to the RTE while allowing for the derivation of dimensionless parameters useful in slurry reactor design.^{47,56,57} Ray-tracing, which involves analyzing the path of individual rays from an emission source based on the optical properties of the incident environment, has previously been applied to determine local radiation fields in UV disinfection reactors.⁵⁸ This technique could be adapted to determine LVRPA in immobilized photocatalyst reactors with relative ease, although incorporating an absorbing and scattering mobile particulate slurry into a ray tracing analysis presents a nontrivial challenge.

Other difficulties result from the lack of a universally accepted method to quantitatively evaluate and compare the

performance of new materials and reactor designs. Photocatalytic water treatment represents a highly variable parameter space that depends on target pollutant, water quality parameters, reaction time, mixing conditions, and light source. To ease knowledge transfer, uncoupling reaction rate constants from the number of photons absorbed is critical. Determination of LVRPA is integral for flow-through reactor design, although it has not been deemed necessary for material evaluations typically performed in a well-mixed batch reactor. If we accept at a minimum that characterization of new catalysts should include measurements of Φ , then a concerted effort to quantify the number of photons in the system, by either radiometry or chemical actinometry, is essential, as this information cannot be derived from reporting irradiation time and lamp type/power alone. Depending on the proposed application and method of evaluation, this Φ may be defined in terms of target pollutant destruction or the generation of a specific oxidizing species such as $\cdot\text{OH}$. Care should be taken to consider whether the reactions in a particular system may occur via bulk-phase or surface-bound $\cdot\text{OH}$, or through pathways involving other oxidative species. Additionally, for accurate reporting of kinetics, a probe compound that does not compete for absorption nor degrade with direct photolysis should be employed. For these reasons, as well as their susceptibility to sensitization, dyes, such as methylene blue, are inappropriate probes for comparing the activity of photocatalytic semiconductors.⁵⁹

Effective comparison is challenging not only among different photocatalytic systems, but between photocatalysis and its competitor AOP technologies. The most commonly applied figure of merit is electrical energy per unit order (EE/O): the electric energy (or alternatively the area of solar radiation) required to degrade a target contaminant by 1 order of magnitude in a unit volume of contaminated water.⁶⁰ For a treatment scenario with low-concentration of target contaminants compared to background scavengers, EE/O is straightforward to calculate, and is a versatile aid to design. Translation from bench-, to pilot-, to full-scale applications can therefore be readily assessed through determination and reporting of EE/O for common pollutants. While values of $\sim <0.5$ to 10 kWh/m³ are considered competitive for drinking water applications,⁶⁰ typical slurry TiO₂/UV systems tend to report values of 10 kWh/m³ or higher, whereas competing AOPs such as UV/H₂O₂ and H₂O₂/O₃ can report less than 1 kWh/m³.^{22,61} Although reporting of EE/O or other metrics, such as electron efficiency,⁶² is encouraged, the limitations of comparing technologies using a single value should be recognized. Care should be taken to include other factors as well, such as the embedded energy requirements (or costs) of applying consumable chemicals.

■ STRATEGIES FOR IMPROVING RESEARCH OUTCOMES

When recent advances in materials science and reactor engineering are combined, opportunities to improve the performance of photocatalytic water treatment may emerge. On the basis of our collective experience, we propose the following strategies for researchers aiming to advance photocatalytic water treatment processes without succumbing to the pitfalls that have stunted progress during the past three decades:

- (1) *Expand the criteria for assessing the performance of photocatalytic water treatment systems.* To create technologies that have a higher likelihood of attracting commercial interest, researchers should expand performance criteria to include factors such as material cost and availability, the feasibility of large-scale production, tendency to foul in the proposed water matrix, and long-term stability and performance under likely operating conditions.
- (2) *Evaluate the performance of photocatalysts under well-defined conditions.* The use of established approaches for quantifying photon fluence and absorption (e.g., radiometry, actinometry, or computational evaluation of LVRPA) is essential, as is the use of probe compounds that do not affect light absorption or otherwise alter the catalyst.⁵⁹ As candidate photocatalysts advance toward practical application, testing should be done under standardized conditions, using well-characterized probe compounds, and solution conditions (e.g., pH, ionic composition, concentration of ROS scavengers) that approximate those encountered in actual treatment systems. An appropriate figure of merit, such as EE/O,⁶⁰ should be reported when comparing the efficiency of different AOPs.
- (3) *Consider creative approaches and seek break-through photocatalysts without neglecting the challenges of adapting materials from other disciplines.* While repurposing emerging materials from related fields can be an effective strategy to develop innovative water treatment photocatalysts, a blind pursuit can lead to the promotion of materials not suitable for practical AOP application. For example, materials developed for water-splitting or photovoltaics also operate under photoinduced charge transfer processes; however, they differ in the nature of their energy conversion processes and are designed with different ideal characteristics in mind. As such, even the most successful of these materials may be ineffective at generating ROS for water treatment.
- (4) *Design and test materials for specific applications.* Many past reports on photocatalyst performance fail to identify the most appealing application for the material. The performance of a photocatalyst depends upon the properties of the contaminant being treated,⁶³ as well as the relative concentrations of other interfering components. As a result, researchers may develop photocatalysts for applications that are impractical or for which industry lacks interest. To overcome this challenge, researchers need either to overcome the major barriers facing traditional applications such as drinking water and municipal wastewater treatment, or to identify niche areas, where photocatalytic water treatment can be competitive with existing AOPs.

