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Photocatalytic Activity of Inorganic Semiconductor Surfaces: Myths, Hype, and Reality

The notion of driving chemical and biochemical reactions on irradiated inorganic semiconductor surfaces has both fundamental and practical importance. The name “heterogeneous photocatalysis” has been coined for this field of endeavor, and it is hardly surprising that the field has literally exploded during the past couple of decades. Nevertheless, process efficiencies remain poor, and quantum yields have been disappointingly low (amounting only to fractions of a percent) even for well-studied semiconductors such as titanium dioxide, TiO_2 . Therefore, the time appears ripe to take stock of what we know and what we do not know about photoinduced processes at the molecular level. While impressive advances have been made in the surface science of oxide semiconductors (especially, TiO_2), much of this understanding resides with surfaces as they exist in pristine, ultrahigh vacuum conditions.^{1,2} On the other hand, little is known about inorganic semiconductor surfaces in contact with air or water and under conditions as they relate to the practical use of such interfaces. Here, we will critically examine what we know about the structural and chemical factors related to such interfaces and what knowledge is further needed to move this field forward. However, before we undertake this exercise, it is useful to set the parameters for the discussion.

Genesis, Concepts, and Confusions. The field’s growth has been (mistakenly, at least in the authors’ view) associated with the well-cited discovery³ that irradiated TiO_2 could assist in the splitting of water. However, oxide semiconductors had long before received considerable scrutiny from the perspective of the electronic theory of chemical catalysis, and this corpus of work dates back at least to the 1960s.⁴ Zinc oxide was a particularly popular choice for the oxide semiconductor candidate in these early studies. Oxide semiconductors were also of interest in the geochemical and environmental chemistry literature especially from the perspective of how the combination of sunlight and rocks affected natural remediation processes.⁵ Popular recognition that irradiated semiconductor surfaces can indeed break down environmental pollutants (such as chlorinated hydrocarbons, cyanide, etc.) stems from papers that did appear^{6–8} just around the time of the Fujishima–Honda discovery; this could offer an explanation for the misplaced identification of the origin of the field of heterogeneous photocatalysis.

Process efficiencies remain poor, and quantum yields have been disappointingly low (amounting only to fractions of a percent) even for well-studied semiconductors such as TiO_2 .

That heterogeneous photocatalysis can be understood on a fundamental level by using electrochemical principles has been

pointed out by one of us.^{9,10} Thus, an irradiated semiconductor particle may be regarded as a short-circuited microelectrochemical cell in which the anodic and cathodic photoprocesses are balanced and the particle attains a (mixed) photopotential that depends on the relative rates of the two “conjugate” half-reactions.⁹ Consider the photooxidation of a hydrocarbon; the conjugate process in this case is the photoreduction of dioxygen, and the faster we can make this process, the more facile the hydrocarbon photooxidation.⁹ Similarly, consider the photoreduction of a metal ion (i.e., photodeposition of a metal) on an irradiated metal oxide surface. In this case, the conjugate reaction may be the photooxidation of a reducing agent (electron donor) such as formate species. Of course, in all of these cases, the reactions involve the photogenerated electron–hole (e^- – h^+) pairs in the irradiated semiconductor.

From a thermodynamics perspective, the key point to note is that in both above scenarios, the overall chemical reaction, namely, the oxidation of a hydrocarbon (by dioxygen) or the reduction of a metal ion (by a reducing agent) is *thermodynamically “downhill”*. In other words, the overall chemical reaction has a negative free-energy change. However, in the dark, both reactions are *kinetically sluggish*; light therefore serves to accelerate the reaction. Hence, the name “photocatalytic” for the process is entirely appropriate.

At this juncture, it is worth noting the oft-misplaced use of the word “photocatalyst” in the literature even in the cases wherein the overall processes are *thermodynamically uphill*. Examples of these include water splitting (into H_2 and O_2) and CO_2 splitting (into a myriad of products depending on the electron stoichiometry; ref 11). Thus, TiO_2 has been repeatedly (and mistakenly, in our opinion) called a “photocatalyst” for the splitting of water!

It is useful to think of two coupled processes in these cases. Photoexcitation allows the system to be “pumped up” against the free-energy gradient. The second step involves driving multiple electrons across the interface to convert the reactants to products; this is where the catalytic aspect of the inorganic semiconductor comes in.

Is the Oxide Semiconductor Surface Intrinsically Catalytic? The fact that strategies such as platinization of the parent oxide semiconductor surface have been utilized would seem to argue against this possibility. However, recent studies indicate that certain oxide surfaces do appear to have the ability to store electrons even without noble metal (e.g., Pt) islands on them; a case in point is p-type Cu_2O . For example, photoexcitation of this semiconductor results in the $6e^-$ conversion of CO_2 to methanol in the absence of any co-catalyst.^{12,13} Many of the surface chemical aspects discussed below can only be readily rationalized within the framework that the oxide surface is intrinsically catalytic toward many substrates.

