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TERMINOLOGY, RELATIVE PHOTONIC EFFICIENCIES AND QUANTUM YIELDS IN HETEROGENEOUS PHOTOCATALYSIS. PART I: SUGGESTED PROTOCOL†

(Technical Report)

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† A draft version of this paper was published previously in part in [*J. Photochem. Photobiol. A: Chem.*, *J. Adv. Oxid. Technol.*; *IAPS Newsletter* and *EPA Newsletter*] to solicit comments and critiques from the scientific and engineering community. Moreover, during the preparation the draft proposal was submitted to a number of distinguished photochemists and photocatalycists to obtain their views.

Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part I: Suggested protocol (Technical Report)

Abstract: The term *photocatalysis* is one amongst several in a quagmire of labels used to describe a photon-driven catalytic process; a simple description of photocatalysis is proposed herein. Other labels such as *quantum yield* and/or *quantum efficiency* used in solid/liquid and solid/gas heterogeneous photocatalytic systems to express process efficiencies have come to refer (incorrectly) to *the ratio of the rate of a given event to the rate of* ***incident*** *photons impinging on the reactor walls and typically for broadband radiation*. There is no accord on the expression for process efficiency. At times quantum yield is defined; often, it is ill-defined and more frequently how it was assessed is not described. This has led to much confusion in the literature, not only because of its different meaning from homogeneous photochemistry, but also because the description of photon efficiency precludes comparison of results from different laboratories owing to variations in light sources, reactor geometries, and overall experimental conditions. The previously reported quantum yields are in fact *apparent* quantum yields, i.e. *lower limits* of the true quantum yields. We address this issue and argue that any reference to quantum yields or quantum efficiencies in a heterogeneous medium is inadvisable until the number of photons ***absorbed*** by the light harvester (the photocatalyst) is known. A practical and simple alternative is proposed for general use and in particular for processes employing complex reactor geometries: the concept of ***relative photonic efficiency*** (ξ_r) is useful to compare process efficiencies using a given photocatalyst material and a given standard test molecule. A quantum yield can subsequently be calculated since $\Phi = \xi_r \, \Phi_{phenol}$, where Φ_{phenol} denotes the quantum yield for the photocatalyzed oxidative transformation of phenol used as the standard secondary actinometer and Degussa P-25 TiO_2 as the standard photocatalyst. For heterogeneous suspensions (only), an additional method to determine quantum yields Φ is also proposed.

INTRODUCTION

Heterogeneous photocatalysis describes a process whereby illumination of a semiconductor particulate (CdS, TiO_2, ZnO, WO_3, ...) with UV-visible light suitable to its bandgap energy ($\geq E_g$) ultimately generates thermalized conduction band electrons (e^-) and valence band holes (h^+) which, subsequent to their separation and other competitive photochemical and photophysical decay channels (see below), are poised at the particulate/solution interface ready to initiate redox chemistries. The energy level at the bottom of the conduction band (LUMOs) reflects the reduction potential of the photo-electrons, whereas the uppermost level of the valence band (HOMOs) is a measure of the oxidizing ability of the photo-holes. The flatband potenial, V_{fb}, fixed by the nature of the material and by the proton exchange equilibria, determines the energy of the two charge carriers at the interface. Hence, reductive and oxidative processes for adsorbed couples with redox potentials more positive and more negative than the V_{fb} of the conduction and valence bands, respectively, can be driven by surface-trapped e^- and h^+ carriers. Figure 1 illustrates a fraction of the complex sequence of events that may take place in a semiconductor photocatalyst.

Taking TiO_2 as an example, initially, irradiation of the semiconductor particle generates a bound electron/hole pair (the exciton), which can either recombine or dissociate to give a conduction band electron and a valence band hole. These separated charge carriers may also recombine, migrate to the surface while scanning several shallow traps (anion vacancies and/or Ti^{4+} for the electrons; and oxygen vacancies or other defect sites for the hole). On the surface, both charge carriers scan the surface visiting several sites to reduce adsorbed electron acceptors (A_{ads}) and to oxidize adsorbed electron donors (D_{ads}) in competition with surface recombination of the surface trapped electrons and holes (e^-_{st} and h^+_{st}) to

