Fundamentals and misconceptions in photocatalysis

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ABSTRACT

Photocatalysis has presently become a major discipline owing to two factors: (i) the intuition of the pioneers of last 20th century and (ii) the mutual enrichment of scientists arising from different fields: photochemistry, electrochemistry, analytical chemistry, radiochemistry, material chemistry, surface science, electronics, and hopefully catalysis. However, heterogeneous photocatalysis belongs to catalysis, which means that all the bases of this discipline must be respected and consequently, it has become imperative to refocus the frame of photocatalysis to avoid misfits and misconceptions: (i) proportionality of the reaction rate to the mass of catalyst (below the plateau due to a full absorption of photons); (ii) implication of the Langmuir–Hinshelwood mechanism of kinetics with the initial rate being proportional to the coverages θ in reactants; (iii) obtention of conversions beyond the *stoichiometric threshold* defined as the number of potential active sites initially present at the surface. Photonics should be respected with the photocatalytic activity being (i) parallel to the absorbance of the photocatalyst and (ii) proportional to the radiant flux Φ, enabling one to determine the quantum yield defined as the ratio of the reaction rate r (in molecules converted per second) to the efficient photonic flux (in photons per second) received by the solid. True photocatalytic normalized tests should be established to prove the real catalytic activity of irradiated solids, independent of non-catalytic side-reactions. In particular, dye decolorization is a misleading test, which only provides a "visible" and apparent "disappearance" of the dye, purely photochemical but not photocatalytic. Thermodynamics have also to be respected. The decrease of photon energy to the visible may be thermodynamically detrimental for the generation of highly active species such as OH$^\circ$. Concerning solid state chemistry, it is now eventually admitted that cationic doping is detrimental for photocatalysis. Anionic doping must be rapidly clarified or otherwise abandoned. In conclusion, all these recommendations have to be addressed and experiments have to be operated in suitable conditions before claiming that one deals with a true photocatalytic reaction, whose veracity can be proved by following a protocol suggested at the end.

1. Historical introduction

At the end of 20th century, heterogeneous photocatalysis appeared as a new emerging "Advanced Oxidation Process" (AOP), as illustrated by the reports in Ref. [1] with more than 2000 publications registered on the subject. Presently, more than 1000 articles are published yearly. Heterogeneous photocatalysis is simultaneously able to be efficient in Green Chemistry, in Fine Chemicals and in emerging "Advanced Oxidation Processes" (AOP) [2–4]. Nowadays, this last domain is preferentially studied [5–7] but people must not forget that photocatalysis is able to provide highly selective mild oxidation for organic fine chemistry [8]. Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously **ad**sorb reactants and **ab**sorb efficient photons ($h\nu \geq E_G$).

Initially, photocatalysis originated from different catalysis laboratories in Europe. In England, Stone first studied the photo-adsorption/desorption of oxygen on ZnO [9] before studying the photocatalytic oxidation of CO on the same solid [10]. He subsequently switched to titania under rutile phase for oxygen photo-adsorption [11] and selective isopropanol oxidation in acetone [12]. This last reference was the first one, to my knowledge, to mention OH$^\circ$ radicals as oxidizing agents formed by neutralization of surface OH$^-$ by photo-holes h$^+$. In addition, this simple and selective reaction was and still remains a direct and simple test to put in evidence some photo-activity of solids. Simultaneously, in Germany, Hauffe was also studying the photocatalytic oxidation of CO on ZnO [13,14] and, actually, this reference was the first one to include the term "photocatalysis" in its title. In the same decade, Juillet and Teichner in France were studying the sintering of ultra-pure oxide powders for nuclear applications and tested their solids through their electrical properties.

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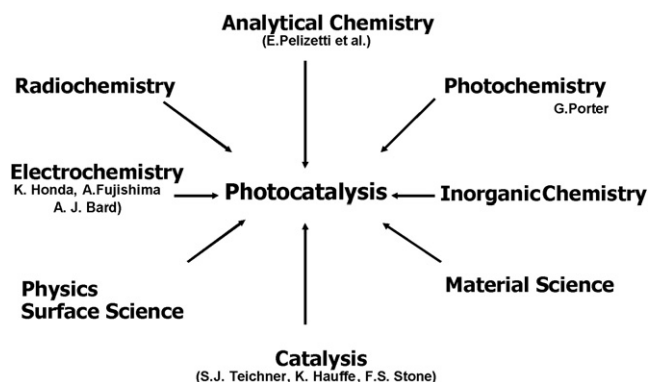
Fig. 1. Contributions to photocatalysis from various sub-disciplines of chemistry.

Fig. 2. Commonly adopted but misleading titania's energy band diagram. Influence of the different physical parameters, which govern the kinetics of photocatalysis: reaction rate r; (A) mass of catalyst m; (B) wavelength λ; (C) initial concentration c of reactant; (D) temperature T; (E) radiant flux Φ.

The erratic results obtained on titania anatase puzzled them till they realized that titania was photosensitive to daylight, especially in sunny days [15]. They subsequently used the photo-activated oxygen species to perform mild and selective oxidations of light alkanes [16,17].

Actually, whereas photocatalysis was developing confidentially in Europe, there was an "earthquake" in or from Japan, according to Bickley [18] with the re-publication in English of a previous work by Fujishima and Honda on the photo-electrolysis of water using a UV-irradiated titania-based anode [19] in the review "Nature" (238 (1972) 37). This constituted the initial event for a globalization of photocatalysis, which had a preferential development in Japan, as illustrated by Ref. [20]. Unfortunately, newcomers in the field of photocatalysis have never read this article and improperly cite it as the starting point of photocatalysis, which is obviously erroneous. From this date, photocatalysis received valuable contributions from other chemical sub-disciplines. Photocatalysis became a major discipline owing to the mutual enrichment of scientists arising from different fields: photochemistry, electrochemistry, analytical chemistry, radiochemistry, material chemistry, surface science, electronics, and hopefully "catalysis" as illustrated in Fig. 1.

Facing the exponential number of publications globally appearing in the literature, the frame of photocatalysis must be urgently refocussed, especially by senior scientists. This is the aim of the present article.

2. Common erroneous features

Several presentations and concept are erroneous or misleading. Two examples are given.

2.1. Energy band diagram

In almost all reviews or introductions on photocatalysis, including my previous own ones [2–4], the energy band diagram is generally presented in the shape of Fig. 2. I realized that it was not logical nor homogeneously presented, when once I was asked by a colleague to explain it to him.