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Table 1. Factors Underpinning Photocatalytic Activity of Inorganic Semiconductor Surfaces

category	factor(s)	impact(s)
optical	energy band gap	photonic efficiency
electronic	carrier mobility	quantum efficiency
structural/morphological	surface area	adsorption
	crystallinity/crystal facet	multiple ^a
	particle size	multiple ^a
	defects	multiple ^a
	crystal phase	multiple ^a
surface chemical	acid–base character	multiple ^a
	surface groups (hydroxyls)	multiple ^a

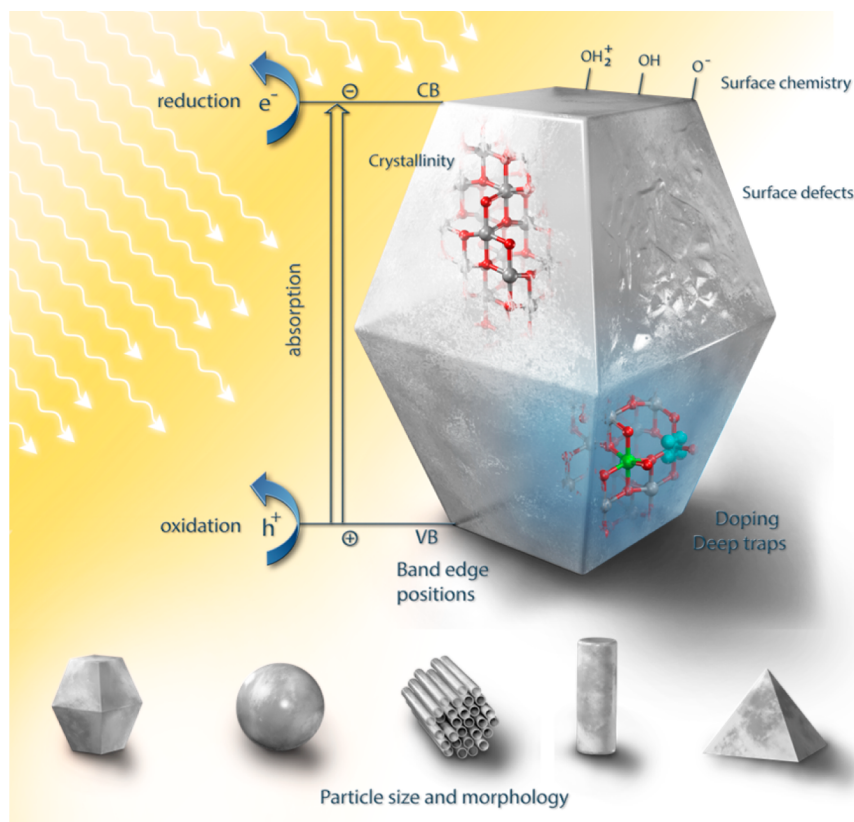
^aImpacts photocatalytic activity in multiple ways; see the text.

To streamline the discussion, factors underpinning the photocatalytic activity of inorganic semiconductor surfaces are listed in Table 1. It is worth emphasizing that the impact of the factors listed on the photocatalytic activity is complex and convoluted. For example, particle size can influence light absorption via the size quantization effect;¹⁴ it can also influence light-scattering events (see below). Thus, in this sense, optical and structural factors are coupled. Particle size can also impact surface area and hence influence adsorption of solution species. Similarly, the acid–base character of the photocatalyst surface can influence adsorption via electrostatic effects induced by charged surface groups. Grouping of the factors into neat boxes should not lead to the mistaken conclusion that they exert effects independent of one another. The chemometrics community addresses such complications by

implicating that the factors “interact” with one another, and hence, the response surface [i.e., three-dimensional plots of the response variable (in this case, the photocatalytic activity) as a function of the factor level] becomes curved rather than planar.¹⁵

If the optoelectronic factors are (temporarily) set aside, it is easy to recognize that every other factor listed in the compilation in Table 1 is no different from what is well-established in the heterogeneous catalysis community on the prerequisites of a “good” catalyst. Scheme 1 also highlights the topics addressed below.