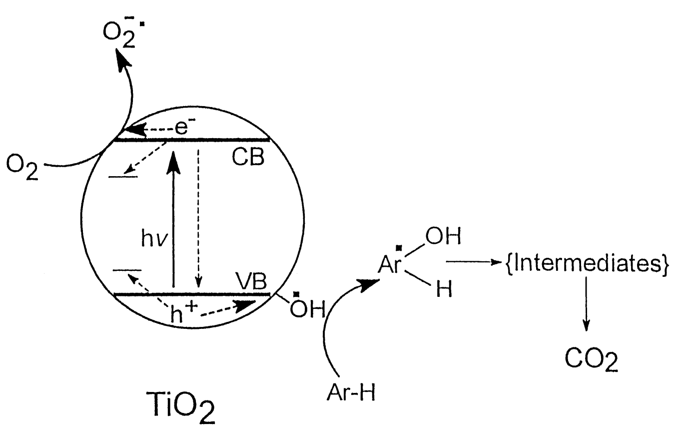


Fig. 1 Sequence of photophysical and photochemical events taking place upon irradiation of a TiO_2 particle with hν greater than E_g together with secondary reactions to total mineralization to CO_2. Phenol is indicated.

produce light emission and/or phonon emission. Oxygen is omnipresent on the particle surface and acts as an electron acceptor whereas OH^- groups and H_2O molecules are available as electron donors to yield the strongly oxidizing $^\bullet OH$ radicals [1a]. Trapping of electrons and holes in pristine naked TiO_2 colloids (size = a few nm;) takes place in less than 30 ps [1–3]. At concentrations of organic pollutant substrates normally found in the environment (a few tens of mg L^{-1}) the $^\bullet OH$ radicals are the primary oxidizing entities to produce, in the case of an aromatic substance, the corresponding $^\bullet OH$-adduct (a cyclohexadienyl radical [5]) that ultimately breaks down into a variety of intermediate products on the way to total mineralization to carbon dioxide.

The function of photo-excited semiconductor particulates then is to act as pools of electrons and holes which can be exploited in several multielectron transfer processes [4]. Thus:

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^-/h^+) \rightarrow e^-_{cb} + h^+_{vb} \qquad \text{(generation/separation)} \qquad (1)$$

$$e^-_{cb} + h^+_{vb} \rightarrow e^-_{tr} + h^+_{tr} \qquad \text{(lattice and/or surface trapping)} \qquad (2)$$

$$e^-_{cb} + h^+_{vb}(\text{and/or } h^+_{tr}) \rightarrow \text{recombination} \qquad (h\nu' \text{ and phonon emission}) \qquad (3)$$

$$e^-_{cb}(\text{and/or } e^-_{tr}) + h^+_{vb} \rightarrow \text{recombination} \qquad (h\nu'' \text{ and phonon emission}) \qquad (4)$$

$$e^-_{tr} + h^+_{tr} \rightarrow \text{recombination} \qquad (h\nu''' \text{ and phonon emission}) \qquad (5)$$

$$Ti{-}^\bullet OH + RH \rightarrow \rightarrow \rightarrow \ldots \text{photoxidations} \qquad (6a)$$

$$e^-_{tr} + \text{compound} \rightarrow \rightarrow \rightarrow \ldots \text{photoreductions} \qquad (6b)$$

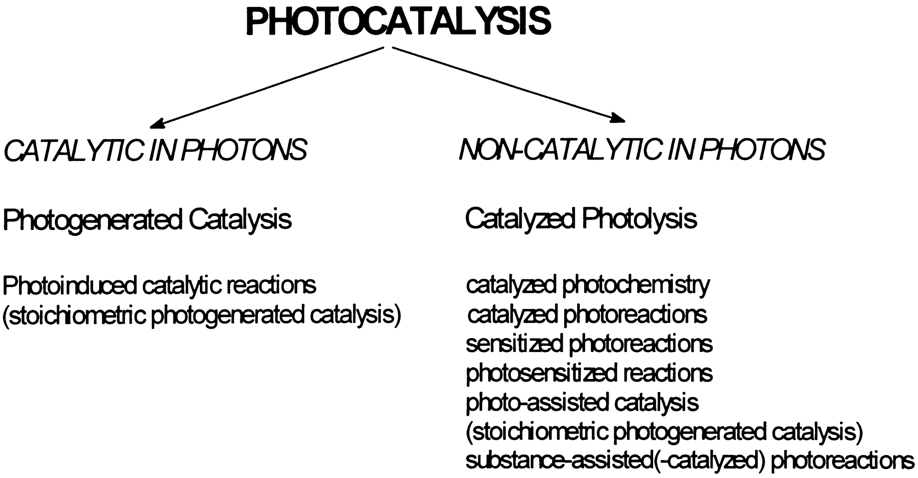
where e^-_{tr} is a trapped electron (e.g. as Ti^{3+}) and h^+_{tr} is a trapped hole denoted here [3,6] as a surface-bound $^\bullet OH$ radical, i.e. as Ti-$^\bullet$OH. Close examination of the field discloses gaps in our understanding of the basic elements that underlie heterogeneous photocatalysis

Issues that require a collective fundamental understanding of heterogeneous photocatalysis are the description of: (i) photocatalysis, (ii) quantum yields, and (iii) turnover numbers, rates and frequencies.