This representation is wrong since it mixes an allegoric and geometrical catalyst particle representation with and into an energy band diagram of titania with the electron energy plotted upwards. Such a representation cannot be understood by a non-initiated reader, as I experimentally checked several times. In addition, it is wrong and misleading since the curved arrows seem to indicate that the photo-excited species formed at the surface escape from this surface to react in the ambient (gas or liquid) fluid phase, which would lead to a kind of radicalar reaction in contradiction with a true heterogeneous catalytic process as stated further. A less aesthetic but more realistic model is given in Fig. 3 with a diagram of
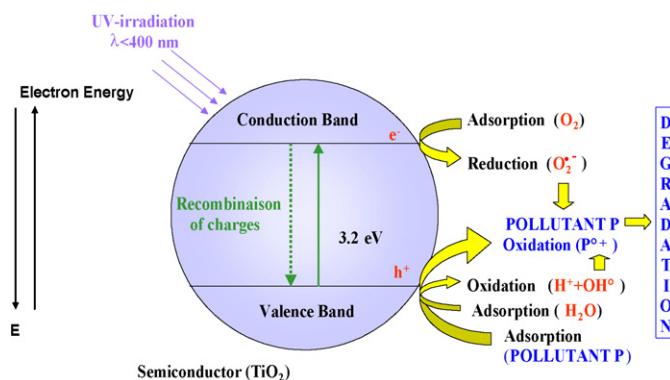
the electron energy as a function of the distance from the surface to the bulk of titania.

As a consequence, photocatalysis mechanism must not be illustrated any more by Fig. 2, although it looks pretty "mediatic", in line with the present tendencies in molecular and homogeneous catalyses.

2.2. Schematic bifunctional Pt/TiO$_2$ photocatalysts

Many articles mention the addition of a noble metal, mainly Pt, to hypothetically improve the photocatalytic activity of titania. Actually, the addition of Pt is only working with bifunctional Pt/TiO$_2$ photocatalysts for hydrogen-involving reactions [21]. Moreover, it has been semiquantitavely shown that (i) Pt is indispensable for hydrogen production in reducing conditions but (ii) it is oppositely detrimental for oxidation reactions [22].

Very often the preparation of Pt/TiO$_2$ photocatalysts is not accurate enough and it is not sure whether the final Pt/TiO$_2$ photocatalysts, especially those obtained by photodeposition, are irreversibly stable, as those obtained in conventional catalysis with reduction by hydrogen [21]. One has to be sure if there remain some cations such as Pt^{IV} or Pt^{2+} on titania, which could later play the role of hidden oxidants when reducing to Pt^0, thus conferring to this catalysts undue oxidative activity. Generally, they are poorly characterized by contrast with conventional heterogeneous catalysts for hydrocarbon- and hydrogen-involving reactions.

Many references illustrate their Pt/TiO$_2$ catalysts as in Fig. 4. Such a representation is totally erroneous as evidenced by TEM.
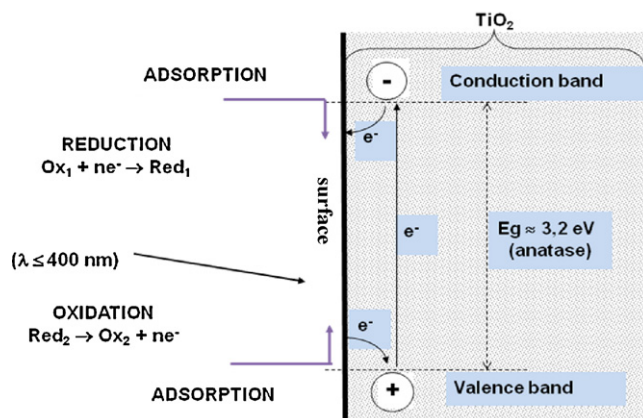

Fig. 3. Correct electron energy band diagram of titania: electron energy E plotted upwards as a function of the distance from the surface to the bulk of the solid.
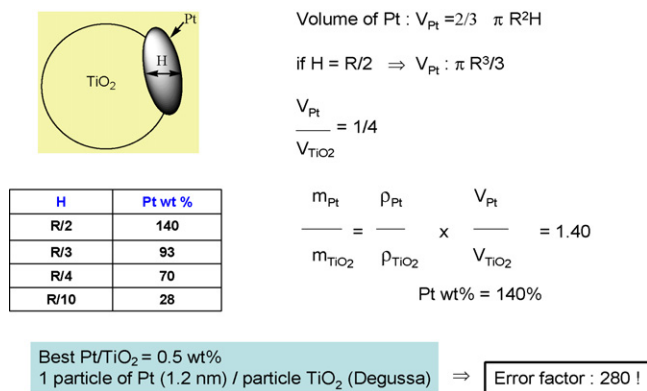
Fig. 4. Erroneous schematic representation of Pt/TiO$_2$ (for explanations, see text).

Platinum deposited on titania via the recipes of conventional and industrial catalysis is generally present as small particles of 1–2 nm, which are characterized by the dispersion D, corresponding to the ratio of the number of surface metal atoms n_S to the total number n_T of metal atoms present.

$$D = \frac{n_S}{n_T}$$

D can be easily measured with simple reactions such as hydrogen chemisorption, oxygen chemisorption or H$_2$–O$_2$ titrations [23]. Assuming a population of homodispersed (i.e. with the same size) metal particles, the mean particle size d expressed in nanometer could be easily related to dispersion D by the simple equation:

$$d\,(\text{nm}) \approx \frac{1}{D}$$

Actually, unity in the numerator is not fortuitous but results from the calculation of the mean surface density of metal atoms, which is almost constant for transition metals [23,24]. For example, a metal with a dispersion of 0.8 (or 80%) is present under the shape of particles having a mean diameter of 1.2 nm. All these results were confirmed by Transmission Electron Microscopy (TEM) [25].

If one considers the purely speculative scheme in Fig. 4, one can calculate the corresponding metal loading. According to the shape given to Pt deposit, it can be assimilated to a spherical calotte, whose volume is equal to $(2/3 \pi R^2 H)$. In Fig. 4, an inserted table gives the calculated Pt loadings as a function of the thickness H, expressed in radius fractions. This clearly demonstrates that the model in Fig. 7 is quite unrealistic. In particular, if one considers that the optimum Pt/TiO$_2$ bifunctional photocatalyst contains 0.5 wt.% Pt [25], the calculation can reach an error factor equal to 280, if thickness H is chosen equal to $H = R/2$, as often found in the literature, similarly to Fig. 4.