Doping and Metal Modification of Parent Oxide Semiconductor Surfaces. A major motivation for metal modification is to impart electron storage capacity to the parent semiconductor surface; this is especially useful when the chemical reaction to be driven involves multiple electrons. This chemical modification may be performed either in the semiconductor bulk or on its surface. At this juncture, it is worth noting that the term “doping” has been mistakenly used by many authors in the literature for metal-modified semiconductors. Doping is a very specific phenomenon that in the solid-state chemistry or microelectronics communities means the controlled introduction of trace-level (subppm) impurities (“dopants”) into the host lattice such that they alter its optoelectronic characteristics. On the other hand, even when (a) the metal is present as a distinctly separate phase and/or (b) is present at levels of the order of a few percent (by mass), the term doping has been mistakenly applied. Within the context of this Viewpoint, we mostly consider *metal-modified* cases where the metal phase is present as discontinuous islands on the parent semiconductor surface.

Scheme 1. Factors Impacting Photocatalytic Activity of a Single (Idealized) Inorganic Semiconductor Particle^a

^aSee also Table 1 above.

Recent studies indicate that certain oxide surfaces do appear to have the ability to store electrons even without noble metal (e.g., Pt) islands on them; a case in point is p-type Cu_2O .

Interestingly, a distinction between *doping* and *alloying* has been made¹⁶ in terms of electronic structure consequences. Thus, doping has been used to signal instances where localized electronic states have been added such that the Fermi level shifts but the band edges are not changed. On the other hand, alloying is differentiated by introducing elements having delocalized bands that if sufficiently close in energy to other band edges, hybridize to form a new band with wider dispersion.¹⁶ However, this distinction still does not conform to the solid-state microelectronics/materials science usage where doping signals very low levels (ppm or less) of the foreign element whereas alloying means that the element is present at variable but much higher levels (a few percent) than the case of dopant species.

Another, more recent discovery concerns the possibility of shifting the photoabsorption profile into the visible range of the electromagnetic spectrum by surface plasmon effects when the semiconductor is decorated by metals such as Au.¹⁷ TiO_2 is not the only semiconductor that has been explored in this regard; others such as bismuth vanadate (BiVO_4) have been modified with metals such as Au.¹⁸ To this end, one of the authors of this Viewpoint has demonstrated the utility of combining anodic electrodeposition with galvanic displacement for preparing Au– Bi_2O_3 ¹⁹ and Au– BiVO_4 ¹⁸ nanocomposites. [Bismuth oxide, Bi_2O_3 , is an oxide that exists in n- as well as p-type semiconductor forms.] In both cases, the Au-modified photocatalysts exhibited faster kinetics (relative to the parent unmodified surfaces) for the decomposition of a dye probe (Figure 1).

The improvement in photocatalytic activity observed upon Au modification (Figure 1) may be rationalized on both optical and electronic grounds. Surface plasmon effects induced by the

presence of Au islands shift the absorption profile of the parent semiconductor into the visible, resulting in enhanced UV–visible absorption relative to the pristine surface. Second, the photogenerated electrons are siphoned off to the Au islands, thereby diminishing the extent of electron–hole recombination.

Quantifying Photocatalytic Activity. Plots such as those contained in Figure 1 have been commonly used by the community to compare the photocatalytic activity of given samples. However, these data shed no light at all on precisely how many of the incident photons were utilized for converting the targeted substrate into products. A well-recognized difficulty pertains to quantifying the number of photons that were absorbed by the semiconductor. Depending on the morphology and other nanoparticle attributes, the light can also be scattered; in fact, multiple scattering events can occur within the reactor confinement. These ideas lead to the notion of a photonic efficiency, that is, how many photons are absorbed versus the number incident on the semiconductor. Related to this parameter is the quantum efficiency, that is, the number of electrons (or holes) utilized in the photochemical process versus the number of photons incident. A large scattering cross section leads to a low photonic efficiency; similarly, facile electron–hole recombination leads to a low quantum efficiency. Facile electron–hole recombination can be caused both by bulk defect states in the semiconductor and by surface trap states (see below).

It is rather unfortunate that the notion of circumventing the above difficulties by defining a relative photonic efficiency²⁰ has been largely overlooked by practitioners of heterogeneous photocatalysis. The basic tenet of the suggested protocol was that by comparing the performance for the test substrate(s) against corresponding metrics for phenol (a standard secondary actinometer), inherent difficulties with precise knowledge of photon absorption (by the photocatalyst sample) and variations associated with the reactor geometry, light source, and so forth could be factored out.²⁰

Polymorphic Phases and Crystal Facets. Studies probing the factors underlying the variant photocatalytic activity of the rutile and anatase forms of TiO_2 have had a long history dating back at least 2 decades. (It is worth noting here that anatase is a *metastable* phase in the thermochemical sense and only reverts

