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Updates on the Roadmap for Photocatalysis

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■ INTRODUCTION

"Here comes the sun, and I say it's alright". The line from the famous and comforting Beatles' song sounds like a perfect slogan for today's crusade toward a more sustainable world. A never-tiring memento that, as long as the Sun shines in the sky, there will always be hope to heal a world suffering from an impressive increase in energetic demand. Sunlight brings a gigantic energy pack, and modern scientists are investing a huge amount of time, resources, and intellectual exercise into best exploiting it. Therefore, the fast-growing number of discoveries on photocatalysis comes as no surprise, and quite obviously they are accompanied by a ballistic number of publications (Figure 1). However, is this latter number truly
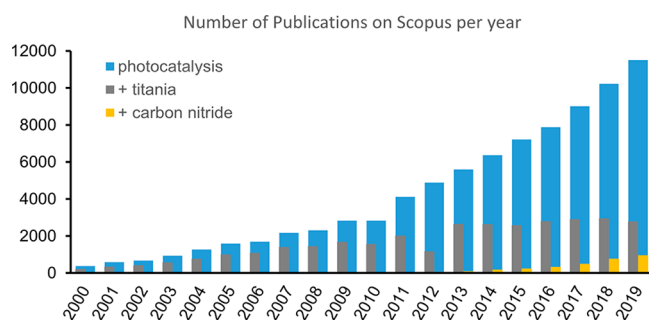
Figure 1. Histogram of number of publications on photocatalysis (blue bars) and on photocatalysis with TiO_2 and C_3N_4 (gray and yellow bars respectively) from 2000 to 2019 (data source: Scopus, March 12th, 2020).

justified or is the chain of events pining for sustainability and clean energy generating an overpopulation of contributions to the topic? Assuming that all such publications always reach a minimum standard of quality and novelty, the question for now must remain unanswered, because research is an unpredictable animal that can feed from any little fruit. However, a different but relevant question could be possibly answered: is it possible to establish a common protocol, set of rules, that makes all these publications useful for moving forward in a harmonized fashion the knowledge on photocatalysis?

Since its acknowledged genesis back in the 1910s,[1] photocatalysis has become a complex world, embracing a considerable number of ecosystems that live by their own rules: rules that are more or less clear and more or less respected. For example, homogeneous and heterogeneous photocatalysts bear notable differences; similarly, a careful

distinction is needed in comparing the processes for which light is used, these being organic conversions, small-molecule (CO_2, H_2O, N_2, etc.) reduction or oxidation, pollutant degradation, and many others. Setting common rules for all these different research streams appears to be a very hard task (if not impossible), but surely the *status quo* of each of these streams in terms of standardization of reported results can be significantly improved. By doing this, we can endow researchers with meaningful coordinates and help them move more comfortably in the photocatalysis world, consequently speeding up the global progress on the topic.

In this viewpoint, we will focus on heterogeneous photocatalysis and briefly summarize critical considerations and good practices for designing catalysts, carrying out experiments, and reporting results in relation to the role of photocatalysis in modern times. In particular, we will deal with the fundamental studies, thus not stretching the discussion to device engineering.

■ I MADE A GOOD CATALYST. OR NOT?

The first fundamental issue relates not only to photocatalysis but to some extent also to catalysis in general: namely, it must be clear and understood "what really is" the catalytically active species. If the proposition is not undeniably confirmed, the merits of the catalyst are misleading, with the risk of sparking further unmotivated research, resulting in a waste of time. Recently, for example, the real activity of certain carbon nanostructures in electrochemical reactions has been under an adverse spotlight by some researchers, and the truly "metal-free" nature has been criticized, on account of the frequent presence of metal impurities in these materials.[2] Transcending any rushed criticism on carbon nanostructures in catalysis, on account of their otherwise proven activity enhancement effects in photocatalysis and electrocatalysis,[3] this aspect should be deeply examined when photocatalysts based on carbon are developed.