■ MOVING AHEAD: DESIGN FOR NICHE APPLICATIONS

The need for energy-efficient AOPs will persist, as advances in analytical techniques and increasingly stringent legislation continue to drive lower contaminant minimum concentration targets for potable use and environmental discharge. For photocatalysis to carve out a place in this growing market, it must be competitive with other AOP technologies, particularly UV/H₂O₂, which is more widely adopted by industry. At pilot-

scale, reports show the EE/O of UV/H₂O₂ tends to be significantly lower than UV/TiO₂.^{22,64} Aside from energy efficiency, homogeneous AOPs are easier to engineer, are not surface area limited, have fewer mass transfer problems, and do not experience catalyst surface fouling. For large scale municipal applications, it is the agreement among industry practitioners, as well as these authors, that current photocatalytic water treatment systems are impractical because they are less efficient and have higher costs than existing UV/H₂O₂, O₃/H₂O₂, and UV/O₃ technologies.^{65,66} However, an unfavorable prospect for large scale application does not preclude the potential of photocatalysis for water treatment in select niche applications; the technology still retains substantive and unique benefits. Tangible short-term outputs based on a valid business model and a clear pathway for technology transfer to industry are overdue, considering the maturity of basic science and, indeed, are critical to shrink the increasingly wider gap between industrial needs and academic research.

Reappraising the unique benefits of photocatalysis over other AOPs may pave the road toward these niches. For example, photocatalysis enables not only oxidation but also reduction, presenting relatively untapped opportunities to reductively remove oxyanions, such as nitrate,⁶⁷ chromate,⁶⁸ and redox-active metal ions, such as Ag⁺.⁶⁹ For several metals, reduction can lead to irreversible fouling through the formation of crystallites on the surface of the catalyst.⁶⁹ In contrast, Cr(VI) can be reduced to less toxic Cr(III) which is easily precipitated out of solution.⁷⁰ This process can be made more favorable by the presence of abundant efficient h⁺ scavengers.⁷¹ Innovative approaches to improve the reductive use of photocatalysis continue to emerge,⁷² albeit still in embryonic phase. The ability to reduce oxygen to form H₂O₂ by select photocatalysts, such as C₃N₄,⁷³ may also become a useful approach to produce AOP precursors on site.

Through the oxidation pathway, the generation of highly oxidative h_{vb}⁺ in addition to ROS can contribute to degradation of recalcitrant organics and even mineralization for niche applications.⁷⁴ Photocatalysis has been proposed as a pretreatment for particularly challenging waters, especially those that occur in smaller volumes compared to municipal waste streams; for example, effluents loaded with lignin (in the pulp and paper mill industry),⁷⁵ dyes (textile industry),⁷⁶ poly/perfluoroalkyl substances (chemical industry),^{77,78} and pesticides (pharmaceutical industry).^{79–81} While reducing toxicity is often the goal, complete mineralization is unrealistic for the vast majority of applications.^{1,82} The resulting incomplete degradation of hazardous pollutants requires careful assessment of the ecotoxicity^{83,84} or human toxicity^{85,86} of the byproducts. The ability of photocatalysis to increase biodegradability requires further attention with emphasis on the development of methods to enable the rapid assessment of contaminant biodegradability. The higher mineralization potential of photocatalysis when applied as a polishing step for pretreated water can also be advantageous in niche applications where cost and time are less restricted, such as the treatment of highly turbid waters containing recalcitrant contaminants, space-station water treatment systems,^{87,88} or the production of ultrapure water for the semiconductor industry.⁸⁹

As a catalytic process, not requiring consumable chemicals is another key benefit of photocatalytic treatment systems. This leads to opportunities in applications where transportation of