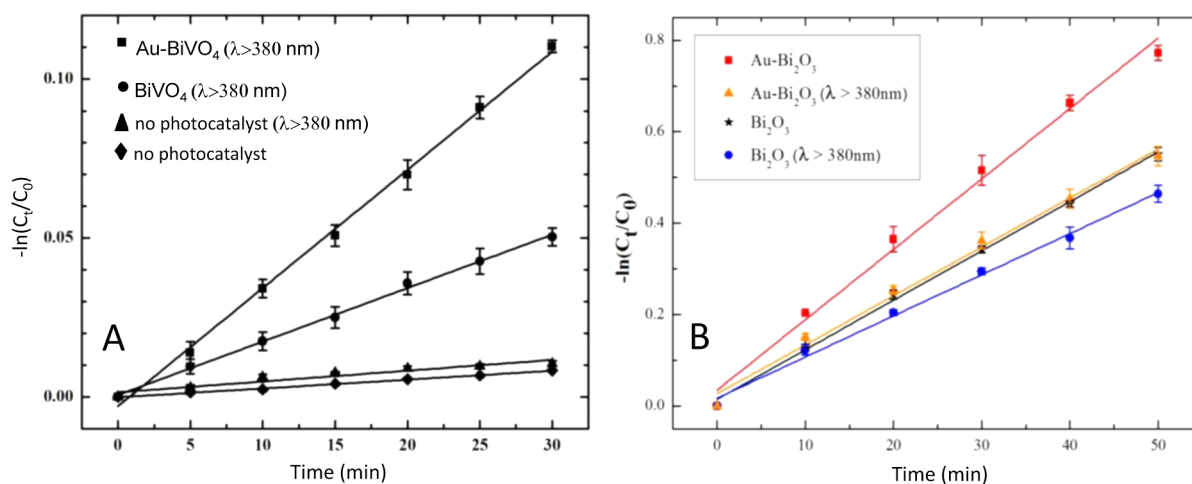


Figure 1. Pseudo-first-order kinetics plots showing the enhancement of photocatalytic activity for the decomposition of a dye (methyl orange) upon Au modification of (a) BiVO_4 and (b) Bi_2O_3 . The original papers (refs 18 and 19) may be consulted for further details. Reproduced with permission from Wiley-VCH and the Electrochemical Society. Copyright 2014: VCH (left) and The Electrochemical Society (right).

to rutile by heating up to temperatures in the region of ~ 600 °C).²¹ Which of the two phases is more photocatalytically active? The answer depends on the conjugate reaction in the overall photocatalytic process. When O_2 is present in the reaction medium, the anatase phase is always more active; on the other hand, rutile shows significant photocatalytic activity when oxidants other than O_2 are present, such as Ag^+ or H_2O_2 .²²

The better photocatalytic activity of anatase relative to rutile is rooted in several (undoubtedly coupled) factors, the more important among them being the (a) higher energy band gap of anatase (~ 3.2 relative to ~ 3.0 eV for the rutile phase) and conduction band edge location, (b) lower O_2 adsorption capacity for rutile, (c) higher preponderance of surface hydroxyl groups in anatase, (d) enhanced carrier recombination in rutile, (e) higher electron mobility in anatase ($4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) versus rutile ($0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$),²³ and (f) lower degree of charge separation in rutile because of a lower density of surface-to-bulk trap states. Information on the precise chemical nature of the trap states (surface or bulk) is currently lacking although surface peroxo groups have been implicated by voltammetric measurements.²⁴ The more stable surface peroxide intermediates generated in situ on the anatase surface during the photo-oxidation process (relative to the rutile surface) would be consistent with the intrinsically higher surface hydroxylation of anatase relative to rutile.

Doping is a very specific phenomenon that in the solid-state chemistry or microelectronics communities means the controlled introduction of trace-level (subppm) impurities ("dopants") into the host lattice such that they alter its optoelectronic characteristics.

Studies^{25,26} on rutile TiO_2 synthesized at low temperatures (as opposed to samples obtained by high-temperature calcination of the anatase phase), challenge the long-standing notion for the superior photocatalytic activity of the anatase form of TiO_2 . For example, flower-like rutile "superstructures" were grown by a solution-phase approach at room temperature, and the morphological evolution as a result of calcination was mapped using scanning electron microscopy.²⁶ Using rhodamine B (RhB) dye as a probe, the room-temperature synthesized samples were observed to have superior photocatalytic activity relative to the calcined ones. A particularly noteworthy aspect of this study was the correlation of surface area and surface charge using active species trapping experiments.²⁶ Thus, the effects of chemical species selective for scavenging holes (sodium oxalate), electrons (potassium dichromate), $O_2^{\cdot-}$ (*p*-benzoquinone), or $\cdot OH$ (isopropanol) were compared for RhB photodegradation.²⁶

Studies oriented toward surface chemical and crystal phase effects on the photocatalytic activity of other oxides besides TiO_2 are rather sparse. An interesting potential candidate for such a study is $BiVO_4$ (see also Figure 1); three phases are known for this material: scheelite-tetragonal, zircon-tetragonal, and scheelite-monoclinic.²⁷ Crystal form-controlled and highly

crystalline $BiVO_4$ powder were synthesized, and the photocatalytic properties were reported for the monoclinic and tetragonal phases.²⁸ The monoclinic form is highly active for O_2 evolution under visible light, and thus, it is not surprising that most of the studies on this material have centered on the O_2 evolution activity (a thermodynamically uphill process; see above) rather than on its photocatalytic attributes.