The presence of metallic contaminants should be evaluated and their possible contribution to the activity ruled out, as their adventitious incorporation in the catalyst structure may
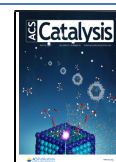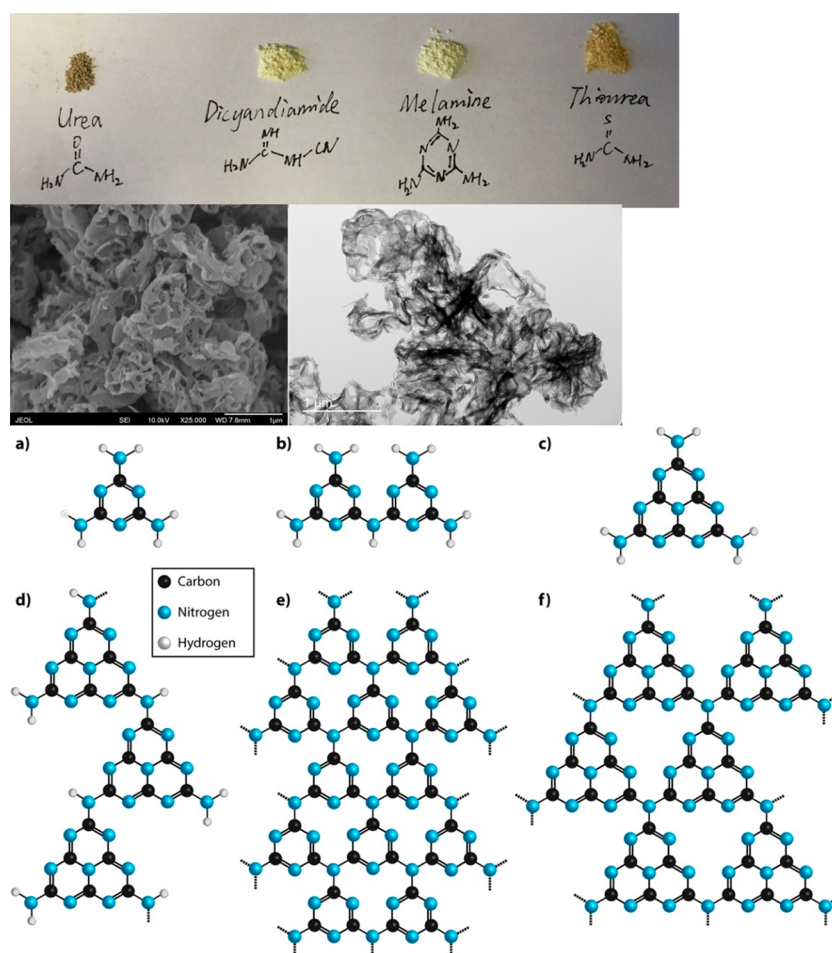
Figure 2. (top to bottom) Different precursors typically used for carbon nitride synthesis and the corresponding final product powder; typical SEM and TEM images of the carbon nitride material and structural motifs for carbon nitride molecules and solid-state structures: (a) melamine; (b) melam, (c) melem; (d) melon; (e) fully condensed triazine-based C_3N_4; (f) fully condensed polyheptazine (tris-triazine) C_3N_4. Adapted with permission from ref 4c, Copyright 2017, Royal Society of Chemistry with permission from Prof. Danmeng Shuai (https://materwatersus.weebly.com/).

dramatically affect the activity, generating for example a reduction in charge recombination rate and thus inflating the claimed catalytic performance. A cross check among various characterization techniques, above all X-ray photoelectron spectroscopy (XPS), elemental analysis, and inductively coupled plasma mass spectroscopy, will confirm the total amount of surface and bulk metal impurities, and allow an understanding if such an amount is catalytically significant in relation to the overall activity.[3c] Just to mention one specific example, graphitic carbon nitride (g-C_3N_4) is a formidable photocatalyst that is enjoying great popularity due to its visible light activity and simplicity in preparation (Figure 2),[4] and the boosting of its photocatalytic performance by metal doping has been well documented,[5] so that it has now become imperative to ascertain whether the apparent activity is tuned by any metal.