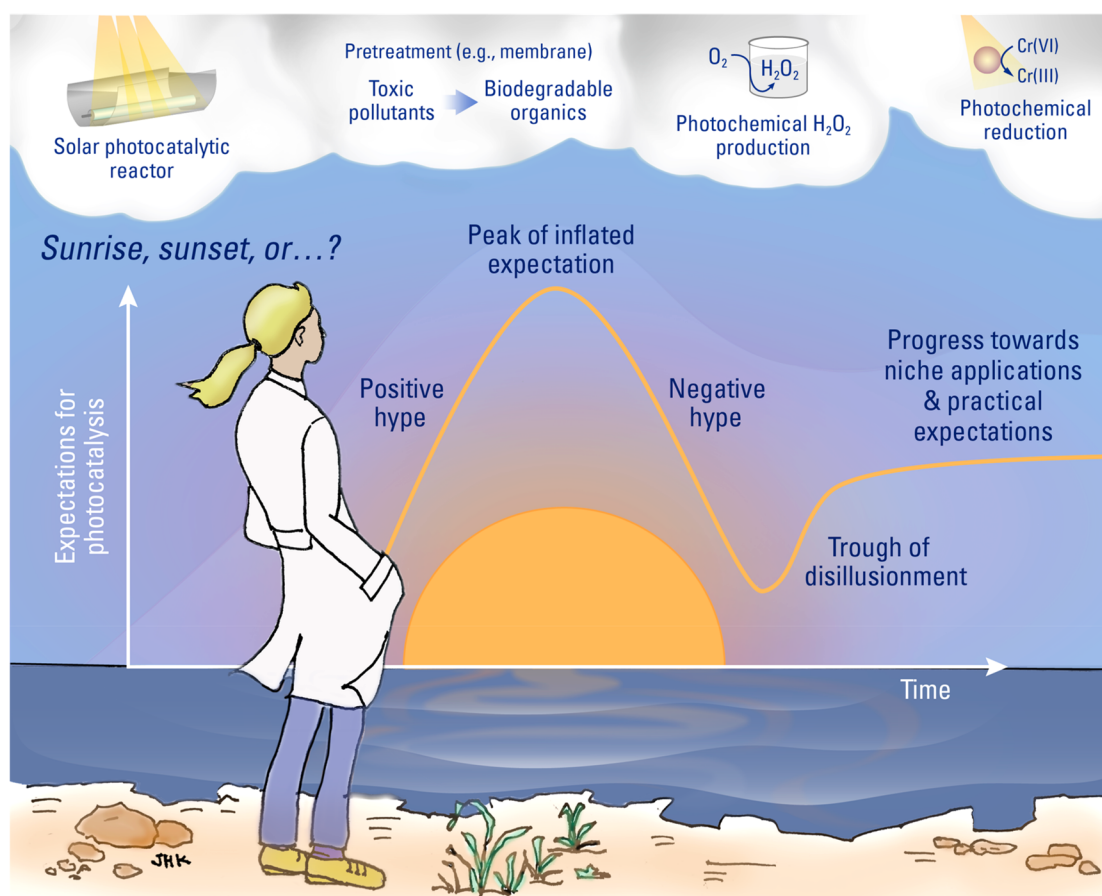


Figure 4. Future Trajectory of Photocatalytic Water Treatment. The development of a new technology can be visualized as following the trace of the sun on the horizon, rising from its initial conception, then reaching a zenith of popularity before arcing back toward the horizon. Photocatalytic water treatment has undeniably experienced a peak of academic hype, leading many detractors to espouse the failure of the technology to live up to its predicted potential. However, it is the opinion of these authors that this need not lead to the sun setting on industrial applications for photocatalytic water treatment, but that real near-term applications can be achieved considering the maturity of basic science. The practical plateau of technical performance will likely fall below peak expectations, as with many new innovations; however, valid business models and a clear pathway for technology transfer to industry can help engineers finally harness the startling benefits of these unique materials.

chemicals is cumbersome (i.e., geographically isolated regions) or in biological systems that may be sensitive to the addition of chemicals. The performance and costs associated with small-scale groundwater pump and treat systems employing photocatalysis can be comparable to conventional treatment technologies,⁹⁰ while negating the need for a continual supply of chemicals. Other emerging opportunities include treatment of waste streams from aquaculture and hydroponics, as both are often practiced in small scale. Aquaculture waters consist of a unique set of contaminants including pathogens, taste and odor compounds, and antibiotics⁹¹ that are not easily treated with conventional systems. Similarly, photocatalytic treatment of recycled hydroponics water can facilitate the breakdown of phytotoxic compounds, leading to increased crop yields without leaving a harmful residual.⁹²

Perhaps its most greatly espoused attribute is that photocatalysis can be solar powered, making photocatalytic treatment ideal for highly cost-sensitive or energy-restrictive applications. Regions that lack access to clean water often lack energy infrastructure, justifying the need for solar-powered, household-based, water treatment interventions in developing regions.⁷ Several researchers have proposed using TiO₂ to enhance solar disinfection (SODIS), demonstrating its

ability to disinfect and decontaminate water faster than SODIS alone.^{93–95} Solar powered applications are intrinsically limited by the low-energy density of sunlight (<1000 W/m²); yet when land area is not restricted and an effective light-harvesting strategy such as a compound parabolic collector is employed, photocatalysis can be an efficient method for the low-energy treatment of small-scale industrial waste streams.^{96–98} Other solar-based applications have emerged for industrial off-grid treatment, including floating photocatalyst structures in oil sands tailing ponds, which are large in area and already operate over very long-time scales.^{99,100} The use of solar-driven photocatalysis has been suggested as a possible means of detoxifying treated drinking waters containing residual algal toxins, but concerns remain regarding cost effectiveness and generation of toxic byproducts.¹⁰¹ At best, such technology might be utilized for this purpose in small, remote communities where piped supply is intermittent and volumes to be treated are small.

■ FUTURE OF PHOTOCATALYSIS: SUNRISE OR SUNSET?

Although longer time frames for acceptance of new technologies in risk-averse industries, such as water treatment,

can be expected,¹⁰² the more than three decades-long delay in technology transfer clearly suggests that photocatalysis for water treatment is not in the sunrise phase of research and development. However, we do not view it as a sunset, either; rather, we see the field overcoming an inflated expectation (a.k.a. academic hype),¹⁰³ exacerbated by its connection to concurrent hypes in the fields of materials science and nanotechnology (Figure 4). While we should not limit our imagination or the boundary of science, it is time for us to reevaluate critically the necessary components of successful research to move the field of photocatalytic water treatment forward.

AUTHOR INFORMATION

Corresponding Author

E-mail: jaehong.kim@yale.edu. Tel: +1-203-432-4386.