All these results confirm that Transmission Electron Microscopy (TEM) examinations with many electronic micrographs are a pre-requisite to invoke platinum (or noble metals) in Pt/TiO$_2$ photocatalysts! By contrast, articles originating from laboratories of Surface Science and containing the term "photocatalysis" in their title are very often full of DRX spectra and of TEM micrographs but contain only a few lines on catalytic results, just as an appendix to justify the title.

2.3. Quantum yield ⟨QY⟩ (or quantum efficiency)

In photochemistry, the quantum yield is defined as a yield, i.e. as the number of molecules converted per quantum absorbed by the medium. In heterogeneous photocatalysis, the situation is more complex. Such a definition of quantum yield could be useful for example to determine the irradiation time necessary to reach a certain conversion in a simple reaction under a given UV-photonic flux. The notion of instantaneous ⟨QY⟩ is closer to the kinetic reality and can be defined as a dimensionless, "doubly kinetic" magnitude equal to the ratio of two rates: the reaction rate r (in molecules converted per second) divided by the efficient photonic flux φ (in UV-photons per second) actually absorbed by the solid.

$$\langle \text{QY} \rangle = \frac{r}{\varphi}$$

This is an instantaneous magnitude directly linked to the parameters governing the reaction rate, in particular to the concentrations or partial pressures. The maximum values of ⟨QY⟩ are obtained at maximum coverage of reactants. The highest QY I ever experimentally observed in my laboratory was ca. 0.40 (or 40%) in the case of methanol dehydrogenation in pure liquid phase, i.e. with $C = 25$ mol/L [25]. On the contrary, for pollutant trace eliminations, ⟨QY⟩ mathematically decreases to less than 1% (<0.01), because of very low coverages resulting from the Langmuir–Hinshelwood equation (see further in Section 4.1).

As a concluding remark of this section, high ⟨QY⟩ can only be obtained at full coverages in reactants. The high ⟨QY⟩ values cited in the literature, that are obtained at very low pressures or concentrations, especially in diluted solutions or in trace elimination or with super-powerful UV-lamps, may appear as suspect.

2.4. Control of electrical powers, energies and photon fluxes used for the turnover frequency determination

High quantum yields are indicative of the facility of the photocatalytic reactions performed. For low ⟨QY⟩, it is not necessary to use over-powered electrical lamps. Actually, it is necessary to know the number of UV-photons emitted per second. Visible photons are inactive, while IR-ones can be detrimental for the initial adsorption of the reactant (see Section 5). Therefore they must be eliminated by a water cell fitted to laboratory photoreactors as described in Refs. [3,16,17]. For the initial solar photoreactors, whose technology was based on thermal solar reactors using concentrators, coolers were required [26]. As mentioned above, radiant UV-fluxes must be adapted to ⟨QY⟩ comprised between a fraction of % and 40–50% in realistic studies.

The notion of turnover frequency ⟨TOF⟩ in heterogeneous catalysis has also to be taken into account. Its definition is the same as in enzymatic or homogeneous catalysis, i.e. the number of molecules converted per second and per active site [23]. It can be determined in heterogeneous catalysis only if the nature and number of active sites have been carefully identified and quantified. It is easy for noble metal-based catalysis since every surface metal atom can be considered as an active site. In that case, Boudart estimates that correct values should range between 10^{-2} and 10^{+2} s^{-1} with a correct mean value around 1 s^{-1} [23]. Low values of ca. 10^{-3} s^{-1} can be incorrect because of large analytical errors. On the opposite, ⟨TOF⟩ higher than 10^{+3} s^{-1} can become limited by diffusion [23]. In heterogeneous photocatalysis, ⟨TOF⟩ is much more difficult to be determined. As an upper limit of the number of active sites n_{sites}, one can choose the maximum value of the surface density of titanol groups Ti-OH, equal to 5×10^{18} OH/m^2 or 5 OH/nm^2 [27]. Therefore, one gets: $n_{\text{sites}} = 5 \times 10^{18}$ OH/m$^2 \times S_{\text{BET}} \times m_{\text{cat}}$.

2.5. Confusion between reaction rate and conversion

In several articles, it is generally mentioned that the reaction rate r is of the (apparent) first order as expected for diluted reaction media. Therefore, one should expect an increase in the rate r as concentration C increases. Very often in published or in submitted articles, a few lines further than the mention that "reaction rate r is of the first order", it is written that the rate decreases when one
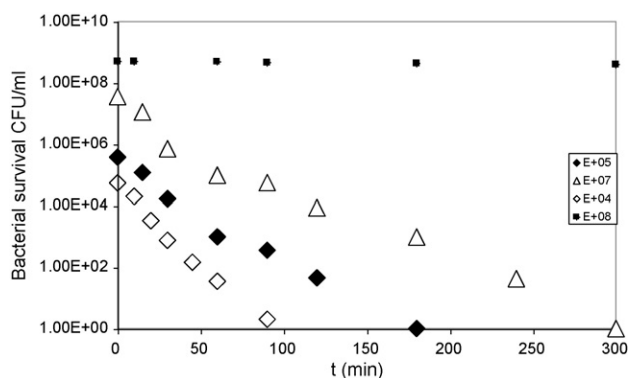
Fig. 5. Kinetics of the bacterial survival decrease of wild type *E. coli* in the presence of UV-irradiated TiO$_2$ Degussa P-25 at different initial concentrations.

increases the concentration. This surprising contradiction is due to the confusion between reaction rate *r* and conversion τ!

Conversion τ is defined as:

$$\tau = \frac{(C_0 - C)}{C_0} = 1 - \frac{C}{C_0}$$

and is generally expressed in %. It must be clearly understood that it is faster to eliminate say 50% of a solution of 10^{-6} mol/L than 50% of a molar solution (1 mol/L) since a photocatalytic reaction is limited by the photon fluxes delivered by the lamps and their corresponding quantum yields.

Actually, in a **true** or apparent first order reaction, the integration of the reaction rate $-dC/dt = kC$ gives $C = C_0 \exp(-kt)$ or Ln $(C/C_0) = -kt$. Therefore, conversion τ is equal to:

$$\tau = \frac{(C_0 - C)}{C_0} = 1 - \frac{C}{C_0} = 1 - \exp(-kt)$$

Consequently, it clearly appears that in a first order reaction, conversion is independent of the initial concentration C_0 but, conversely, the rate and the number of converted molecules per time unit are proportional to C_0.