The O_2 evolution activity was mapped as a function of the postsynthesis calcination temperature ranging from 350 to 800 °C for $BiVO_4$ synthesized by homogeneous coprecipitation.²⁹ In all of the cases, only the scheelite-monoclinic phase was observed.²⁹ Both the V–O bond length (as monitored via Raman spectroscopy) and the energy band gap (as assessed by Tauc plots)³⁰ monotonically decreased with increasing calcination temperature.²⁹ Correspondingly, the O_2 evolution photoactivity (using simulated sunlight) increased with increasing calcination temperature.²⁹ The effect of particle size was also probed, and these results will be addressed in a subsequent section below. Studies comparing the photocatalytic activity of this material for the three crystal forms are still lacking, at least to our knowledge.

Specific crystal facets can have higher photocatalytic activity than others. This is well exemplified by a study on hydrothermally synthesized "starlike" $BiVO_4$ crystals.³¹ These samples were much more active for methylene blue photodecomposition than bulk oxide powder. In particular, this material has a higher atom density on the (010) lattice planes, and therefore, samples exposing more of these family of planes showed higher activity. The photocatalytic activity of this oxide was also attributed to distortion of the Bi–O polyhedron in the monoclinic phase.³¹

Most available anatase TiO_2 crystals are dominated by the thermodynamically stable {101} facets. However, this stability trend can be reversed by tweaking surface chemistry, a paradigm demonstrated by synthesizing fluorine-terminated surfaces where the {001} planes are energetically favored relative to {101} during crystal growth.³² High photocatalytic activity has been reported for faceted titania particles such as those having decahedral or octahedral shapes (see, for example, ref 33.) In another study, facet-mediated photodegradation of RhB was studied on hematite ($\alpha\text{-Fe}_2O_3$) architectures, namely, 1D nanorods, 2D nanoplates, and 3D nanocubes.³⁴ The dominant facets in these architectures were {001} and {110} (for the 1D), {001} (2D), and {012} (3D), respectively; the photocatalytic activity was ordered thus $1D > 3D \gg 2D$ for the dye photodegradation.³⁴ The observed differences were attributed to the direct consequence of the availability of surface iron sites on the three types of facets in the order $\{110\} > \{012\} \gg \{001\}$.

This is an area of heterogeneous photocatalysis deserving further study. Even the photoelectrochemical stability of the material can be influenced by crystal face orientation, as demonstrated recently for electrosynthesized Cu_2O films.³⁵

Crystallinity and Crystallite Size. Crystallinity is well-accepted in solid-state science to improve charge-transport dynamics; therefore, this parameter should be crucial in dictating the photocatalytic activity of a given inorganic semiconductor. Thus, amorphous titania has been shown to exhibit negligible activity for several photocatalytic reactions.³⁶ The general approach for tuning crystallinity (and crystallite size) is by thermal annealing of either the amorphous phase or of small particles. Unfortunately, calcination affects both parameters, complicating clear conclusions to be made about the *individual*