ORCID

Pedro J. J. Alvarez: 0000-0002-6725-7199

Ezra L. Cates: 0000-0003-0793-0246

Wonyong Choi: 0000-0003-1801-9386

John Crittenden: 0000-0002-9048-7208

Qilin Li: 0000-0001-5756-3873

Xie Quan: 0000-0003-3085-0789

T. David Waite: 0000-0002-5411-3233

Paul Westerhoff: 0000-0002-9241-8759

Jae-Hong Kim: 0000-0003-2224-3516

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSF Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment (NEWT, EEC-1449500). D.L.S.'s contribution was supported by the Engineering Research Center for Reinventing the Nation's Urban Water Infrastructure (RENUWIT, EEC-1028968).

REFERENCES

- (1) Ollis, D. F.; Pelizzetti, E.; Serpone, N. Photocatalyzed destruction of water contaminants. *Environ. Sci. Technol.* **1991**, *25* (9), 1522–1529.
- (2) Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37.
- (3) Okamoto, K. I.; Yamamoto, Y.; Tanaka, H.; Tanaka, M.; Itaya, A. Heterogeneous photocatalytic decomposition of phenol over TiO₂ powder. *Bull. Chem. Soc. Jpn.* **1985**, *58* (7), 2015–2022.
- (4) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95* (1), 69–96.
- (5) Henan Bright Commercial Co., Ltd. Factory sales nano-titanium dioxide TiO₂ degussa P25. https://www.alibaba.com/product-detail/Factory-sales-Nano-Titanium-Dioxide-tio2_60601130450.html?spm=a2700.7724838.2017115.1.6d0263f8Q9brPJ (accessed 5/2/2018).
- (6) Khan, A.; Balakrishnan, K.; Katona, T. Ultraviolet light-emitting diodes based on group three nitrides. *Nat. Photonics* **2008**, *2*, 77.
- (7) Loeb, S.; Hofmann, R.; Kim, J. H. Beyond the pipeline: Assessing the efficiency limits of advanced technologies for solar water disinfection. *Environ. Sci. Technol. Lett.* **2016**, *3* (3), 73–80.
- (8) Grčić, I.; Li Puma, G. Six-flux absorption-scattering models for photocatalysis under wide-spectrum irradiation sources in annular and flat reactors using catalysts with different optical properties. *Appl. Catal., B* **2017**, *211*, 222–234.
- (9) Serpone, N. Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. *J. Photochem. Photobiol., A* **1997**, *104* (1), 1–12.
- (10) Zhang, J.; Nosaka, Y. Quantitative detection of OH radicals for investigating the reaction mechanism of various visible-light TiO₂ photocatalysts in aqueous suspension. *J. Phys. Chem. C* **2013**, *117* (3), 1383–1391.
- (11) Sun, L.; Bolton, J. R. Determination of the quantum yield for the photochemical generation of hydroxyl radicals in TiO₂ suspensions. *J. Phys. Chem.* **1996**, *100* (10), 4127–4134.
- (12) Zhang, J.; Nosaka, Y. Mechanism of the OH radical generation in photocatalysis with TiO₂ of different crystalline types. *J. Phys. Chem. C* **2014**, *118* (20), 10824–10832.
- (13) Stafford, U.; Gray, K. A.; Kamat, P. V. Photocatalytic degradation of 4-chlorophenol: The effects of varying TiO₂ concentration and light wavelength. *J. Catal.* **1997**, *167* (1), 25–32.
- (14) Mills, A.; Morris, S. Photomineralization of 4-chlorophenol sensitized by titanium dioxide: a study of the initial kinetics of carbon dioxide photogeneration. *J. Photochem. Photobiol., A* **1993**, *71* (1), 75–83.
- (15) Lepore, G. P.; Langford, C. H.; Víchová, J.; Vlček, A. Photochemistry and picosecond absorption spectra of aqueous suspensions of a polycrystalline titanium dioxide optically transparent in the visible spectrum. *J. Photochem. Photobiol., A* **1993**, *75* (1), 67–75.
- (16) Cornu, C. J. G.; Colussi, A. J.; Hoffmann, M. R. Quantum Yields of the photocatalytic oxidation of formate in aqueous TiO₂ suspensions under continuous and periodic illumination. *J. Phys. Chem. B* **2001**, *105* (7), 1351–1354.
- (17) Mierzwa, J. C.; Rodrigues, R.; Teixeira, A. C. S. C., Chapter 2: UV-hydrogen peroxide processes. In *Advanced Oxidation Processes for Waste Water Treatment*; Ameta, R., Ed.; Academic Press, 2018; pp 13–48.
- (18) Liao, C. H.; Gurol, M. D. Chemical oxidation by photolytic decomposition of hydrogen peroxide. *Environ. Sci. Technol.* **1995**, *29* (12), 3007–3014.
- (19) Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **1992**, *26* (5), 1005–1013.
- (20) Brame, J.; Long, M.; Li, Q.; Alvarez, P. Inhibitory effect of natural organic matter or other background constituents on photocatalytic advanced oxidation processes: Mechanistic model development and validation. *Water Res.* **2015**, *84*, 362–371.
- (21) Katz, A.; McDonagh, A.; Tijging, L.; Shon, H. K. Fouling and inactivation of titanium dioxide-based photocatalytic systems. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45* (17), 1880–1915.
- (22) Benotti, M. J.; Stanford, B. D.; Wert, E. C.; Snyder, S. A. Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Res.* **2009**, *43* (6), 1513–1522.
- (23) Hurum, D. C.; Agrios, A. G.; Gray, K. A.; Rajh, T.; Thurnauer, M. C. Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO₂ Using EPR. *J. Phys. Chem. B* **2003**, *107* (19), 4545–4549.
- (24) Choi, W.; Termin, A.; Hoffmann, M. R. The role of metal ion dopants in quantum-sized TiO₂: correlation between photoreactivity and charge carrier recombination dynamics. *J. Phys. Chem.* **1994**, *98* (51), 13669–13679.
- (25) Suri, R. P. S.; Liu, J.; Hand, D. W.; Crittenden, J. C.; Perram, D. L.; Mullins, M. E. Heterogeneous photocatalytic oxidation of hazardous organic contaminants in water. *Water Environ. Res.* **1993**, *65* (5), 665–673.
- (26) Banerjee, S.; Pillai, S. C.; Falaras, P.; O'Shea, K. E.; Byrne, J. A.; Dionysiou, D. D. New insights into the mechanism of visible light photocatalysis. *J. Phys. Chem. Lett.* **2014**, *5* (15), 2543–2554.
- (27) Chen, X. B.; Liu, L.; Yu, P. Y.; Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* **2011**, *331* (6018), 746–750.