On the other hand, this element of confusion regarding impurities is not exclusive to carbon nanomaterials. Adsorbed foreign metal cations on electrocatalytic metallic surfaces has been recognized to bring positive or negative effects in many processes.[6] Similarly in photocatalysis, even by famous semiconductors such as TiO_2, it is a matter of fact that inclusion of foreign metals can create a positive synergy as well as a visible light region shift in the absorption spectra of TiO_2.[7]

The central message is therefore to carry out a rigorous characterization of the prepared photocatalysts by a combination of techniques and finally ensure that the catalyst's activity is reproducible and is not dependent on serendipitous contaminations. Reproducibility implies repetition (not less than three times) of the catalytic experiments with different batches of the same catalyst, with a report of the standard deviation. Unfortunately, many articles discuss the activity on a single catalytic test, which has a large uncertainty. The design of the photocatalyst should be carried out with inclusion of a rigorous purification step to get rid of any presumably occurring impurity. If a nanocarbon is used as one of the phases in catalyst formulation, thorough acid washing prior to its use is a standard preliminary step, as typical impurities include transition metals such as nickel, cobalt, iron, and copper that can be relatively easily dissolved in mineral acid. Attention should be paid to the use of high-purity acid to avoid possible secondary contamination. For some metal derivatives that are used in the synthesis, other side components may be incorporated that are not easily removed with simple acid washing. Moreover, in some cases, even the aforementioned base metals are not totally removed, although levels may be lowered to ppb.[8] However, we suggest that if any tiny doubt arises on the effective participation of unremovable metal

traces, some efforts should be made to design some structural/activity experiments so that the activity can be robustly assigned to specific catalyst moieties.[9] A study of the metal content/catalyst activity relationship could provide indirect proof that the activity is not likely related to the presence of the metal impurity.

REPORTING ACTIVITY DATA: ESTABLISHING A COMPREHENSIVE ANALYSIS OF THE FIGURES OF MERIT

The reporting of the catalyst activity is an infamous aspect of the confusion that surrounds photocatalytic studies. The problem is that many authors provide only a partial analysis (often dictated by convenience), and in many cases erroneous, of how "good" their photocatalyst is. In their recent review, Qureshi and Takanabe provide a detailed and exhaustive discussion on how the figures of merit of a photocatalyst ought to be diligently scrutinized.[10] Here we will expose in more general terms the common shortcomings. It must be first noticed that the complexity of reporting activity data is in general exacerbated when the catalyst is heterogeneous. For a homogeneous catalyst, parameters such as the turnover number (TON) and turnover frequency (TOF) can be reliably estimated, but this does not hold true for heterogeneous systems, where the number of active sites is not unequivocally measured and therefore do not make much sense, requiring adaptations or assumptions. In reality, the use of TOF is still generating some confusion and debate among scientists, as the IUPAC definition is concise and is interpreted differently. For example, the TOF for heterogeneous catalysts is mostly calculated over the number of active sites, but when this is too difficult or impossible to evaluate, it is simply calculated over the moles of catalysts. In the first case, surely the calculation is from a theoretical perspective more accurate to define the intrinsic activity, but on the other hand, it can be very subjective (active sites are in many cases assumed). Moreover, the fact that only a percentage of the catalyst is active is a way to inflate its activity, as in practice the material is still made by using that amount of metal in the synthesis, which has a cost. Hence, in general terms, units of measure for TOF (per moles of catalysts, per number of active sites, etc.) must be always clearly specified. It should also be reminded that the TOF is a kinetic-dependent quantity, where the mechanism and the rate order of the reaction are to be taken into account. Measuring TOF at high (at times total) conversions generates false values, being very different from that calculated at low conversions, as the TOF depends on reagent (and sometimes product) concentration. The instantaneous TOF, calculated from the derivative at a specified concentration, could give an unequivocal value,[11] but this is often impractical to do. However, it can be mathematically proven that calculating the TOF at lower conversions is in most cases the more appropriate course. But do TON and TOF make some sense for hetereogeneous photocatalysis? To some extent yes, if they are used as a mere rough estimation, but they should not be used as a main or unique defining parameter to evaluate a photocatalyst. To exacerbate complexity, many photocatalytic reactions investigated currently are triple-phase reactions, including a solid catalyst, a liquid medium, and a gaseous reagent (for example, CO_2, CO, N_2, etc.) that must dissolve in the liquid, and therefore the kinetics may be limited by diffusion. In reference to heterogeneous photocatalysis, additional considerations emerge, and the TON

and TOF seem to be even less appropriate, because even assuming a complete knowledge of the percentage of the active metal phase, the number of *photocatalytically* active centers is still unknown. In fact, the heterogeneous nature of the catalyst implies that some of the potentially active surface is not illuminated due to shading, taking no part in the catalysis. Hence, the efficiency must be somehow related to the fraction of light that is effectively used by the catalyst. The concept of *quantum yield* (QY) has been introduced long ago, defined for a photochemical reaction as