To illustrate this misunderstanding in kinetics, I have chosen an example in my laboratory to respect the anonymity of several authors in the literature with erroneous interpretations based on the confusion of rate vs conversion. Let us consider the effect of the initial concentrations of *E. coli* in a very large range of almost 4 orders of magnitude on the photocatalytic disinfection efficiency of TiO$_2$ Degussa P-25 [28].

The bacterial survival of wild type *E. coli* (*E. coli* 849), performed at different initial concentrations, is depicted in the semi-log plot of Fig. 5. Indeed, the use of a semi-log plot was aimed at presenting all the results in a same figure for $1 < C_0 < 5 \times 10^7$ CFU/mL. As expected, longer times are required for bacterial inactivation at higher bacterial concentrations to reach a given conversion. Facing Fig. 5, students in the lab spontaneously claimed: "*the lower the concentration, the higher the reaction rate!*", similarly to what is often briefly and crudely written in the literature.

2.6. Respect to thermodynamics and photonics

The energetics of photocatalysis is based on the energy *E* of the photons, i.e. $E \geq E_G = 3.2$ eV. This energy represents 308 kJ/mol and/or 73.7 kcal/mol, i.e. a strong supply in energy. Consequently, it enables titania to produce very strong oxidizing agents, the photoholes h$^+$. This virtual positive charge is chemically supported by O$^-$ surface or bulk lattice anions of titania. This is the chemical oxidizing species, very strongly electrophilic. In particular, it is responsible for the generation, in presence of adsorbed water, of

OH$^\circ$ radicals, the second best oxidizing agent after F$_2$.

$$p^+ + H_2O \rightarrow H^+ + OH^\circ$$

or

$$O^- + H_2O \rightarrow O^{2-} + H^+ + OH^\circ$$
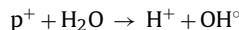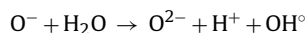
The tentative to decrease the photon energy towards the visible to "harvest the abundant visible energy spectrum of the sun" should take into account the necessity of passing over a minimum energy threshold since, otherwise, the energy supply for the activation and the generation of such highly cracking and degrading species that are OH$^\circ$ radicals would become thermodynamically detrimental.

2.7. Minimum conversion required to exceed the "stoichiometric threshold"

For demonstrating the *true catalytic nature* of a photocatalytic reaction, the conversion has to be carried out beyond a certain percentage corresponding to the catalytic threshold. It is defined as the minimum number of molecules that have to be converted to be greater than the maximum number of potential active sites initially present at the surface of a mass *m* of titania photocatalyst used in the reaction. If we admit for titania that the maximum surface site density is equal to 5×10^{18} sites/m^2 according to Boehm [27], therefore one should obtain a minimum number n_{min} of molecules converted equal to: $n_{min} = (5 \times 10^{18}) \times m \times S_{(BET)}$. For example, if a photoreactor contains 1 g of titania Degussa P-25 (with $S_{(BET)} = 50$ m^2/g), which is fully illuminated and respects the laws mentioned above, a given photocatalytic reaction could be declared "truly catalytic" only if the number of converted molecules is higher than $n_{min} = (5 \times 10^{18}) \times m \times S_{(BET)} = 2.5 \times 10^{20}$ molecules/g$_{cat}$, i.e. 4.2×10^{-4} molecules/g$_{cat}$. Actually, a true catalytic system should work with ratios n/n_{min} of several orders of magnitude. For example, ratios n/n_{min} much higher than 10^3 could be obtained in alcohol dehydrogenation [21].

The test for the respect of the stoichiometric threshold is particularly important for dealing with a true catalytic process. In the problem of air and/or water purification, one is faced with traces elimination. The disappearance of such traces can be easily measured and quantified but disappearance does not mean degradation. It can also result from non-catalytic artifacts (adsorption, electron transfer reactions, side photochemical reactions, etc.) as evidenced in indigo carmine decoloration in the visible [29].
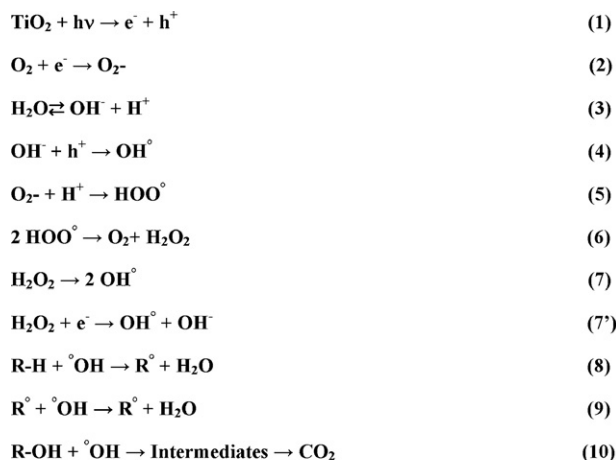
2.8. Mass balance determination

All the studies in photocatalysis, should include an exhaustive overall mass balance analysis. Two examples can explain this necessity.

2.8.1. Mass balance of organic nitrogen

First, in the photocatalytic degradation of azo-dyes, the nitrogen mass balance, established on the final contents in NH$_4^+$ and NO$_3^-$ could only reach ca. 30–35% [3,4]. A thorough complete analysis indicated an unsuspected evolution of gaseous nitrogen in the air. Actually, this amount of N$_2$ (g) corresponded to a 100% selective conversion of the –N=N– azo-groups. Such a result underlines the environmentally friendly character of the photocatalytic degradation of azo-dyes, whose interest is accentuated when one realizes that azo-dyes represent 45% of the global industrial dye production.