- (28) Zhao, C.; Pelaez, M.; Dionysiou, D. D.; Pillai, S. C.; Byrne, J. A.; O'Shea, K. E. UV and visible light activated TiO₂ photocatalysis of 6-hydroxymethyl uracil, a model compound for the potent cyanotoxin cylindrospermopsin. *Catal. Today* **2014**, *224*, 70–76.
- (29) Shiraiishi, Y.; Sakamoto, H.; Sugano, Y.; Ichikawa, S.; Hirai, T. Pt–Cu bimetallic alloy nanoparticles supported on anatase TiO₂: Highly active catalysts for aerobic oxidation driven by visible light. *ACS Nano* **2013**, *7* (10), 9287–9297.
- (30) Chen, C.; Ma, W.; Zhao, J. Semiconductor-mediated photodegradation of pollutants under visible-light irradiation. *Chem. Soc. Rev.* **2010**, *39* (11), 4206–4219.
- (31) Tsukamoto, D.; Shiraiishi, Y.; Sugano, Y.; Ichikawa, S.; Tanaka, S.; Hirai, T. Gold Nanoparticles located at the interface of anatase/rutile TiO₂ particles as active plasmonic photocatalysts for aerobic oxidation. *J. Am. Chem. Soc.* **2012**, *134* (14), 6309–6315.
- (32) Xiong, Z.; Ma, J.; Ng, W. J.; Waite, T. D.; Zhao, X. S. Silver-modified mesoporous TiO₂ photocatalyst for water purification. *Water Res.* **2011**, *45* (5), 2095–2103.
- (33) Zhang, Y.; Tang, Z. R.; Fu, X.; Xu, Y. J. TiO₂–graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: Is TiO₂–graphene truly different from other TiO₂–carbon composite materials? *ACS Nano* **2010**, *4* (12), 7303–7314.
- (34) Liu, Z.; Bai, H.; Sun, D. Facile fabrication of hierarchical porous TiO₂ hollow microspheres with high photocatalytic activity for water purification. *Appl. Catal., B* **2011**, *104* (3), 234–238.
- (35) Yu, J. G.; Su, Y. R.; Cheng, B. Template-free fabrication and enhanced photocatalytic activity of hierarchical macro-/mesoporous titania. *Adv. Funct. Mater.* **2007**, *17* (12), 1984–1990.
- (36) Chen, P. C.; Tsai, M. C.; Yang, M. H.; Chen, T. T.; Chen, H. C.; Chang, I. C.; Chang, Y. C.; Chen, Y. L.; Lin, I. N.; Chiu, H. T.; Lee, C. Y. The “cascade effect” of nano/micro hierarchical structure: A new concept for designing the high photoactivity materials – An example for TiO₂. *Appl. Catal., B* **2013**, *142–143*, 752–760.
- (37) Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S. T.; Zhong, J.; Kang, Z. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* **2015**, *347* (6225), 970–974.
- (38) Niu, P.; Liu, G.; Cheng, H. M. Nitrogen vacancy-promoted photocatalytic activity of graphitic carbon nitride. *J. Phys. Chem. C* **2012**, *116* (20), 11013–11018.
- (39) Wang, W.; Tade, M. O.; Shao, Z. Research progress of perovskite materials in photocatalysis- and photovoltaics-related energy conversion and environmental treatment. *Chem. Soc. Rev.* **2015**, *44* (15), 5371–5408.
- (40) Kim, J.; Lee, C. W.; Choi, W. Platinized WO₃ as an environmental photocatalyst that generates OH radicals under visible light. *Environ. Sci. Technol.* **2010**, *44* (17), 6849–6854.
- (41) Pan, C.; Zhu, Y. A review of BiPO₄, a highly efficient oxyacid-type photocatalyst, used for environmental applications. *Catal. Sci. Technol.* **2015**, *5* (6), 3071–3083.
- (42) Park, H.; Kim, H. I.; Moon, G. H.; Choi, W. Photoinduced charge transfer processes in solar photocatalysis based on modified TiO₂. *Energy Environ. Sci.* **2016**, *9* (2), 411–433.
- (43) Pelaez, M.; Nolan, N. T.; Pillai, S. C.; Seery, M. K.; Falaras, P.; Kontos, A. G.; Dunlop, P. S. M.; Hamilton, J. W. J.; Byrne, J. A.; O'Shea, K.; Entezari, M. H.; Dionysiou, D. D. A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal., B* **2012**, *125*, 331–349.
- (44) Dong, S.; Feng, J.; Fan, M.; Pi, Y.; Hu, L.; Han, X.; Liu, M.; Sun, J.; Sun, J. Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review. *RSC Adv.* **2015**, *5* (19), 14610–14630.
- (45) Van Gerven, T.; Mul, G.; Moulijn, J.; Stankiewicz, A. A review of intensification of photocatalytic processes. *Chem. Eng. Process.* **2007**, *46* (9), 781–789.
- (46) Benotti, M. J.; Stanford, B. D.; Wert, E. C.; Snyder, S. A. Evaluation of a photocatalytic reactor membrane pilot system for the removal of pharmaceuticals and endocrine disrupting compounds from water. *Water Res.* **2009**, *43* (6), 1513–1522.