PHOTOCATALYSIS

A suitable description of the term ***photocatalysis***, whether in homogeneous or heterogeneous media, seems to elude acceptance as attested by the spectrum of specific labels used to describe a variety of mechanistic possibilities for a given process [7,8]. We have adopted the view [8] that the terminology *photocatalysis* refers simply to a catalytic reaction involving light absorption by a catalyst or by a substrate [9,10], although there is no universal agreement on an appropriate definition. Without reference to a special or specific mechanism, photocatalysis has also been described [7] as *the acceleration of the rate of a photoreaction by the presence of a catalyst*; further, as a label to indicate that *a catalyst may accelerate the photoreaction by interaction with a substrate either in its ground state or in its excited state and/or with the primary photoproduct, depending on the mechanism of the photoreaction.* This description also encompasses [11] *photosensitization*, yet such a process, defined officially [9] as *a process by which a photochemical or photophysical alteration occurs in one molecular entity as a result of* *initial absorption of radiation by another molecular entity—the photosensitizer*, is by no means necessarily catalytic without the knowledge of the turnover number and/or quantum yield. The issue seems to rest entirely on the role of the photons. Where in a process the quantum yield is **greater than one** (as occurs in photoreactions involving radicals) the process may be considered *catalytic in photons,* and where the quantum yield is **less than or equal to one**, the process may be taken as being *noncatalytic in photons*.

In an excellent account, Salomon [12] proposed that a broad definition of photocatalysis should be operationally divided into two distinct classes: (i) ***photogenerated catalysis***, and (ii) ***catalyzed photolysis***. The former implicates only ground states of the catalyst and the substrate in the catalytic step which is thermodynamically spontaneous (exoergic), whereas in the latter either the nominal catalyst or the substrate, or both, are in an excited state during the catalytic step. Later, Kutal [7,13] clarified and illustrated Salomon's formal schemes, and Hennig [14] suggested consistent labels that applied to observed experimental evidence. This led to the appearance of a quagmire of mechanism-specific labels: (i) ***photo***catalysis [10,11,15], (ii) ***photogenerated*** catalysis [12], (iii) ***catalyzed*** photolysis [12], (iv) ***photoinduced*** catalytic reactions [14], (v) ***stoichiometric photogenerated*** catalysis [12], (vi) **photo-assisted** catalysis [14,16], (vii) ***catalyzed*** photoreactions [13,17], (viii) ***catalyzed*** photochemistry [13], (ix) ***sensitized*** photoreactions [13,14], (x) ***photosensitized*** reactions [15], and (xi) '***substance-assisted(-catalyzed)'*** photoreactions [18], where 'substance' refers to a transition metal complex or to a semiconductor if dealing in the field of heterogeneous photocatalysis. Unquestionably, this quagmire of labels can only lead to confusion. A definition to be useful, as echoed by Kisch [11], must be such as to facilitate communication amongst researchers in the different areas of chemistry, as the principal aim of chemists is to discover novel chemical transformations through (photo)catalysis. We summarize in the scheme below Salomon's classification; for an elaborate account and illustration of these various labels the work of Chanon & Chanon is worth consulting [10] (Scheme 1).



Scheme 1

To the extent that many of the labels alluded to pertain to a specific mechanism, the label becomes useful only in so far as the mechanism of the chemical transformation is reliable and until such time as the mechanism has not been revised by more recent experimental evidence [8]. This calls immediate attention to the usage of the less descriptive and recommended (albeit unfulfilling) label *photocatalysis* to denote simply a process that is ***photon-driven*** and is ***catalytic*** upon establishing the turnover number of the given process to demonstrate that the process is indeed catalytic [8].

For a process to be labeled catalytic, the turnover number must be greater than unity. Unfortunately, the expression *turnover number* has its own limitations in heterogeneous photocatalysis; problems associated with its description shall be taken up at a later date [19].