A second example concerns the degradation of pesticides and of dyes containing a strongly aromatic triazinic ring. Although the HPLC analyses indicated the formation of cyanuric acid C$_3$H$_3$N$_3$O$_3$ as the unique final product, the Total Organic Carbon (TOC) analyzer indicated a total conversion of the organic matter as CO$_2$. The truth

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$O_2 + e^- \rightarrow O_2^- \quad (2)$$

$$H_2O \rightleftarrows OH^- + H^+ \quad (3)$$

$$OH^- + h^+ \rightarrow OH^\circ \quad (4)$$

$$O_2^- + H^+ \rightarrow HOO^\circ \quad (5)$$

$$2\,HOO^\circ \rightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 \rightarrow 2\,OH^\circ \quad (7)$$

$$H_2O_2 + e^- \rightarrow OH^\circ + OH^- \quad (7')$$

$$R-H + {}^\circ OH \rightarrow R^\circ + H_2O \quad (8)$$

$$R^\circ + {}^\circ OH \rightarrow R^\circ + H_2O \quad (9)$$

$$R-OH + {}^\circ OH \rightarrow Intermediates \rightarrow CO_2 \quad (10)$$

Loss of one carbon atom via the "photo-Kolbe" reaction:

$$R-COO^- + h^+ \rightarrow R-COO^\circ \rightarrow R^\circ + CO_2$$
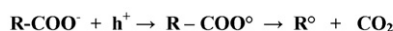
Fig. 6. Successive elementary reactions in a total oxidative degradation reaction involving some transient radical intermediates.

was that HPLC analyses were correct, whereas the TOC-analyzer was unable to destroy $C_3H_3N_3O_3$ into three CO_2 molecules for their IR detection because of the too high stability of cyanuric acid. The consequence was that the assertion by Pelizzetti et al. according to which cyanuric acid could not be destroyed by photocatalysis, was still true [30].

2.8.2. Mass balance in radicalar unpaired electrons

The electrical charge neutralization of adsorbed ions at the surface of titania by photogenerated electrons and/or holes generates transient radicals which are symbolized by dots in superscript. For instance, one can cite OH° generation:

$$OH^- + h^+ \rightarrow OH^\circ$$
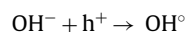
or the photo-Kolbe reaction [31].

$$R-COO^- + h^+ \rightarrow R-COO^\circ \rightarrow R^\circ + CO_2(g)$$
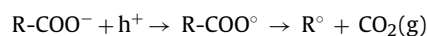
It has to be clearly established that dotted unpaired electrons belonging to radicals are true stoichiometric partners. Every chemical equation must be equilibrated with respect to them. Each radical definitively disappears via a termination reaction by coupling with another radical, either identical such as in the transient formation of hydrogen peroxide:

$$OH^\circ + OH^\circ \rightarrow H_2O_2$$

or distinct such as in the transient formation of alcoholic intermediate compounds:

$$R^\circ + OH^\circ \rightarrow R-OH$$
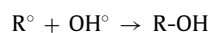
A complete reaction scheme has to take into account all the transient radicals involved, as summarized in Fig. 6.

2.9. True photocatalytic normalized tests

In line with the applications and commercialization of photocatalytic devices (air purifiers, domestic refrigerators, self-cleaning materials, etc.), photocatalytic normalized tests have to be clearly defined and disseminated. In addition to the above recommendations, a real photocatalytic activity test can be erroneously claimed if a non-catalytic side-reaction or an artifact does occur. Many tests are based on dyes decolorization, which is easy to perform with a UV–visible spectrophotometer. However, these tests
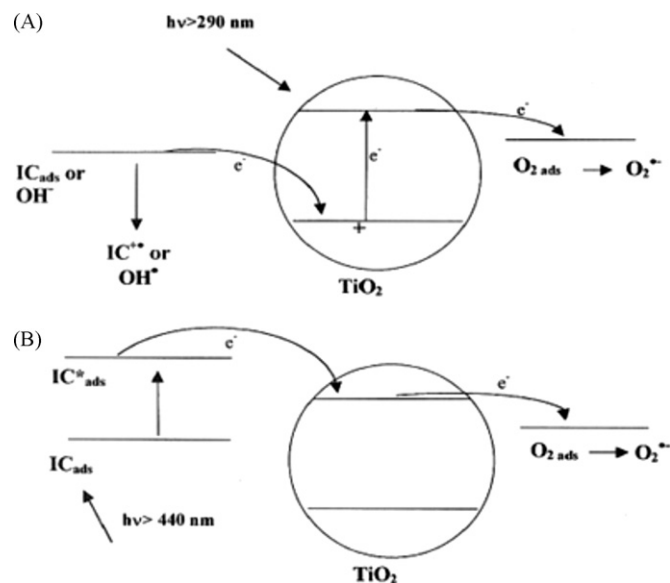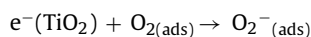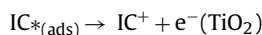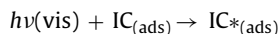

Fig. 7. Degradation of Indigo Carmine dye under UV-irradiation (A) and electron transfer from excited IC* molecules without hole formation under visible light (B).

can represent the most "subtle pseudo-photocatalytic" systems, hiding the actual non-catalytic nature of the reaction involved. This was quantitatively demonstrated with the apparent photocatalytic "disappearance" of indigo carmine dye [29]. Whereas indigo carmine IC was totally destroyed by UV-irradiated titania, its color also disappeared when only using visible light. Actually, IC was decolorized but its corresponding Total Organic Carbon (TOC) remained intact. The loss of color actually corresponded to a limited stoichiometric transfer to titania of electrons originating from indigo molecules, once photo-excited in the visible as IC*. This is quite possible since the electronic energy level of IC* is higher than that of the conduction band of titania.

This electron transfer destroys the regular distribution of conjugated bonds within the dye molecule and causes its decolorization. Once transferred to titania, the electron participates to an additional iono-sorption of molecular oxygen as O_2^-. This is described by the following equations and illustrated in Fig. 7.

$$h\nu(vis) + IC_{(ads)} \rightarrow IC*_{(ads)}$$

$$IC*_{(ads)} \rightarrow IC^+ + e^-(TiO_2)$$

$$e^-(TiO_2) + O_{2(ads)} \rightarrow O_2^-{}_{(ads)}$$

When the same reaction was performed with a higher concentration of IC providing an initial number of molecules higher than the stoichiometric threshold described above, the solution remained totally colored with indeed the same constant initial TOC value.

By contrast, our laboratory has been selected as expert in a European Contract [32] including the two European self-cleaning glass producers, Saint Gobain (F) and Pilkington (GB) to propose a true photocatalytic test to certify the true photocatalytic nature of the activity of such solids [33]. They were based on palmitic and stearic acid oxidative degradation [34,35], since both fatty acids are indicative of greasy stains on glass resulting from human sebum on tips of fingers or from cooking or from ordinarily polluted ambient air.

As a consequence, all standardization tests, exclusively based on dye decolorization, should be banished.