- (47) Li Puma, G.; Brucato, A. Dimensionless analysis of slurry photocatalytic reactors using two-flux and six-flux radiation absorption–scattering models. *Catal. Today* **2007**, *122* (1), 78–90.
- (48) Ling, L.; Tugaoen, H.; Brame, J.; Sinha, S.; Li, C.; Schoepf, J.; Hristovski, K.; Kim, J. H.; Shang, C.; Westerhoff, P. Coupling light emitting diodes with photocatalyst-coated optical fibers improves quantum yield of pollutant oxidation. *Environ. Sci. Technol.* **2017**, *51* (22), 13319–13326.
- (49) Karches, M.; Morstein, M.; Rudolf von Rohr, P.; Pozzo, R. L.; Giombi, J. L.; Baltanás, M. A. Plasma-CVD-coated glass beads as photocatalyst for water decontamination. *Catal. Today* **2002**, *72* (3), 267–279.
- (50) Plesch, G.; Gorbár, M.; Vogt, U. F.; Jeseník, K.; Vargová, M. Reticulated macroporous ceramic foam supported TiO₂ for photocatalytic applications. *Mater. Lett.* **2009**, *63* (3), 461–463.
- (51) Athanasekou, C. P.; Romanos, G. E.; Katsaros, F. K.; Kordatos, K.; Likodimos, V.; Falaras, P. Very efficient composite titania membranes in hybrid ultrafiltration/photocatalysis water treatment processes. *J. Membr. Sci.* **2012**, *392–393*, 192–203.
- (52) Lee, C. G.; Javed, H.; Zhang, D.; Kim, J. H.; Westerhoff, P.; Li, Q.; Alvarez, P. J. J. Porous electrospun fibers embedding TiO₂ for adsorption and photocatalytic degradation of water pollutants. *Environ. Sci. Technol.* **2018**, *52* (7), 4285–4293.
- (53) Matafonova, G.; Batoev, V. Recent advances in application of UV light-emitting diodes for degrading organic pollutants in water through advanced oxidation processes: A review. *Water Res.* **2018**, *132*, 177–189.
- (54) Chen, J.; Loeb, S.; Kim, J. H. LED revolution: fundamentals and prospects for UV disinfection applications. *Environ. Sci.: Water Res. Technol.* **2017**, *3* (2), 188–202.
- (55) Dotson, A. D.; Rodríguez, C. E.; Linden, K. G. UV disinfection implementation status in US water treatment plants. *J. - Am. Water Works Assoc.* **2012**, *104* (5), E318–E324.
- (56) Grčić, I.; Li Puma, G. Photocatalytic degradation of water contaminants in multiple photoreactors and evaluation of reaction kinetic constants independent of photon absorption, irradiance, reactor geometry, and hydrodynamics. *Environ. Sci. Technol.* **2013**, *47* (23), 13702–13711.
- (57) Otálvaro-Marín, H. L.; Mueses, M. A.; Crittenden, J. C.; Machuca-Martinez, F. Solar photoreactor design by the photon path length and optimization of the radiant field in a TiO₂-based CPC reactor. *Chem. Eng. J.* **2017**, *315*, 283–295.
- (58) Ahmed, Y. M.; Jongewaard, M.; Li, M.; Blatchley, E. R. Ray tracing for fluence rate simulations in ultraviolet photoreactors. *Environ. Sci. Technol.* **2018**, *52* (8), 4738–4745.
- (59) Barbero, N.; Vione, D. Why dyes should not be used to test the photocatalytic activity of semiconductor oxides. *Environ. Sci. Technol.* **2016**, *50* (5), 2130–2131.
- (60) Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric-and solar-driven systems (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 627.
- (61) Liu, L.; Chen, F.; Yang, F.; Chen, Y.; Crittenden, J. Photocatalytic degradation of 2,4-dichlorophenol using nanoscale Fe/TiO₂. *Chem. Eng. J.* **2012**, *181–182*, 189–195.
- (62) Xie, R.; Meng, X.; Sun, P.; Niu, J.; Jiang, W.; Bottomley, L.; Li, D.; Chen, Y.; Crittenden, J. Electrochemical oxidation of ofloxacin using a TiO₂-based SnO₂-Sb/polytetrafluoroethylene resin-PbO₂ electrode: Reaction kinetics and mass transfer impact. *Appl. Catal., B* **2017**, *203*, 515–525.
- (63) Ryu, J.; Choi, W. Substrate-specific photocatalytic activities of TiO₂ and multiactivity test for water treatment application. *Environ. Sci. Technol.* **2008**, *42* (1), 294–300.
- (64) Autin, O.; Hart, J.; Jarvis, P.; MacAdam, J.; Parsons, S. A.; Jefferson, B. Comparison of UV/TiO₂ and UV/H₂O₂ processes in an annular photoreactor for removal of micropollutants: Influence of