$$QY(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

where the above QY refers to the absorbed photons of wavelength λ. A core problem for heterogeneous systems is widely acknowledged to be the unknown number of photons that have been actually absorbed, due to the additional scattering and reflection phenomena. For this reason the concept of *apparent quantum yield* (AQY) has been introduced, referring to the number of incident photons of a given wavelength per time and volume that reach the *inside* of the photoreactor.[12] Measurement of the QY is in most cases performed using monochromatic light, which does not consider that this parameter depends on the excitation wavelength.[13] Recently, models were proposed where the QY (or AQY) could be calculated from reaction rates under simulated solar or polychromatic light, which can be better adapted to more complicated photocatalytic materials, including for instance heterojunctions.[14] If monochromatic light is chosen for AQY evaluation, the choice of the wavelength must be as much as possible consistent with the optical features of the photocatalyst. If the catalyst can absorb light of different wavelengths, then reporting the AQY measured with a single monochromatic light source may be misleading. Ultimately, the as-calculated quantum yield should include all of the experimental details in addition to the wavelength used, such as for example the shape of the reactor and the exact time duration of the catalytic experiments upon which the number of moles of product and the number of photons were counted; the latter is relevant, as the rate of product formation might not be constant over time.

Another common practice in attempts to define the merits of photocatalysts is to report rates of product formed by the total mass of catalyst. This common habit of reporting activity can cause a flawed analysis of the catalyst. In fact, the enhancement of activity observed in reporting reaction rate per unit mass, especially for multicomponent catalysts, may be in principle due to simple geometric effects, and this can be confirmed by measuring the rate over the surface area of the catalyst. In a study of Au/TiO_2 photocatalysts for H_2 evolution, it was found that the micro- and nanostructured catalysts exhibited a significant difference in activity when they are normalized by mass. However, normalization by unit area confirmed resulted in equivalent activities, thus confirming that the electronic transfer dynamics of the catalysts were not particle size dependent.[15] We recommend that both data reporting procedures be provided by authors. This does not totally remove all the elements of uncertainty on the real catalysis (the surface area should be combined with a morphological and complete analysis of the material porosity, as it is not guaranteed that all of the surface is illuminated), but we believe it would be a more robust method of reporting activity.

In particular, rates per gram of catalyst can be useful for a preliminary rough evaluation and technological relevance as they provide an immediate idea of the final cost of the catalyst for possible industrial production. On the other hand, surface area normalization bears a more scientific meaning. In any case, the rates of production must be accompanied by AQY data.

To sum up, scrutiny of the photocatalytic activity should be an important part of the design, seriously evaluated to a deep level of details, possibly in relation to other experiments that give information on the kinetics and the mechanism. Given the higher and higher complexity of recent photocatalysts, where multiphase materials are interfaced with a specific hierarchy, we do not discourage a set of different ways of reporting the activity.

■ DOING A CORRECT CATALYST BENCHMARKING

Following the combined experiments carried out to evaluate the photocatalytic activity in the most possible inclusive way, the next step is to understand how the newly reported catalyst ranks among existing catalysts. The benchmarking cannot prescind from all the considerations illustrated earlier. Many studies poorly address this important part of the work and merely compare the material versus standard reference catalysts, such as for example TiO_2 Degussa P25. This surely gives an initial flavor of the catalysts, but the comparison does not always makes sense, and it is also not sufficient to justify publication. It may seem obvious, but there is first a philosophical question: does the paradigm of reporting activity versus Degussa P25 still hold in modern times? We have been bombarded by the brand new policies of editors, industry, grant commissions, and so on that it is imperative that future photocatalytic studies should focus on the exploitation of visible light irradiation. It is a coherent perception that, given the strong connection of photocatalysis with sustainability, future realistic developments hinting at green energy and processes must hinge on exploitation of sunlight. Much of the energy irradiated by the sun falls in the range of the visible spectrum (43%), and even more is actually furnished by the infrared component (52%), but this is at the moment difficult to use for semiconductor photocatalysis, as the energy is too small to generate the required charge separation in most semiconductors. It is, however, worth noting that a few pioneering works on the exploitation of IR radiation have emerged,[16] which bears intriguing promise for future research trends. Certainly the ultraviolet portion (5%) is far too little, and so there is the general feeling that wide-band-gap (larger than ~3.0 eV) semiconductors by themselves can no longer play the leading role and have become obsolete unless they are investigated for the development of strategies built around multicomponent structural configurations, such as Z-schemes and p−n junctions. For this reason, it seems contradictory that the activity must be indistinctly benchmarked versus a UV-active semiconductor such as Degussa P25.