3. Problematic doping

Photocatalytic studies are sometimes focusing too much on peculiar subjects as sometimes complains Comyns [36]. It could perhaps be the case of doping with numerous, even too numerous publications on it. They started 30 years ago with cationic doping. No correct improvement in photo-activity could be recorded since a correct improvement in catalysis requires a benefit by at least a factor of two, or even better by one order of magnitude. This was never observed in literature. I have personally only observed detrimental effects since 1984 [37,38].
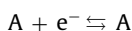
3.1. Cationic doping

It has to be reminded that doping consists in dissolving controlled and moderate quantities of heterovalent cations in lattice sites of Ti^{4+} host cations to apply the "induction valence law" defined in electronics [39] and illustrated in Fig. 8.

It is now generally and finally admitted that cationic doping is detrimental for photocatalysis. Chromium doping was catastrophic (i) for oxygen chemisorption [33] and (ii) for all kind of reaction performed in various media as illustrated in Fig. 9. This was clearly and quantitatively explained by the fact that doping cations act as recombination centers [3,4]. In the case of substitutional doping of titania by M^{3+} dissolved trivalent cations (M = Fe, Cr, Ga), according to Fig. 9, each doping agent creates one acceptor center A:

$$(-Cr^{3+}-) + e^- \leftrightarrows [(-Cr^{3+}-)e^-]$$

or

$$A + e^- \leftrightarrows A$$
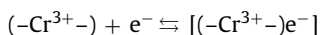
The filled acceptor centers attract photo-holes and become empty after neutralization:

$$A^- + h^+ \leftrightarrows A$$
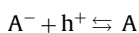
The resulting balance gives: $e^- + h^+ \leftrightarrows N$ with N = neutral center. Since Cr-doping contains 0.86 at.%, there results: $[Cr^{3+}] = 2.50 \times 10^{20}$ ions/cm^3. Even if cationic doping is by definition low in at.%, the concentration in Cr is much larger than the instantaneous concentration of electrons and holes, $[e^-]$ and $[h^+]$. In undoped samples, the recombination rate R is given by:

$$R = k_R[e^-][h^+] = k_R[e^-]^2$$

i.e. of the second order. For doped sample, the recombination rate becomes:

$$R' = k_R([e^-] + [A^-])[h^+] = k_R([e^-] + [2.50 \times 10^{20}])[h^+] \approx k'_R[h^+] >> R$$

There results that recombination rate R is strongly increased by p-type doping. A similar demonstration shows that n-type doping agents behave also as electron-hole recombination centers. Therefore, cationic doping has to be given up.

3.2. Anionic doping

Anionic doping has been a new innovative concept with the narrowing of the band gap energy [40]. For nitrogen doping (N-doping different from n-type doping), according to the valence induction law [35], it must be proved (i) that nitrogen is be present in a nitride state N^{3-}, (ii) that N^{3-} anions are in O^{2-} lattice bulk positions and (iii) that, in oxidizing working conditions, titania has no tendency to self-clean expulsing N^{3-} anions from the anionic sub-lattice via their oxidation with a favorable decrease of the ionic radius of element N from 1.71 Å to 0.55, 0.25, 0.16 and 0.13 Å corresponding to

the oxidation numbers of N equal to −3, 0, +1, +3 and +5, respectively. Concerning anionic doping, my personal position is "Wait and see".

4. Respect for the fundamentals of heterogeneous catalysis

Because of the diversity in origins of laboratories working on photocatalysis, there are some misfits and some misconceptions, especially in recent articles originating from laboratories having no culture in heterogeneous catalysis. As in heterogeneous catalysis, heterogeneous photocatalysis follows the 5 step process of chemical engineering, presented in Fig. 10. The only difference with photocatalysis resides in step 3. Instead of thermal activation, photocatalysis implies the activation of the solid by photons. As a consequence, step 3 subsequently includes (i) the absorption of photons by the solid, (ii) the creation of electrons and holes and (iii) the subsequent electron transfer reactions. It has to be noted that the photons must be absorbed by the solid, i.e. their energy $h\nu$ should be $\geq E_G$ (E_G = band gap energy). As a consequence, photocatalysis is quite different from a hypothetic photochemistry in the adsorbed phase.

4.1. Langmuir–Hinshelwood mechanism

Actually, photocatalysis as heterogeneous catalysis obeys the Langmuir–Hinshelwood mechanism in most cases with the rate of reaction r being chosen as the expression of the catalytic activity. It is proportional to the surface coverages of reactants. In a bimolecular reaction:

$$A + B \rightarrow C + D$$
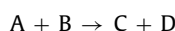
rate r varies as:

$$r = k\theta_A\theta_B$$

Each coverage θ_i varies as:

$$\theta_i = \frac{K_i X_i}{(1 + K_i X_i)}$$

where K_i is the adsorption constant (in the dark) and X_i represents either the concentration in the liquid phase or the partial pressure P_i in the gas phase. Therefore reaction rate r becomes:

$$r = k\theta_A\theta_B = \frac{k K_A \cdot K_B \cdot X_A \cdot X_B}{(1 + K_A X_A)}(1 + K_B X_B)$$

where k is the true rate constant. It has to be recalled that, besides the mass of catalyst, reaction rate constant k exclusively depends on a single parameter, temperature according to the Arrhenius' law:

$$k = k_0 \exp(-E_a/RT), \text{ with } E_a = \text{true activation energy}$$

Similarly, adsorption constants K_i only vary with temperature T according to van t'Hoff's law

