Environmental green chemistry as defined by photocatalysis

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Abstract

Photocatalysis is efficient in several fields. Firstly, in selective mild oxidation: oxidation of gas and liquid hydrocarbons (alkanes, alkenes, *cyclo*-alkanes, aromatics) into aldehydes and ketons. Primary and secondary alcohols are also oxidized into their corresponding aldehydes or ketones. The high selectivity was ascribed to a photoactive neutral, atomic oxygen species. Once platinized (only 0.5 wt.% Pt) titania may catalyze reactions involving hydrogen (deuterium-alkane isotopic exchange and alcohol dehydrogenation). For fine chemicals, high initial selectivities enable titania to address most of the twelve principles of "green chemistry", such as the synthesis of 4-*tert*-butyl-benzaldehyde, an important intermediate in perfume industry by direct selective oxidation of 4-*tert*-butyl-toluene with air. A new field recently appeared: thio-photocatalysis. Oxygen was replaced by sulfur, using H_2S as a convenient and reactive source. For instance, the conversion of propene in 1-propanthiol was successfully obtained. The reaction was performed using either CdS or TiO_2. The latter was much more active than CdS. In environmental photocatalysis, titania becomes a total oxidation catalyst once in presence of water because of the photogeneration of $OH^{\bullet}$ radicals by neutralization of OH^- surface groups by positive holes. Many toxic inorganic ions are oxidized in their harmless upper oxidized state. The total degradation of organic pollutants (pesticides, herbicides, insecticides, fungicides, dyes, etc. . . .) is the main field of water photocatalytic decontamination. The UVA solar spectrum can de advantageously used as demonstrated by many campaigns performed in the solar pilot plant at the "Plataforma Solar de Almeria" (Spain).

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1. Introduction

Heterogeneous photocatalysis has recently appeared as a new emerging "advanced oxidation process" (AOP), with more than 2000 recent publications on the subject [1]. Heterogeneous photocatalysis is simultaneously able to be efficient in green chemistry [2], in fine chemicals, and in emerging "AOP". This has been recently established [3–11].

When a divided semiconductor is illuminated with photons of energy higher than or equal to its band gap energy, photo-electrons, e^- and photoholes (or positons) h^+ are created. In a fluid reaction medium, reactants can adsorb and react either with electrons (acceptor molecules such as O_2) or with holes (donor molecules). Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb reactants, and to absorb efficient photons. The five main parameters which govern the kinetics are (i) the mass of catalyst, (ii) the wavelength, (iii) the initial concentration (or pressure) of the reactant, (iv) the radiant flux, and (v) exceptionally the temperature in extreme conditions with respect to room temperature ($T < -10\,^{\circ}C$ and $T > 80$–$100\,^{\circ}C$).

How can photocatalysis be efficiently operating in both opposite fields constituted by fine chemicals and environmental chemistry? Indeed photocatalysis is alternatively able to induce mild and selective oxidation reactions, and total oxidation reactions leading most elements to their higher oxidation state, in particular leading organic carbon to the +4 oxidation state in CO_2.

This is mainly due to the absence (mild oxidations), and to the presence (total oxidation) of water. In the first case, the active species is a neutral atomic O* species [12], whereas in the presence of water (or humid air), $OH^{\bullet}$ radicals (second best universal oxidant) lead to total oxidation. Their formation is summarized in the following Table 1.