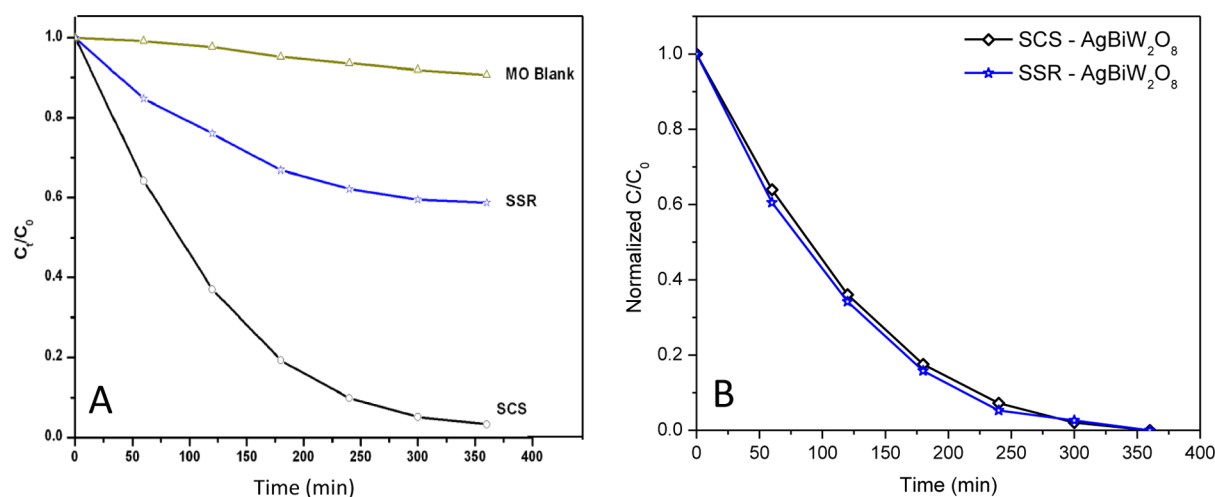


Figure 2. Comparison of photocatalytic activity for AgBiW₂O₈ before (A) and after (B) surface area normalization. The data are for the photocatalytic decomposition of a probe dye (methyl orange or MO; refer to the text) and are compared for a SCS sample and another derived from a SSR by other authors (ref 46). Copyright permission from Wiley-VCH.

effect of crystallinity and crystallite size. The way around this would be to synthesize and characterize a series of samples with well-defined crystallinity and crystallite size without having to resort to thermal pretreatment. This has been done in a study on anatase nanoparticles prepared by supercritical flow synthesis.³⁷ The crystallite size ranged from 6 to 27 nm (with a fixed crystallinity of ~87%), whereas another series varied the crystallinity from 12 to 82% with a fixed crystallite size of ~9 nm.

Rather surprisingly, the degree of crystallinity was found to exert only a negligible effect on the photodecomposition of phenol.³⁷ In contrast, crystallite size had a dramatic effect and interestingly influenced the production distribution profiles.³⁷ When small anatase nanoparticles were used, phenol was selectively photooxidized to benzoquinone as an intermediate.³⁷ Conversely, hydroquinone was found to be the dominant intermediate product when large anatase nanoparticles were used.³⁷

It is well-established in the heterogeneous catalysis community that the catalyst support can exert a key role on the degree of crystallinity and crystallite size of the supported nanoparticles. A corresponding example of such effects in the photocatalysis literature is provided by a study on the effect of porous amorphous silica minerals on supported TiO₂ photocatalysts.³⁸ Other studies addressing the influence of particle size are also noted,^{39,40} although it is not clear to what extent crystallinity variations confounded the effects observed in these studies.

Defects. Defects play a critical role in dictating the photocatalytic activity through their role in influencing the optoelectronic characteristics or in affecting carrier transit through the material after photoexcitation. Defects play a role in carrier trapping events both in the material bulk and on its surface. Perhaps a best known defect in the photocatalysis community is Ti³⁺ sites in the TiO₂ host lattice; these defect sites may be introduced, for example, by annealing titania powder in a reducing (e.g., hydrogen-containing) environment. The initially white powder immediately turns blue, signaling that “color centers” have been introduced. This color rapidly fades when the reduced material reacts with ambient oxygen. While metal “dopants” have been introduced to modify the optoelectronic characteristics of titania (a topic well reviewed

by previous authors and hence omitted here), a more recent innovation has been the introduction of nonmetals such as N or C. For example, metal oxynitrides show photocatalytic activity under visible light—a manifestation of band edge lowering.⁴¹

Analyzing the defect structure upon alloying or co-alloying a photocatalytic material is not commonplace. An exception to this trend is furnished by a study on co-alloying of anatase TiO₂ with Nb and N.¹⁶ The resultant material showed a 7-fold increase in the rate of methylene blue photodegradation compared to the parent (unalloyed) TiO₂ phase.¹⁶ Both Ti³⁺ and F⁺ centers (and oxygen vacancies) were identified as defects in the co-alloyed material that after annealing under ammonia flow appeared as an orange powder with ~2.0 eV band gap.¹⁶

While X-ray photoelectron spectroscopy provides useful information on the species introduced into the host lattice (and their oxidation states), this information obviously is surface-selective. Low-temperature electron paramagnetic resonance (EPR) is a versatile technique for probing defects in solids and was deployed in the study cited above.¹⁶ Similar EPR studies on TiO₂ have shown the formation of trapped electrons or Ti³⁺ states and trapped holes in the crystal lattice and/or surface hydroxyl groups.^{42,43} The molar amounts of defect sites (M_d) in several TiO₂ photocatalyst powders were determined using photoinduced reactions of electron accumulation in deaerated solutions containing sacrificial hole scavengers.⁴⁴

Surface Area. Any discussion of the physical attributes of a given catalyst must start with its surface area, and this is no different for a photocatalyst material. Of course, this parameter manifests most directly in photocatalysis in dictating the amount of substrate species that can be initially bound by adsorption. However, many of the parameters discussed in the previous subsections (e.g., crystallite size) also are inextricably intertwined with surface area. A hierarchical approach serves to parse out the effects of the various factors by normalizing the photocatalytic activity with respect to surface area. Thus, plots of the photocatalytic activity versus time for given series of samples can be renormalized in the vertical direction by factoring out the influence of surface area.