Table of comparisons with state of the art catalysts are appearing with more frequency in current publications. They are more useful if chosen with care, sense, and fairness. Tables should compare not one but as many performance parameters as possible, as far as this is possible. Reporting only a comparison between quantum yields does not say much about either the stability or the selectivity of the catalyst, two equally important terms of comparison. The choice of duration of the experiment for calculating the yield is arbitrary and therefore can be easily bent to the authors' convenience, losing objectivity, especially when the rates of product formation are not constant. Moreover, a catalyst with a higher QY or AQY could be only artificially superior, as it does not rule out a contribution to the evolved product by means of other mechanisms operating in the dark (parallel experiments in the dark under same conditions of temperature, catalyst loading, etc. must be invariably carried out). Another important aspect is that the experiments for AQY are normally carried out with monochromatic light sources, and as mentioned above, quantum yields vary with excitation wavelengths. Tables of comparisons exclusively discussing quantum yield ideally require a comparison made with polychromatic light sources or at least between photocatalysts principally absorbing in the same narrow wavelength range (a condition difficult to achieve). Obviously a comparison should also be made versus catalysts explored under the same catalytic conditions (reaction media, temperature, catalyst loading, etc.). The terminology is another aspect that should not be underestimated, as it can create confusion. As defined earlier, the QY and AQY refer to the amount of reactant consumed (or product formed); other IUPAC definitions more often used in heterogeneous photocatalysis consider *quantum efficiency* (QE) and *photonic efficiency* (PE), the former referring to the rate of photochemical events divided by the absorbed photon flux and the latter to the ratio of the photoreaction rate measured for a specified time interval to the rate of incident photons.[17] Authors need to make sure they are comparing the same parameters. Overall, we discourage a benchmarking made exclusively on QY, QE, or PE, as in our opinion this is incomplete and potentially misleading (Figure 3).[18] Other
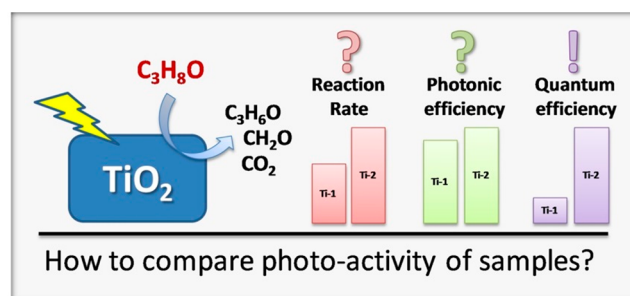
Figure 3. Visual comparison of two TiO_2 catalysts for 2-propanol degradation based on three different activity parameters (reaction rate, photonic efficiency, and quantum efficiency). Depending on the chosen parameter, the two catalysts display unequal levels of activity improvement. Reprinted from ref 18. Copyright 2017, with permission from Elsevier.

activity data can offer additional key information: reporting the rates of product formation over an extended time provides an assessment of the stability of the catalyst and a rough indication of possible different mechanisms, and a comparison on these terms is essential for the design of catalysts to be transferred to an industrial scale. The rates to be compared should be reported both per mass of catalyst and per surface area, for the reasons explained above.

Finally, a seemingly too long step is in our belief also something that should be contemplated in future publications: namely, a comparison made on the current cost of the photocatalytic package. This aspect seems estranged from academic work, dealing with fundamental knowledge and therefore in principle not to be hampered by money

restrictions. However, we must accept that research is more and more connected to industry and that funding is partially determined by an economic analysis of the project proposals; therefore, this aspect can no longer be neglected. It is customary in recent publications to advance claims on the importance of the reported materials because of the absence of precious metals, which have long been (and still are) included as cocatalysts.[19] This is a too general speculation, which does not say much about how actually cheaper the material is; as a matter of fact, not including a precious metal (often used at a small mass loading) is not necessarily a cheaper choice, as the material could still be based on costly precursors or tedious reaction conditions (solvent, temperature, purification, etc.) that eventually end up inflating the cost of the suggested catalyst. It is perhaps time to attempt some quantification of the cost associated with the proposed photocatalyst, not only because in modern times it is an essential aspect but also because it will encourage optimizations in this respect by other scientists.