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Table 1
Main features of photocatalytically driven fine and environmental chemistry

Features	Fine chemicals	Environmental catalysis
Main reaction	Mild oxidation	Total oxidation
Initial selectivity	100%	No selectivity
Final products for organics	$>\!C\!=\!O$	
Medium	Dry medium	Water, humid air
Active species	O*	OH°
Reaction of formation	$(TiO_2) + h\nu \rightarrow e^- + h^+$	
	$O_{(ads)}^- + h^+ \rightarrow O_{(ads)}^*$ $(H_2O \rightleftarrows H^+ + OH^-) + h^+ \rightarrow H^+ + OH°$	

2. Experimental

2.1. Catalysts

All the reactions described and discussed have been performed using titania Degussa P25, worldwide recognized as a reference photocatalyst. It is constituted by homodispersed non-porous polyhedral particles of a mean diameter $\bar{d}$ equal to ca. 32 nm, containing 20–30% rutile in anatase. Its surface BET surface area S is equal to $50 \pm 2 \, \text{m}^2/\text{g}$ in good agreement with the textural relationship.

$$\bar{d} = \frac{6}{\rho \times S}$$

ρ being the volumic mass of titania ($3.85 \times 10^3 \, \text{kg/m}^3$)

2.2. Photoreactors

Various photoreactors were used according to the reaction medium studied. Gas phase reactions were performed either in fixed bed reactors used either as differential gas flow reactors or as batch reactors.

Liquid phase reactions were performed in a batch thermostated photoreactors of $100 \, \text{cm}^3$ as described in Fig. 1 or in bigger one (1 L) when the sampling required larger volumes
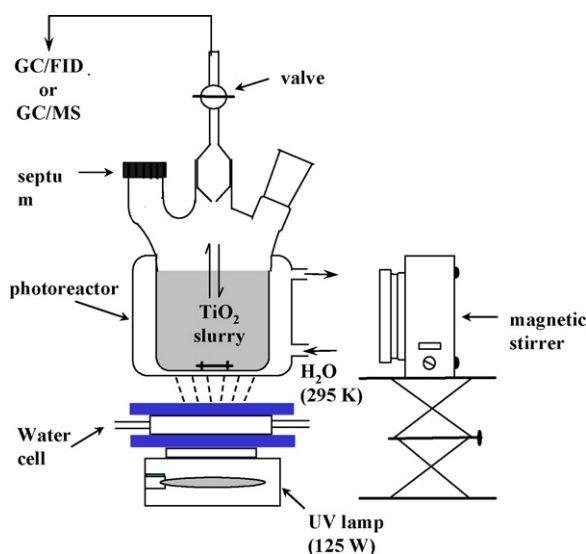

Fig. 1. Schematic of a batch slurry photoreactor.

to withdraw for analysis, especially in the case of dye degradation.

2.3. Analyses

Reactants and both intermediate, and final products were analyzed using gas chromatography, mass spectrometry for isotope exchange reactions, HPLC, and HPLC-MS for intermediates identification and UV–vis spectrometry, especially for dyes disappearance kinetics.

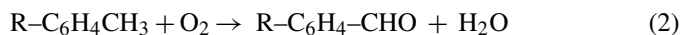## 3. Selective photocatalytic mild oxidation in fine chemicals

3.1. Functionalization of light n-alkanes

Photocatalysis is the only catalytic process able to functionalize light *n*-alkanes at room temperature into carbonyl-containing molecules (mainly aldehydes + ketons) either in the gas or in liquid phase ($C \geq 2$).

$$CnH_{2n+2} + O_2 + [TiO_2 + h\nu + air] \rightarrow CnH_{2n}O + H_2O \quad (1)$$
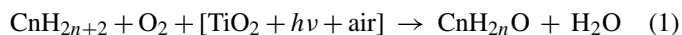
3.2. Selective mild oxidation of other hydrocarbons

Cyclo-alkanes (CnH_{2n}) are selectively oxidized in cycloketons. For instance, cyclohexane and decalin are oxidized into cyclohexanone and 2-decalone, respectively with an identical selectivity (86%). The selectivity in ketons increases with the presence of aromatic rings. For instance, tetralin gives mainly 2-tetralone. Substituted aromatic hydrocarbons such as alkyltoluenes or *O*-xylenes are 100% regio-selectively oxidized on the methyl group into alkylbenzaldehydes, both in gas or liquid phase, by mere irradiation of titania at room temperature [2]:

$$R–C_6H_4CH_3 + O_2 \rightarrow R–C_6H_4–CHO + H_2O \quad (2)$$

The photocatalytic mild oxidation of olefins (propylene, cyclohexene) gives a 100% initial selectivity in epoxides, which, however, decompose when increasing the conversion because of their high inherent reactivity.