Consider a set of data on combustion-synthesized silver bismuth tungstate, AgBiW₂O₈.⁴⁵ Figure 2A contains a set of curves for this material in which the activity of a combustion-

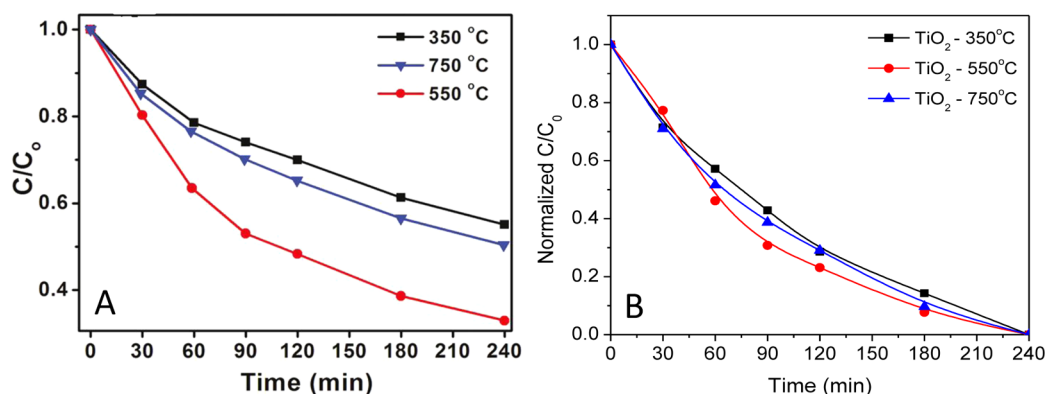


Figure 3. Comparison of photocatalytic activity for TiO_2 nanosheet samples before (A) and after (B) surface area normalization. The original data are from ref 47.

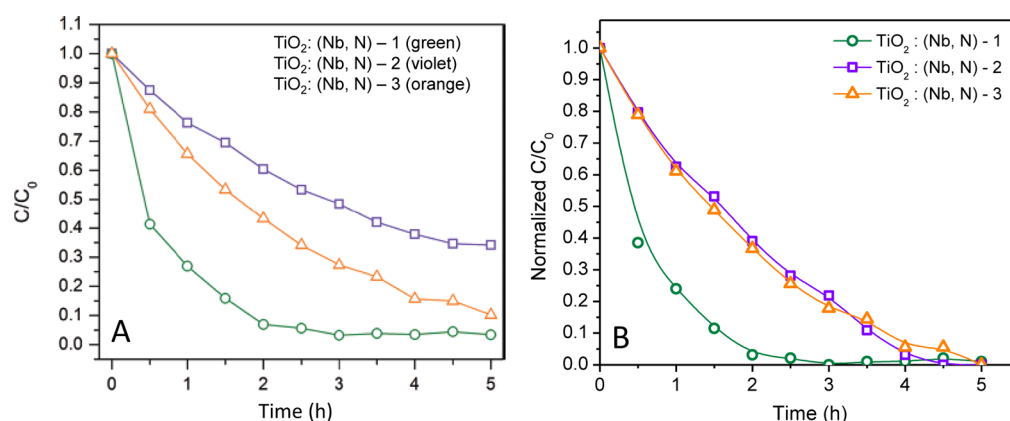


Figure 4. Comparison of photocatalytic activity for Nb and N co-alloyed TiO_2 before (A) and after (B) surface area normalization. The original data are from ref 16.

synthesized sample (SCS) for the photodegradation of methylene orange dye is compared with that of another sample (synthesized by previous authors) by a solid-state reaction (SSR) route.⁴⁶ A blank is also included to show that the dye degradation is negligible in the absence of the photocatalyst. The activity of the SCS sample is vastly superior to the SSR case. However, to what is this variation in activity attributable? The renormalized curves for the SCS and SSR samples taking into account their variant surface area (Figure 2B) immediately reveal that all of the difference in activity is simply attributable to surface area differences. The two curves now are virtually indistinguishable. Thus, no other factors (as discussed in the earlier subsections above) need be invoked here.