■ PHOTOCATALYSIS UPDATED TRENDS: HOT PIPELINES AND UNDERSTANDING YOUR CATALYST

In this final section, a very brief overview will be given on what are today's hot topics in photocatalysis: the processes, the scientific goals, and the expected future milestones. The discussion cannot ignore the synergy of photocatalysis with sustainability, where the concept of sustainability overarches several themes such as climate change, green energy, better use of resources, and others that are keeping politicians, activists, and business operators very busy. Due to the continuous damage that we all are inflicting on a more and more suffering planet, it is mandatory to make dramatic changes in our behaviors. The complexity of such much-discussed themes is somehow disheartening, as a large number of pieces ought to come together to solve the puzzle. Still, photocatalysis can make a valuable contribution to ease the pressure. For this reason, a massive wave of research is occurring over the development of innovative materials and alternative processes to afford the so-called "solar fuels",[20] where energy fuels and vectors are prepared by starting from nonfossil substrates. Recapture and conversion of CO_2 in principle fulfills the ideal carbon-neutral energetic cycle, simultaneously generating fuels and decreasing CO_2 levels in the atmosphere.[21] Exploiting solar light to chemically cleave atom bonds in CO_2 and form new bonds is nonetheless a difficult task, with a notable required energy, in particular in view of the efforts to trigger the process with visible light. Consequently, an arsenal of diverse approaches are being proposed, including the development of alternative materials and multicomponent hybrids with tuned properties, to enhance activity and selectivity.[22] As far as CO_2 reduction is concerned, the analytical aspects are very critical, as a fraction of the carbon products could be generated not through the reduction process but from partial decomposition of the catalytic material. Therefore, especially for experiments based on a small scale, where the amounts of products are very low, the effective mechanism must be carefully confirmed with multiple analytical techniques, including the use of $^{13}CO_2$ to exactly trace product origins.[23] While the number of publications on this subject is proliferating, current endeavors are successfully achieving the so-called "artificial photosynthesis", where CO_2 reduction is coupled with H_2O oxidation, with the two half-reactions

catalyzed in one pot by a single synthetic material, exploiting for example Z-schemes (Figure 4) or facet engineering.[24]
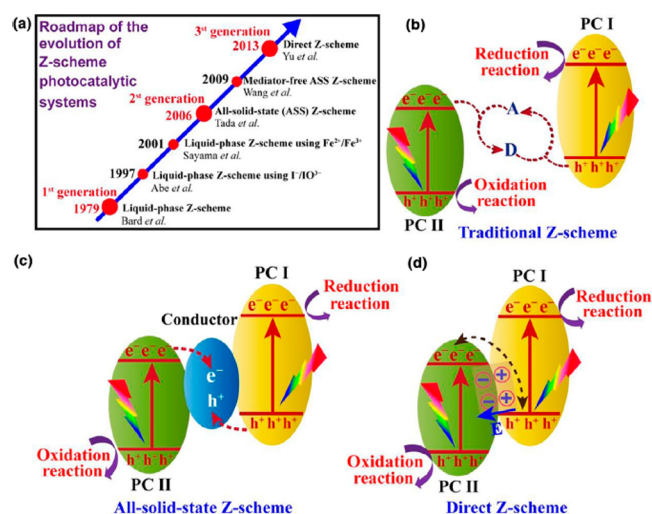

Figure 4. (a) Z-scheme photocatalyst evolution roadmap. (b−d) Schematic illustration of the different types of Z-schemes, respectively: traditional, all-solid-state, and direct. A and D denote the electron acceptor and donor, respectively. E denotes the electric field. Reprinted from ref 24e. Copyright 2018, with permission from Elsevier.