water parameters on metaldehyde removal, quantum yields and energy consumption. *Appl. Catal., B* **2013**, *138–139*, 268–275.

(65) von Gunten, U. Oxidation processes in water treatment: are we on track? *Environ. Sci. Technol.* **2018**, *52* (9), 5062–5075.

(66) Cates, E. L. Photocatalytic water treatment: So where are we going with this? *Environ. Sci. Technol.* **2017**, *51* (2), 757–758.

(67) Doudrick, K.; Yang, T.; Hristovski, K.; Westerhoff, P. Photocatalytic nitrate reduction in water: Managing the hole scavenger and reaction by-product selectivity. *Appl. Catal., B* **2013**, *136–137*, 40–47.

(68) Testa, J. J.; Grela, M. A.; Litter, M. I. Heterogeneous photocatalytic reduction of chromium(VI) over TiO₂ particles in the presence of oxalate: Involvement of Cr(V) species. *Environ. Sci. Technol.* **2004**, *38* (5), 1589–1594.

(69) Prairie, M. R.; Evans, L. R.; Stange, B. M.; Martinez, S. L. An investigation of titanium dioxide photocatalysis for the treatment of water contaminated with metals and organic chemicals. *Environ. Sci. Technol.* **1993**, *27* (9), 1776–1782.

(70) Cheng, Q.; Wang, C.; Doudrick, K.; Chan, C. K. Hexavalent chromium removal using metal oxide photocatalysts. *Appl. Catal., B* **2015**, *176–177*, 740–748.

(71) Marks, R.; Yang, T.; Westerhoff, P.; Doudrick, K. Comparative analysis of the photocatalytic reduction of drinking water oxoanions using titanium dioxide. *Water Res.* **2016**, *104*, 11–19.

(72) Choi, Y.; Koo, M. S.; Bokare, A. D.; Kim, D. H.; Bahnemann, D. W.; Choi, W. Sequential process combination of photocatalytic oxidation and dark reduction for the removal of organic pollutants and Cr(VI) using Ag/TiO₂. *Environ. Sci. Technol.* **2017**, *51* (7), 3973–3981.

(73) Kim, H. I.; Choi, Y.; Hu, S.; Choi, W.; Kim, J. H. Photocatalytic hydrogen peroxide production by anthraquinone-augmented polymeric carbon nitride. *Appl. Catal., B* **2018**, *229*, 121–129.

(74) Liu, Y.; Yao, W.; Liu, D.; Zong, R.; Zhang, M.; Ma, X.; Zhu, Y. Enhancement of visible light mineralization ability and photocatalytic activity of BiPO₄/BiOI. *Appl. Catal., B* **2015**, *163*, 547–553.

(75) Kansal, S. K.; Singh, M.; Sud, D. Studies on TiO₂/ZnO photocatalysed degradation of lignin. *J. Hazard. Mater.* **2008**, *153* (1), 412–417.

(76) Pekakis, P. A.; Xekoukoulotakis, N. P.; Mantzavinos, D. Treatment of textile dyehouse wastewater by TiO₂ photocatalysis. *Water Res.* **2006**, *40* (6), 1276–1286.

(77) Sahu, S. P.; Qanbarzadeh, M.; Ateia, M.; Torzkadeh, H.; Maroli, A. S.; Cates, E. L. Rapid degradation and mineralization of perfluorooctanoic acid by a new petitjeanite Bi₃O(OH)(PO₄)₂ microparticle ultraviolet photocatalyst. *Environ. Sci. Technol. Lett.* **2018**, *5* (8), 533–538.

(78) Xu, B.; Ahmed, M. B.; Zhou, J. L.; Altaee, A.; Wu, M.; Xu, G. Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors. *Chemosphere* **2017**, *189*, 717–729.

(79) Oller, I.; Gernjak, W.; Maldonado, M. I.; Pérez-Estrada, L. A.; Sánchez-Pérez, J. A.; Malato, S. Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *J. Hazard. Mater.* **2006**, *138* (3), 507–517.

(80) Konstantinou, I. K.; Albanis, T. A. Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Appl. Catal., B* **2003**, *42* (4), 319–335.

(81) Minero, C.; Pelizzetti, E.; Malato, S.; Blanco, J. Large solar plant photocatalytic water decontamination: Degradation of atrazine. *Sol. Energy* **1996**, *56* (5), 411–419.

(82) Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* **2010**, *44* (10), 2997–3027.

(83) Malato, S.; Cáceres, J.; Fernández-Alba, A. R.; Piedra, L.; Hernando, M. D.; Agüera, A.; Vial, J. Photocatalytic treatment of diuron by solar photocatalysis: Evaluation of main intermediates and toxicity. *Environ. Sci. Technol.* **2003**, *37* (11), 2516–2524.