### 3.3. Selective oxidation of alcohols and of hydroxyl-containing molecules

Primary and secondary alcohols, either gaseous or liquid, are 100% selectively oxidized in their corresponding aldehydes and

ketons.

$$R-CHOH-R' + O_2 + [TiO_2 + h\nu + air] \rightarrow R-CO-R' + H_2O \tag{3}$$
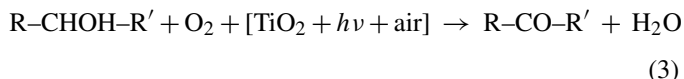
In particular, the oxidation of isopropanol into acetone was chosen as a photocatalytic test for measuring the efficiency of passivation of TiO_2 or ZnO-based pigments in paintings against weathering.

A similar oxidation reaction can be obtained by bifunctional photocatalysis using Pt/TiO_2.

$$R-CHOH-R' + [Pt/TiO_2] \rightarrow R-CO-R' + H_2 \tag{4}$$
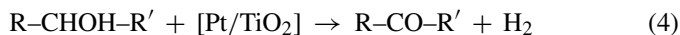
It requires working in *vacuo* or in the absence of air. It is not only a 100% selective mild oxidation reaction but also constitutes a "chemical storage of light energy".

4. Other selective photocatalytic reactions

### 4.1. Photocatalytic reactions involving hydrogen

In photocatalytic reactions involving hydrogen, either as a reactant (deuterium-alkane isotopic exchange) or as a product (alcohol dehydrogenation), the catalyst (such as Pt/TiO_2) requires the presence of a noble metal acting as a cocatalyst necessary (i) to dissociate the reactant (D_2) and (ii) to recombine H atoms into dihydrogen. This belongs to the field of bifunctional photocatalysis using TiO_2-deposited noble metal catalysts [13].

4.2. Selective mono-deutero-labeling of alkanes

Conventional catalysis by metals is not selective at all in alkane-deuterium isotopic exchange [13].

$$C_nH_{2n+2} + x\ D_2 \rightarrow C_nH_{2n+1}D + C_nH_{2n}D_2 + C_nH_{2n-1}D_3$$
$$+\cdots C_nD_{2n+2} + y\ HD \tag{5}$$
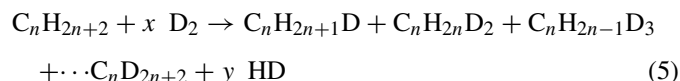
By contrast, photocatalysis gives a 100% selective labeling in mono-deutero-alcane:

$$C_nH_{2n+2} + D_2 \rightarrow C_nH_{2n+1}D + HD \tag{6}$$
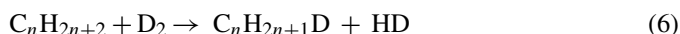
This reaction is not only 100% selective in mono-deutero-alkane but also is 100% regio-selective since labeling occurs with the preferential exchange of a primary H atom (as exemplified on propane):

$$C_3H_8 + D_2 \rightarrow D-CH_2-C_2H_5 + HD \tag{7}$$
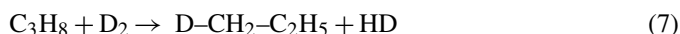
4.3. Photocatalytic dehydrogenation

The photocatalytic dehydrogenation of primary and secondary alcohols, either gaseous or liquid, is 100% selective in the formation of their corresponding aldehydes and ketons, that is, in the formation of carbonyl-containing molecules.

$$R-CHOH-R' + [Pt/TiO_2] \rightarrow R-CO-R' + H_2 \tag{8}$$
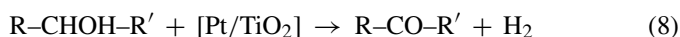
It requires working in the absence of oxygen or air (in *vacuo* or in inert atmosphere). It is not only a 100% selective mild oxidation reaction, but also constitutes a "chemical storage of light energy". The photocatalytic production of hydrogen from chemicals or from biomass on Pt/TiO_2 photocatalyts constitutes another aspect of green chemistry with the conversion of (solar) light in a chemical energy vector, hydrogen [13,14].