$$K_i = (K_i)_0 \exp(-\Delta H_i/RT)$$

where ΔH_i is the enthalpy of adsorption of reactant i. Therefore, even if the true photocatalytic rate constant k is independent of T, reaction rate r depends on temperature because of the two temperature-dependent coverages θ_A and θ_B. In addition, it is not rare, alas, to find in the literature or in submitted articles that both k and K vary with the concentration of reactant! Generally, one of the two reactants (for instance B) is either in excess or maintained as constant. Therefore, $\theta_B = 1$ or θ_B = constant. For example, θ_B is equal to one in a pure reactant liquid phase; alternatively, θ_B can be constant but <1, as for instance B = oxygen in oxidation reactions
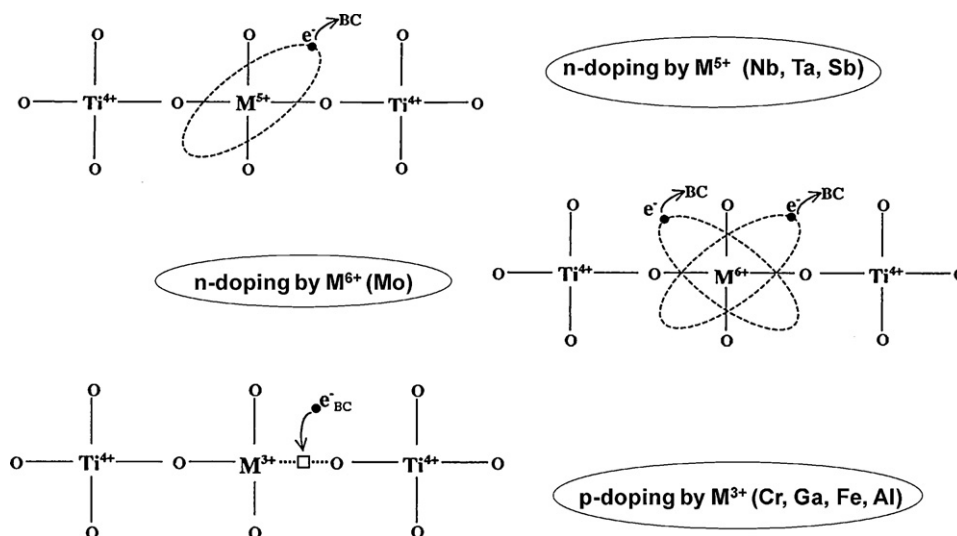
Fig. 8. Schematic n- and p-type doping of titania.

either in ambient air ($P_{O_2} \approx 1/5$ atm) or in liquid phase through its dissolution via Henry's law. Therefore:

$$r = k\theta_B\theta_B = k'\theta_A = \frac{k'K_AC_A}{(1+K_AC_A)}$$

with $k' = k\theta_B$ = pseudo-true rate constant. There are two limit cases:

 (i) $C = C_{max} \Rightarrow \theta_A = 1$ and thence $r = k'$
(ii) $C \ll C_{max} \Rightarrow \theta_A = (K_A C_A)/(1+K_A C_A) \approx K_A C_A$ and thence

$r \approx k'·K_A \ C_A = k_{app} \ C_A$ with k_{app} = apparent first order rate constant. Activation energy can be deduced from the slope of the Arrhenius plot:

$$\frac{\partial \ln k_{app}}{\partial(1/T)} = \frac{-E_{app}}{R} \Rightarrow E_{app} = E_a + \Delta H_A$$

4.2. Allusions to Eley–Rideal mechanism

In some studies, an Eley–Rideal mechanism is sometimes invoked but without any justification nor demonstration. Such a mechanism is based on the assumption that, in a bimolecular (A + B) reaction, one reactant (A) reacts in the adsorbed phase, whereas the other one B reacts directly from the fluid phase. There results that the reaction rate r is proportional (i) to the coverage θ_A and (ii) to the concentration C_B or to the partial pressure P_B, in liquid and gas phase, respectively.

$$r = k\theta_A C_B \text{ or } r = k\theta_A P_B$$

There results that the kinetic order of reactant B must remain permanently equal to +1 in the whole range of concentrations or pressures. Therefore, before claiming for free that one deals with an Eley–Rideal mechanism, a necessary and very simple test consists in plotting $\log r = f(\log C_B)$ or $f(\log P_B)$: if the slope remains permanently equal to +1 in the whole range of C_B or P_B, this mechanism will be confirmed. However, it is very rare. Personally, I estimate that it does not exist, since, otherwise, the separated and simultaneous redox exchanges of electrons and holes with both opposite reactants at titania's surface would not be possible.

5. Respect of the fundamentals of heterogeneous photocatalysis

Five physical parameters govern titania's photo-activity, identified to the temporal reaction rate r. Their influences are illustrated in Fig. 11. They are (i) the mass of catalyst, (ii) the wavelength, (iii) the initial concentration (or pressure) of the reactant, (iv) exceptionally the temperature in extreme conditions with respect to room temperature ($T < -10\,°C$ and $T > 80–100\,°C$) and (v) the radiant flux, as constantly repeated in previous articles to lie due emphasis upon their importance for a realistic and true photocatalysis systems [2,4].

In Fig. 11A, one can observe that the reaction rate r is proportional to the mass m of catalyst before reaching a plateau due to the full absorption of photons by the photocatalytic bed.

The initial proportionality between r and m is the same as that for conventional thermo-activated catalysis. This means that the activity or reaction rate is proportional to the total number of active sites n_t at the surface of the catalyst.

$$n_t = m \times S_{BET} \times d_S$$

where S_{BET} is the specific area and d_S the areal density of sites whose maximum is estimated to be $\leq 5 \times 10^{18}/m^2$ [27]. It has to be noted that the curve of Fig. 11A is quite general. Whatever the design of the photoreactor or the regime chosen (static or dynamic, slurry or fixed bed, solar or artificial light irradiation), the curve $r = f(m)$ will always exhibit an initial linear variation followed by a plateau. For new materials using deposited sub-micrometric layers of titania, the catalytic activity is still proportional to the number of layers before leveling off.

Such a curve should be determined in any study, in particular to determine the mass m_{opt} corresponding to the maximum absorption of photons reaching the catalytic bed.

Fig. 11B represents $r = f(\lambda)$. Such a curve has to be established with monochromatic light and requires a pretty easy and rapid reaction to have an accurate measurement of r.

It can be observed that this curve parallels that of the light absorption by the solid and enables one to determine the energy band gap E_G by catalytic measurements. Such a curve has to be confronted with thermodynamics as seen further.
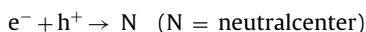
Fig. 11C illustrates the Langmuir–Hinshelwood mechanism described above, whereas the Arrhenius plot of Fig. 11D directly depends from Fig. 11C as demonstrated in [2,3]. The two extreme

Medium	Reaction	Inhibition factor
liquid organic	Cyclo-C_6H_{12} + O_2 ⟶ cyclo-$C_6H_{10}O$ + H_2O	25
liquid organic	CH_3-$CHOH$-$CH_{3\,(liq)}$ + $\frac{1}{2}$ O_2 ⟶ H_2O + CH_3–CO-CH_3	25
gaseous organic	CH_2=CH-$CH_{3\,(g)}$ + $\frac{1}{2}$ O_2 ⟶ CH_2-CH-CH_3 (with O)	55
aqueous phase	$HC_2O_4^{-}{}_{(aq)}$ + $\frac{1}{2}$ O_2 + H^+ ⟶ $2CO_2$ + H_2O	~ 85
surface	^{18}O=$^{18}O_{(g)}$ + $^{16}O_S$ ⟶ ^{18}O=$^{16}O_{(g)}$ + $^{18}O_S$	~ 10^3

Fig. 9. Inhibition factor ($\text{rate}_{(TiO_2\ Degussa)}/\text{rate}_{(Cr^{3+}/TiO_2)}$) due to Cr^{3+}-doping in different reactions performed in different media.

cases can be qualitatively accounted for as follows. Since adsorption is a spontaneous and exothermic phenomenon, low temperatures favor adsorption including that of the final products which become inhibitors. On the opposite, high temperatures are detrimental for the adsorption of the reactants and the reaction rate declines [2–4].