Hydrogen evolution through pure water splitting or by valorization of biomass is another vastly investigated heterogeneous photocatalysis research topic.[25] H_2 is a particularly appealing molecule not only because of the high expectations in the development of alternative energy schemes but also because of its importance in many other processes, such as oil refining, ammonia synthesis, fine chemical synthesis, hydrodesulfurization (HDS), and so on.[26] With regard to H_2 evolution, some confusion has arisen in the past, where the process was indistinctly referred to as "water splitting", opening a debate on the correct terminology. In fact, the pure splitting of the water molecule is a thermodynamically challenging process because of the half-reaction of water oxidation, rather than the proton reduction to hydrogen. For this reason, the former half-reaction is a bottleneck that compromises success for many catalysts that are reported as "water splitting catalysts". Indeed, such catalysts are able to form reasonable amounts of H_2, but only if electron donor species are used in the reaction, which in practice replace the water molecule as hole quenchers, due to their more favorable oxidation potential.[27] We note with relief that such confusion has been gradually disappearing in most recent years, with papers being more clear on whether the process is pure water splitting or H_2 evolution using sacrificial electron donors (SED). Information on the destiny of the SED must be provided, with a rigorous analysis of oxidation products, to have a correct mechanistic view.[28] Moreover, understanding the fate of the sacrificial electron donor is essential, because there may be undesired roles that are overlooked in a first analysis. For example, the as-formed oxidation product could compete for the reduction reaction by the catalyst, thus decreasing the H_2 productivity.[29] Today's challenge is more focused on achieving the more difficult water splitting, with the purpose of making a solar fuel (H_2) by a fully sustainable pathway. On the other hand, H_2 evolution with use of sacrificial donors bears interest because it

can provide fundamental insights in material development studies.[30] Moreover, if the sacrificial donor is an organic compound, the oxidation reaction can be exploited (in concomitance with H_2 evolution) for the synthesis of value-added compounds,[31] provided that the reactivity is under selectivity control, or for pollutant degradation.[32] An emerging field is related to the sustainable synthesis of ammonia from water and N_2,[33] able to replace the energy-intensive traditional Haber–Bosch process.[34] The endeavor is motivated by the high relevance of ammonia in the synthesis of fertilizers, fibers, and other commodities. As this synthesis is based on two thermodynamically challenging processes, the oxidation of water and the reduction of N_2 ($\Delta G° = 339$ kJ mol^{-1}; the dissociation energy for an N≡N bond is 941 kJ mol^{-1}), the hurdles are considerable, and at present amounts of the NH_3 generated are still very low.[35] However, progress is continuously being reported.[36] It must be noted that a notorious problem with these studies is associated with the technical difficulties in the reliable quantification of the as-produced ammonia, that put a question mark on the reported data. Rigorous protocols have been suggested for the electrochemical synthesis,[37] and similar care should be used in carrying out photocatalytic N_2 fixation. Apart from the energy and activation of small molecules, a vast realm of photocatalytic applications include organic transformations for the synthesis of industry-relevant molecules. While homogeneous catalysts have been traditionally more explored,[38] heterogeneous reactions are becoming more and more popular, especially driven by the cost effectiveness of the catalytic material, as in the case of graphitic carbon nitride.[4b,39] Finally, research on the degradation of pollutants for cleaning water or air is still progressing, although it is experiencing oscillating interest and is at the moment a less hot topic.[40]

From a different perspective, which does not concentrate on the process, photocatalysis is also gazing at innovative materials, exploring strategies to enhance photoabsorbance, charge carrier lifetimes, stability, and others. While Z-scheme configurations of the semiconductors are currently well established and highly promising,[41] research is focusing on other methodologies and materials to improve the photo-activity or other important properties. Covalent organic frameworks (COF) bear robustness, versatility, and excellent textural properties, relying on extended π-conjugated frameworks that improve the photochemical response.[42] Plasmonic metals have been known for some time as photocatalytic components, where the tunable surface plasmon resonance effects allow the possibility of exploiting a large portion of the solar spectrum. They can thus usefully interact with semi-conductors by different mechanisms, enhancing rates of product formation to a significant extent.[43] As far as plasmonic metals are concerned, it is significant to distinguish the catalytic contribution derived from thermal effects, due to the ability of plasmonic nanoparticles to act as "hot spots" and localize heat, thus promoting activity.[44] This exciting property of plasmonic nanoparticles has been exploited in various applications (Figure 5), where the time scale levels of the events following thermally induced generation of hot carriers suits specific exploitation of the particular process.[45]