4.4. Thio-photocatalysis

It consists in replacing oxygen as a reactant by sulfur, its next neighbor in group VI, for redox thio-reactions. However, sulfur cannot be used, since it is solid at room temperature (as S_8 crown molecules). We chose H_2S as a convenient and reactive source. For instance, the conversion of propene in 1-propanthiol was successfully obtained:

$$CH_3-CH=CH_2 + H_2S \rightarrow CH_3-CH_2-CH_2-SH \tag{9}$$
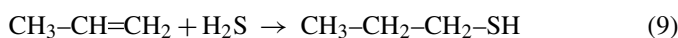
This result was unexpected since secondary 2-propanthiol is preferentially obtained in conventional processes. The reaction was performed using either CdS or TiO_2. In addition, TiO_2 was much more active than CdS, underlining the adaptability of its surface to new and aggressive environments [15].

5. Photocatalysis *versus* green chemistry. Case study of selective mild oxidation of aromatics

The twelve principles of green chemistry, a new concept in chemistry, are reported in next Table 2 after Ref. [16].

As an example of a green chemical photocatalytic reaction, let us consider the synthesis of an important intermediate in industrial fine (perfume) chemistry (4-*tert*-butyl-benzaldehyde). Actually, it is environmentally–hostilely prepared in industry by the stoichiometric oxidation of 4-*tert*-butyl-toluene (4-TBT) by permanganate. This reaction occurs with a lot of (in-) organic by-products:
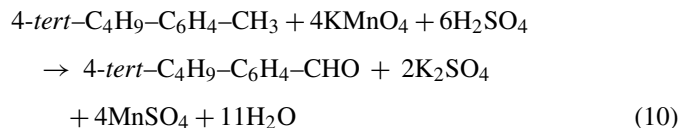
$$4\text{-}tert\text{-}C_4H_9-C_6H_4-CH_3 + 4KMnO_4 + 6H_2SO_4$$
$$\rightarrow 4\text{-}tert\text{-}C_4H_9-C_6H_4-CHO + 2K_2SO_4$$
$$+ 4MnSO_4 + 11H_2O \tag{10}$$

Table 2
The twelve principles of green chemistry[a]

1. Prevention
2. Atom economy
3. Less hazardous chemical syntheses
4. Designing safer chemicals
5. Safer solvents and auxiliaries
6. Design for energy efficiency
7. Use of renewable feedstocks
8. Reduce derivatives
9. Catalysis
10. Design for degradation
11. Real-time analysis for pollution prevention
12. Safer chemistry for accident prevention

[a] Anastas, P.T., Warner, J.C., Green chemistry: Theory and Practice, Oxford University Press: New York, 1998, p. 30. By permission of Oxford University Press.

By contrast, the oxidation of 4-TBT is 100% selective, both in gas or liquid phase, in 4-*tert*–butyl–benzaldehyde by the mere near-UV irradiation of titania in ambient air at room temperature:

$$4\text{-}tert\text{–}C_4H_9\text{–}C_6H_4CH_3 + O_2$$
$$\rightarrow 4\text{-}tert\text{–}C_4H_9\text{–}C_6H_4\text{–}CHO + H_2O \tag{11}$$
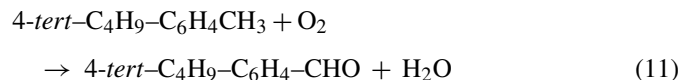
The photocatalytic oxidation of 4-TBT is a typical example of "green chemistry" with the use of air and a cheap, stable, and recyclable titania catalyst which does not need solvents nor heating but only UVA light provided by lamps whose technology is permanently improving.