Eventually, Fig. 11E illustrated the relationship $r = f(\Phi)$, Φ being the radiant flux of the light source (in W/m^2). At moderate radiant fluxes, r is proportional to Φ below a maximum value, indicated by a dashed line, above which the rate declines from proportionality to follow a square root variation as $r \propto \Phi^{1/2}$. I made the demonstration at the end of the seventies but I published it much later in invited reviews [3,4]. However, a similar demonstration had been independently and much earlier published by Egerton in Ref. [41], which has to be historically considered as the first one on the subject. They clearly indicate that too high radiant fluxes greatly increase the identical concentrations in photo-electrons and photo-holes. Consequently, the electron-hole recombination reaction,

$$e^- + h^+ \rightarrow N \quad (N = \text{neutral center})$$

HETEROGENEOUS PHOTO CATALYSIS

1) Transfer of the reactants in the fluid phase

2) Adsorption of the reactants at the surface of the catalyst

3) Reaction in the adsorbed phase

    3.1 Absorption of photons by the solid (no photochemistry)

    3.2 Creation of photo-induced electrons and holes

    3.3 Electron Transfer Reactions (Ionosorption, charge neutralization, radical formation, surface reactions...)

4) Desorption of the final products

5) Removal of the final products in the fluid phase

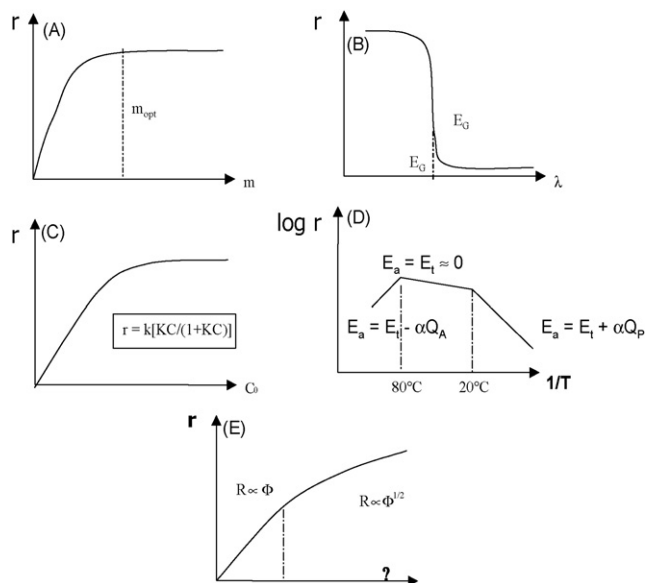**Fig. 10.** The basic 5 step process common to heterogeneous catalysis and to heterogeneous photocatalysis.

which has a recombination rate r_R of the second kinetic order:

$$r_R = k_R[e^-][h^+] = k_R[e^-]^2$$

which parabolically increases with the charge concentration. Consequently, there is a loss (or a waste) in noble UV-light energy and the system does not operate in optimum conditions. In addition, since electron-hole recombination is exothermic, such high radiant fluxes may risk to increase the temperature of the catalyst, thus entering in the left-hand side domain in Fig. 11D where increasing temperatures make the reaction rate decline. In addition, the electron-hole recombination energy dissipates

Fig. 11. Influence of the different physical parameters, which govern the kinetics of photocatalysis: reaction rate r; (A) mass of catalyst m; (B) wavelength λ; (C) initial concentration c of reactant; (D) temperature T; (E) radiant flux Φ.

only via a thermal process since any chemiluminescence could never be detected, according to negative results obtained in 1977 [42].

For information, an intense solar UV-radiant flux, recorded at Plataforma Solar de Almeria (37° latitude) at noon in June, is close 38 W/m^2 [43]. Using a Philips HPK 125 UV-lamp (125 electrical Watts), the change in regime from $r \propto \Phi$ to $r \propto \Phi^{1/2}$ was obtained at $\Phi = 250$ W/m^2.

Therefore it is useless to use over-powered lamps especially with small photoreactors as often read in the literature.

6. Conclusions

This article was aimed at underlining some misconceptions in studies on photocatalysis originating from scientists whose main field is not heterogeneous catalysis. The following protocol can be proposed to make a kind of check up before initiating an experimental work and/or its interpretation.

(1) Check that the photoreactor is operating with a mass of catalyst close to m_{opt}, the optimum mass shown in Fig. 11A, which directly depends of the photoreactor design.
(2) Avoid touse over-powered lamps, especially with small photoreactors, since (i) the photocatalytic regime is less efficient as seen in Fig. 11E and (ii) side-effects can occur, principally thermal ones as illustrated in Fig. 11D.
(3) Consider that maximum quantum yields ⟨QY⟩ can only be obtained at full surface coverages in reactants. ⟨QY⟩ values, obtained at very low pressures or concentrations, especially in diluted solutions or in trace elimination, must be mathematically very low, according to ⟨QY⟩ definition.
(4) Avoid confusion between reaction rate $r = -dC/dt$ and conversion $\tau = (C_0 - C)/C_0$.
(5) Demonstrate the true catalytic nature of a photocatalytic reaction by reaching a high enough conversion to convert a number of molecules higher than the initial number of adsorptive or active sites. The latter number is defined as the "catalytic threshold".
(6) Do not use dubious standardization tests based on non-truly photocatalytic systems such as dye decolorization, despite their facile use.
(7) Avoid "mediatic" illustrations for photocatalytic mechanisms, which are not correct with respect to thermodynamics and to heterogeneous catalysis.
(8) The use of Transmission Electron Microscopy (TEM) is a prerequisite to characterize platinum Pt/TiO$_2$ (or noble metals) bifunctional photocatalysts.
(9) Cationic doping of titania is rather detrimental for catalysis and should avoided. Concerning anionic doping, the situation has to be imminently clarified.

In conclusion, all these recommendations have to be addressed before claiming that one deals with a true photocatalytic reaction, operated in suitable conditions.

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