Figure 3A provides another set of data on TiO_2 nanosheets grown by the hydrothermal method;⁴⁷ they were subsequently calcined at temperatures indicated in the figure. Renormalization results in a lower degree of dispersion in the conversion curves in the vertical direction (Figure 3B). The differences between the 350 and 750 °C samples virtually disappear, diagnosing that the small difference in performance between them in Figure 3A was *mostly* a manifestation of the surface area difference. On the other hand, the 550 °C set of data do appear to have different photocatalytic activity to a small but perceptible degree (Figure 3B). The 550 °C sample had better reported crystallinity than the 350 °C sample and relative to the 750 °C sample (having the best crystallinity) had a unique bicrystalline network, considered by the original authors of this

study to have a favorable influence on the photocatalytic activity.⁴⁷

As a last example of the interpretative advantages to be accrued by surface area renormalization, consider the data for methylene blue photodegradation from an afore-discussed study on N and Nb co-alloyed TiO_2 .¹⁶ Samples 1–3 in Figure 4A are all derived from sol–gel synthesis but received different postsynthesis treatments. Sample 1 was first annealed in an ammonia atmosphere, sample 2 was then also annealed in an oxygen atmosphere (i.e., after the ammonia treatment), while sample 3 was first annealed in flowing oxygen followed by the same nitrogen treatment in ammonia. The photocatalytic activity obviously is highest for sample 1 in the order (Figure 4A) sample 1 \gg sample 3 > sample 2.¹⁶ Renormalization (for the variant surface area) preserves the superior photocatalytic activity of sample 1, but the differences between the other two samples now become much less pronounced (Figure 4B).

Unlike sample 1, both samples 2 and 3 lacked the defects (Ti^{3+} and F^+ centers) as analyzed by EPR in the original study.¹⁶ Further, sample 1 had the lowest-energy band gap (~ 2.0 eV) as opposed to ~ 2.44 and 2.29 eV for samples 2 and 3, respectively.¹⁶ The renormalization approach facilitates better visualization of the importance of defects (and other effects) once the surface area variations are factored out, as in Figure 4B.

Previous authors of photocatalysis studies have factored out surface area variations by renormalizing rate constants with respect to this parameter (see, for example, refs 34 and 48).

This tactic was also employed in studies of nanoparticle dissolution in geochemical environments (for example, ref 49). On the other hand, graphical renormalization of the kinetics data per the methodology prescribed in Figures 2B, 3B, and 4B provides for better visualization of the effects of other parameters (e.g., crystallinity, defect density, etc.). In some (simple) scenarios (e.g., Figure 2B), surface area variations could account for all of the photocatalytic activity differences, while in other (more complicated) situations (e.g., Figures 3B and 4B), other factors are also important for some samples but not in all.

Photocatalytic Activity–Structural/Physical Property Relationships and Concluding Remarks. Only limited attention has been paid to the development of quantitative relationships; these studies have almost exclusively focused on TiO_2 . For example, in one such study, empirical reproduction of photocatalytic properties was claimed from a linear combination of six oxide properties.⁵⁰ However, as stated at the outset of this Viewpoint, multivariate analyses taking into account factor interactions can provide further insights. This represents an opportunity for the chemometrics community.

It should be abundantly clear from the above paragraphs that attempts to delve into the many factors that govern photocatalytic activity have been largely TiO_2 -centric. This trend ought not to be too surprising given the rich history of study of this material by the heterogeneous photocatalysis community. However, it is the opinion of the authors of this Viewpoint that for tangible (and quantum) progress to be made in securing the photocatalysis process efficiencies at levels that would spur process scale-up efforts and industry adoption, the dragnet for other photocatalyst candidates must be cast wider. Unlike corresponding trends in photoelectrochemical energy conversion,¹⁴ the heterogeneous photocatalysis community has not suffered debilitating swings in research funding; however, the discipline appears to have been mired in a “ TiO_2 rut”.

Rather than try and improve the visible wavelength response of TiO_2 , we believe that the photocatalysis community would be better served by systematic efforts to vigorously search for other inorganic semiconductor candidates with comparable robustness but better optoelectronic and surface properties.

Interestingly enough, even for this particular material, the practical applicability of this process for indoor air cleaning and conditioning as well as for surface disinfection applications appears to have surpassed corresponding advances in the development of liquid-based remediation approaches. This trend undoubtedly reflects one handicap of the current state-of-the-science in heterogeneous photocatalysis, securing high reaction fluxes at photocatalyst–liquid interfaces. To improve energy efficiency, the process must also be made solar-compatible so that the electrical cost of driving UV lamps can be circumvented. Rather than try and improve the visible wavelength response of TiO_2 , we believe that the photocatalysis community would be better served by systematic efforts to

vigorously search for other inorganic semiconductor candidates with comparable robustness but better optoelectronic and surface properties. The challenges here are quite different from what the solar photovoltaics community faces in that the intrinsic processes and the materials attributes needed are different in the two application scenarios.

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Notes

Views expressed in this Viewpoint are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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