The high selectivity was ascribed to the oxidation by a photoactive neutral, atomic oxygen species, detected by photoconductivity, and resulting from the neutralization of dissociatively chemisorbed $O^-_{(ads)}$ species by positive photo-generated holes h^+.

$$O^-_{(ads)} + h^+ \rightarrow O*_{(ads)} \tag{12}$$

This reaction only occurs in gas or liquid pure organic phase in the absence of water.

As a consequence, it can be easily observed that photocatalysis is directly concerned with all the twelve principles of green chemistry (Table 2), especially with the nine first ones.

5.1. Environmental photocatalysis

Besides the selective mild oxidation of organics performed in gas or liquid organic phase, UV-irradiated titania becomes a total oxidation catalyst once in presence of water because of the photogeneration of OH° radicals by neutralization of OH^- surface groups by positive holes (Eq. (12)).

$$OH^- + h^+ \rightarrow OH^\circ \tag{13}$$

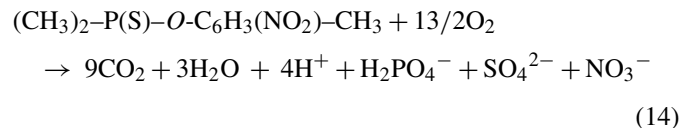### 5.2. Types of pollutants removed by photocatalysis

5.2.1. Inorganic pollutants

Many toxic inorganic ions are oxidized in their harmless upper oxidized state. For example, SO_3^{2-}, HSO_3^-, $S_2O_3^{2-}$, S^{2-}, and HS^- are oxidized into innocuous SO_4^{2-} ions, whereas PO_3^{3-} is oxidized into PO_4^{3-}. NO_2^- and NH_4^+ ions are oxidized into NO_3^-, whereas CN^- is oxidized into OCN^-, and subsequently into NO_3^- and CO_3^2. In parallel, heavy metal cations (Ag^+, Hg^{2+}, Pd^{2+}, Au^{3+}, Rh^{3+}, Pt^{IV}) can be reduced by the photoelectrons, and then deposited on titania as crystallites without screening its surface. Noble metals could be removed from baths and separated from common metals, especially photographic Ag.
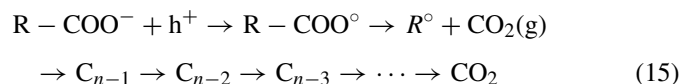
5.2.2. Organic pollutants

This is the main field of water photocatalytic decontamination. Most of aliphatic and aromatic pollutants are totally mineralized into CO_2 and innocuous inorganic anions. More complex molecules such as pesticides (herbicides, insecticides, fungicides etc. ...) or dyes are totally destroyed. This results

from the unselective attack of organics by OH° radicals, known as the second strongest oxidant (after fluorine).

In particular, the dangerous chemicals used in weapons (TNT, organophosphoruS, etc.) are totally destroyed. For example, phenitrothion completely disappeared according to the stoichiometry:

$$(CH_3)_2\text{–}P(S)\text{–}O\text{-}C_6H_3(NO_2)\text{–}CH_3 + 13/2O_2$$
$$\rightarrow 9CO_2 + 3H_2O + 4H^+ + H_2PO_4^- + SO_4^{2-} + NO_3^- \tag{14}$$

The unselective attack of organics by OH° radicals oxidizes a C–H bond into a carboxylic group, which decarboxylates according to the photo-Kolbe reaction:

$$R - COO^- + h^+ \rightarrow R - COO^\circ \rightarrow R^\circ + CO_2(g)$$
$$\rightarrow C_{n-1} \rightarrow C_{n-2} \rightarrow C_{n-3} \rightarrow \cdots \rightarrow CO_2 \tag{15}$$

This reaction accounts for the loss of C atoms as $CO_2(g)$ in total degradation.