(84) Cai, Q.; Hu, J. Decomposition of sulfamethoxazole and trimethoprim by continuous UVA/LED/TiO₂ photocatalysis: Decomposition pathways, residual antibacterial activity and toxicity. *J. Hazard. Mater.* **2017**, *323*, 527–536.

(85) Cantavenera, M. J.; Catanzaro, I.; Loddo, V.; Palmisano, L.; Sciadrello, G. Photocatalytic degradation of paraquat and genotoxicity of its intermediate products. *J. Photochem. Photobiol., A* **2007**, *185* (2), 277–282.

(86) Liviác, D.; Creus, A.; Marcos, R. DNA damage induction by two halogenated acetaldehydes, byproducts of water disinfection. *Water Res.* **2010**, *44* (8), 2638–2646.

(87) Antoniou, M. G.; Dionysiou, D. D. Application of immobilized titanium dioxide photocatalysts for the degradation of creatinine and phenol, model organic contaminants found in NASA's spacecrafts wastewater streams. *Catal. Today* **2007**, *124* (3), 215–223.

(88) Liu, X.; Chen, M.; Bian, Z.; Liu, C. C. Studies on urine treatment by biological purification using Azolla and UV photocatalytic oxidation. *Adv. Space Res.* **2008**, *41* (5), 783–786.

(89) Degenova, J.; Shadman, F. Recovery, reuse, and recycle of water in semiconductor wafer fabrication facilities. *Environ. Prog.* **1997**, *16* (4), 263–267.

(90) Turchi, C. S.; Mehos, M. S.; Link, H. F. *Design and Cost of Solar Photocatalytic Systems for Groundwater Remediation*; U.S. Department of Energy Office of Scientific and Technical Information, 1992. DOI: 10.2172/1114050.

(91) Bian, Z.; Cao, F.; Zhu, J.; Li, H. Plant pptake-assisted round-the-clock photocatalysis for complete purification of aquaculture wastewater using sunlight. *Environ. Sci. Technol.* **2015**, *49* (4), 2418–2424.

(92) Sunada, K.; Ding, X. G.; Utami, M. S.; Kawashima, Y.; Miyama, Y.; Hashimoto, K. Detoxification of phytotoxic compounds by TiO₂ photocatalysis in a recycling hydroponic cultivation system of asparagus. *J. Agric. Food Chem.* **2008**, *56* (12), 4819–4824.

(93) Byrne, J. A.; Fernandez-Ibanez, P. A.; Dunlop, P. S. M.; Alrousan, D. M. A.; Hamilton, J. W. J. Photocatalytic enhancement for solar disinfection of water: A review. *Int. J. Photoenergy* **2011**, *2011*, 1–12.

(94) Malato, S.; Fernandez-Ibanez, P.; Maldonado, M. I.; Blanco, J.; Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catal. Today* **2009**, *147* (1), 1–59.

(95) Alrousan, D. M. A.; Dunlop, P. S. M.; McMurray, T. A.; Byrne, J. A. Photocatalytic inactivation of *E. coli* in surface water using immobilised nanoparticle TiO₂ films. *Water Res.* **2009**, *43* (1), 47–54.

(96) Spasiano, D.; Marotta, R.; Malato, S.; Fernandez-Ibanez, P.; Di Somma, I. Solar photocatalysis: materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. *Appl. Catal., B* **2015**, *170–171*, 90–123.

(97) Feitz, A. J.; Boyden, B. H.; Waite, T. D. Evaluation of two solar pilot scale fixed-bed photocatalytic reactors. *Water Res.* **2000**, *34* (16), 3927–3932.

(98) Colina-Márquez, J.; Machuca-Martínez, F.; Li Puma, G. Photocatalytic mineralization of commercial herbicides in a pilot-scale solar CPC reactor: Photoreactor modeling and reaction kinetics constants independent of radiation field. *Environ. Sci. Technol.* **2009**, *43* (23), 8953–8960.

(99) McQueen, A. D.; Hendrikse, M.; Gaspari, D. P.; Kinley, C. M.; Rodgers, J. H.; Castle, J. W. Performance of a hybrid pilot-scale constructed wetland system for treating oil sands process-affected water from the Athabasca oil sands. *Ecol. Eng.* **2017**, *102*, 152–165.

(100) Leshuk, T.; Krishnakumar, H.; de Oliveira Livera, D.; Gu, F. Floating photocatalysts for passive solar degradation of naphthenic acids in oil sands process-affected water. *Water* **2018**, *10* (2), 202.

(101) Feitz, A. J.; Waite, T. D.; Jones, G. J.; Boyden, B. H.; Orr, P. T. Photocatalytic degradation of the blue green algal toxin microcystin-LR in a natural organic-aqueous matrix. *Environ. Sci. Technol.* **1999**, *33* (2), 243–249.

(102) Kiparsky, M.; Sedlak, D. L.; Thompson, B. H., Jr.; Truffer, B. The innovation deficit in urban water: The need for an integrated

perspective on institutions, organizations, and technology. *Environ. Eng. Sci.* **2013**, *30* (8), 395–408.

(103) van Lente, H.; Spitters, C.; Peine, A. Comparing technological hype cycles: Towards a theory. *Technol. Forecast. Soc. Change* **2013**, *80* (8), 1615–1628.