Since the early 2000s, the light-induced heating of plasmonic metal nanoparticles has found applications in photothermal cancer therapy, catalysis, steam generation, and desalination. Significant advances have been made in the development of thermo-plasmonic thin-film systems, which overcome the
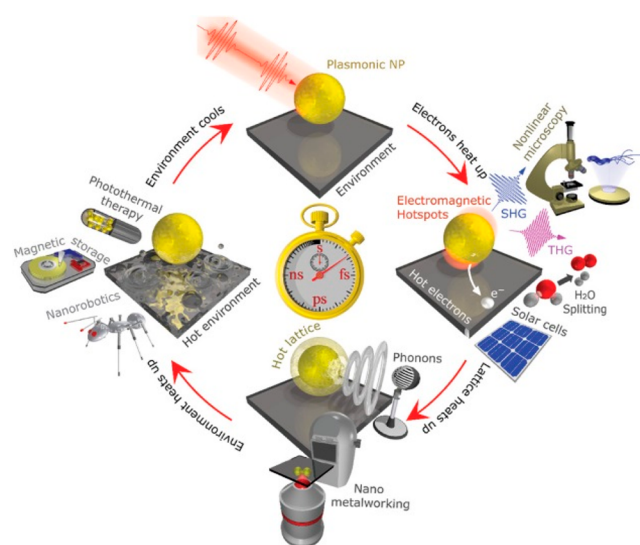
Figure 5. Temperature cycle in plasmonic nanoparticles upon illumination. After illumination (femtosecond time scale), electromagnetic hotspots are generated. These hotspots can enhance nonlinear optical processes for advanced imaging applications. Hot electrons can also be created to be exploited in catalysis. Subsequently, phonons are generated in the picosecond range by lattice heating for nanometal-working techniques. Next, on the nanosecond time scale, environment heating enables applications in photothermal therapy, magnetic storage, and nanorobotics. Finally, the environment cools and the cycle can repeat. Reprinted from ref 45, with permission from Wiley.

intrinsically low thermal stability of nanoparticles and have also found applications in areas such as templated growth of nanostructures, optical nanotweezers, heat-assisted magnetic recording, and energetic materials. It is expected that the field will significantly increase in the near future, with emerging materials such as TiN.[46] As far as photocatalysis is concerned, discerning and quantifying the contributions of hot carriers generated by the nonradiative decay of surface plasmons and carriers generated by photoexcitation are complicated. However, recent ingenious works have shown that this can be achieved, as shown by Zhou et al., who introduced the concept of *light-dependent activation barrier* to understand the electronic and thermal excitation contribution in catalytic ammonia decomposition.[47]

Another recently explored avenue aiming at alleviating the big problem of fast charge recombination in semiconductors contemplates the exploitation of polarization. The polarization electric field can promote the migration of electrons and holes to different regions of the semiconductor or accelerate the charge transfer on the surface of photocatalysts when they are employed as cocatalysts.[48] Piezoelectrics are, for instance, a class of materials that have been proven to be promising in photocatalysis as a consequence of their noncentrosymmetric structure.[49] The last message of this section is that the way to approach photocatalysis has a multiple nature and depends on the interests and competencies of the scientist. In all cases, the benefit to the overall photocatalysis community is evident but is also hinged on the rigor and quality of the experiments. Without going into any specific reference, we finally believe that the inclusion of computational work into the design of advanced photocatalytic materials represents a considerable help for the photocatalysis community and its growth and that collaborative work between the experimental and computa-

tional scientists will generate a leap forward in knowledge and progress.

CONCLUSIONS

Heterogeneous photocatalysis has become a rapidly expanding galaxy with multiple diverse subjects being explored and developed. It is recognized that each different stream of research inevitably has a certain autonomy due to the different issues addressed and the variability of the specific technical challenges. For this reason, an attempt to standardize all the topics in terms of reported data under a common umbrella of rigid rules is to a certain extent a chimera. Surely, a few general good practices can be shared and must be followed, but it must also be accepted that the different subtopics of photocatalysis should enter into their own class when it comes to reporting data. Despite the notable progress, there is still too much confusion in papers associated with photocatalysis, where terms of comparison are often unclear or mistakenly arbitrary. The inhomogeneity in reporting figures of merit is a classic sensible point, as well as the correct establishment of the true mechanistic nuts and bolts, that can be largely unreliable on account of the deficient assessment of the catalyst's structural features. It is time to make an effort and propose agreed guidelines in each of the photocatalysis subjects, so that future research will be more efficient and less time and money wasted.

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Notes
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