5.3. Fate of nitrogen in organics photocatalytic degradation

Nitrogen has always been a complex element in chemistry because of its apparent inertness as N_2, and of its multiple oxidation states, ranging from −3 to +5. Nitro-compounds were found to decompose into nitrite, easily oxidized into nitrate. Amino groups have been found to decompose into ammonium ions, slowly oxidizable into nitrate.

Eventually, nitrogen atoms incorporated into triazinic aromatic rings were found to resist oxidation, remaining in their −3 oxidation state. This was examplified by a partial oxo-degradation of *s*-triazine into cyanuric acid $C_3H_3O_3N_3$. Fortunately, cyanuric acid is innocuous because of its very high stability. It constitutes one of the very few examples of organics resisting photocatalytic degradation at room temperature. This is due (i) to the three bonds of N atoms involved in the aromatic ring skeleton (i.e. without aliphatic substituents) and (ii) to the maximum formal oxidation state of carbon (+4), already reached in $C_3H_3O_3N_3$.

Concerning the degradation of (–N=N–) azo-groups in large dye organic molecules, the mass balance in *n*-containing final
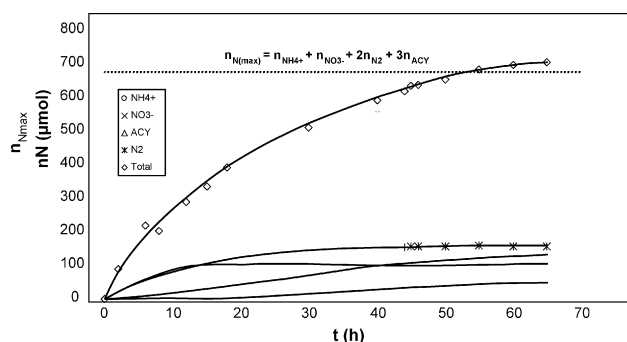

Fig. 2. Kinetics of *n*-containing compound evolution, either in the aqueous or the gas phase during the photocatalytic degradation of Congo Red dye.

products in the degradation of azo-dyes could not be obtained in aqueous phase analyses. Actually, we could quantify N_2 evolution in air, and demonstrate that the photocatalytic degradation of azo-groups is 100% selective in generating nitrogen gas.

For example, N_2 evolution from Congo Red (the "terror" of printers and of paper-makers) is given in Fig. 2. During its photocatalytic degradation the total nitrogen balance could be permanently established.

However, in the case of Amaranth a prohibited cancerigen alimentary dye, the 100% gaseous N_2 expected could not be reached. The only 85% N_2 obtained were due to the presence of 15% of a hydrazone isomeric form of Amaranth.

5.4. Solar-driven photocatalytic detoxification of organic pollutants

Various contaminants (phenol, 4-chlorophenol, 2, 4-D, benzofurane, malic acid, formatanate, Congo Red) previously studied in our laboratory, were later photodegraded in the solar pilot plant at the "Plataforma Solar de Almeria" (PSA, Spain) [17]. The same kinetics of disappearance and the same intermediate products were found indicating identical reaction pathways. The rate was found proportional to the overall light flux including both direct and diffuse UV-light. The total mineralization followed by TOC disappearance was obtained generally within less than 1 h residence time, that is, faster than the CO_2 evolution in lab experiments. This was ascribed to a more adapted reactor design, based on a plug-flow photoreactor connected to a tank, the ensemble corresponding to a resulting batch photoreactor.

Later, PSA and LACE were associated in two European programs (Solwater and Aquacat), and there resulted a new totally autonomous solar photoreactor, presented in Fig. 3, able to potabilize water by decontamination (chemicals), and by disinfection (bacteria).

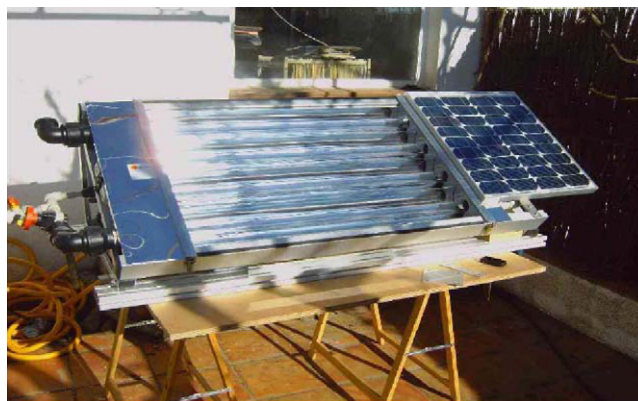Disinfection is illustrated by the photocatalytic degradation of *E. Coli* (Fig. 4).

Fig. 3. Solwater and Aquacat autonomous solar photoreactor prototype for water potabilization.

These results clearly confirmed that solar photocatalysis is a cheap way to decontaminate water in arid sunny areas. In addition, they confirm that solar activation, with a 3% UVA energy content, is suitable for activating titania-coated objects.

6. Conclusions: present challenges for photocatalysis

Since the number of publications on photocatalysis presently increases exponentially, especially from emerging countries, and from other communities such as materials science, experts in photocatalysis are now confronted to new challenges. Some of them concern the following points.

1. Are we "condemned" to exclusively work with titania?
2. Can TiO_2 be photosensitized in the visible by doping? (It is already known that cationic doping is not efficient and rather detrimental whereas anionic doping is under investigation).
3. Can we find a new photocatalyst different from TiO_2, and directly active in the visible?
4. Can invisible titania thin layers be efficient enough when deposited on "self-cleaning" objects?
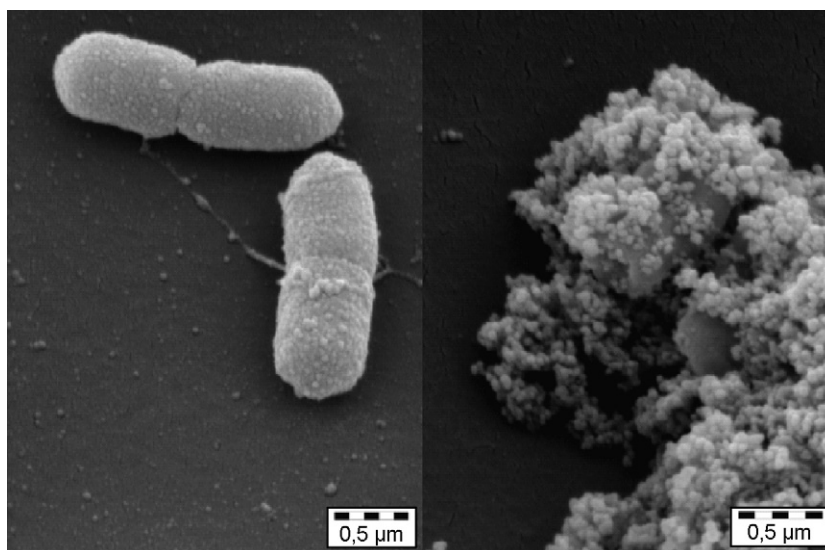

Fig. 4. Killing of *E. Coli* before (left), and during the adsorption before attack by UV-irradiated titania particles (right). Micrographs by C. Guillard et al. (LACE).

5. Is photocatalysis suitable for preparative fine chemistry?
6. Is photocatalysis enough bactericide in water and in air?
7. Can photocatalysis be employed as a new medical tool (cancericide effect)?
8. Are we able to define a few standardized, and globally accepted tests for each photocatalytic application?
9. Are we able to adapt to chemical engineering culture to promote environmental and "green" applications of photocatalysis?

Acknowledgements

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