EFFICIENCIES IN AN INDUSTRIAL ENVIRONMENT

In an industrial environment where the efficiency of a given process is a significant component to determine its economic viability, Bolton *et al*. [20] have proposed the Figures of Merit '*Electrical Energy per Order*' (*EE/O*) and '*Electrical Energy per Unit Mass'* (*EE/M*). Braun [21] has proposed the figure of merit '*Energetic Efficiency of Degradation*' (*EED*) given as mg/L of organic carbon in a given solution volume irradiated per kilowatt-hour (kWh) of electrical energy used, or the more recent suggestion of using volume-corrected efficiencies (mg C per kWh) [22], to afford comparisons between the different methods of water treatment technologies. This presumably includes the analytical procedure into any comparison between different processes, different reactors, and different light sources, among others. Just like the *EE/O*, the *EED* is useful in an economic analysis of various given processes.

In practical oxidative degradations, as envisaged in water treatment technologies, not only is the simple disappearance of the pollutant relevant but conversion of total organic carbon (TOC) into inorganic carbon CO_2 is also important. The pertinent process is the complete mineralization of all organic carbons to insure that the substrate(s) and any intermediate product(s) formed during the degradative process have also been degraded [23]. In some cases, conversion to an innocuous product may be acceptable (e.g. atrazine to cyanuric acid [24]) if the end product is environmentally friendly.

Unfortunately, the *EE/O*, *EE/M*, *EED* and other figures of merit do not provide that fundamental quantity that describes the extent to which the absorbed photon (the efficiency) contributes to drive a certain event. In homogeneous photochemistry, this parameter is the quantum yield, Φ. We therefore seek to define and experimentally attain something identical in heterogeneous photocatalysis. It should be noted that *EE/O* and *EE/M* scale with Φ^{-1} [20].

QUANTUM YIELD IN HOMOGENEOUS PHOTOCHEMISTRY

We begin by recalling the meaning of quantum yield in homogeneous photochemistry and the constraints under which it is measured.

Knowledge of the **quantum yield** (defined as *the number of defined events which occur per photon absorbed by the system* OR *as the amount (mol) of reactant consumed or product formed per amount of photons (einstein) absorbed* [9]) is central to homogeneous photochemistry. Photochemists routinely determine quantum yields of reactant disappearance, product formation, light emission, and of various other events occurring in some photochemical process. Many of these events have been examined in great detail by several laboratories, and the reported quantum yield data are precise and reproducible [25].

Ferrioxalate {$[Fe(C_2O_4)_3]^{3-}$, for UV and visible region to ≈ 500 nm;}, Reinecke's salt {$[Cr(NH_3)_2(SCN)_4]^-$; for the visible region}, uranyl oxalate {$[UO_2(C_2O_4)_2]^{2-}$ for the UV region}, and more recently Aberchrome 540 {for the 310–370 nm; and the 436–546 nm; ranges} [9,25,26] are typical secondary standards used to measure the photon flow incident on the photolytic cell {for details of the experimental protocols, appropriate references [9,25–27] may be consulted}. These substances are the *chemical actinometers* because the product quantum yield is rather insensitive to temperature changes, and to changes in reactant concentration, photon flow, and the wavelength of the absorbed light. Procedures are well established and analysis of products is simple and precise [25]. Utilization of such actinometric substances has simplified determination of the photon flow compared to the earlier more tedious radiometric procedures [9,26]. Placing the actinometer in the same photolysis cell used for the subsequent photochemical study, while maintaining the same optical train, avoids corrections for differences between the fraction of incident light ***reflected*** from the front window of the photolysis cell if different cells were used.

If the photochemical reaction of the actinometer (Ac) is:

$$\mathrm{Ac} \rightarrow \mathrm{B} \tag{7}$$

and Ac is the ***only*** substance that absorbs light at the wavelength of irradiation λ, the rate $R_{\mathrm{Ac},\lambda}$ at which photons are absorbed by Ac (photon flow) is then given by:

$$R_{\mathrm{Ac},\lambda} = R_{\mathrm{o},\lambda}(1 - 10^{-A_\lambda^{\mathrm{Ac}}}) \quad \text{(photons/min } or \text{ einstein/min)} \tag{8}$$

where $A_\lambda{}^{\mathrm{Ac}}$ is the absorbance of Ac at wavelength λ. Operationally, $A_\lambda{}^{\mathrm{Ac}} \geq 2$ during the entire irradiation period *t* to ensure that the light harvester collects $\geq 99\%$ of the photon flow, such that $R_{\mathrm{Ac},\lambda} \approx R_{\mathrm{o},\lambda}$ where $R_{\mathrm{o},\lambda}$ is the incident photon flow from the irradiation source given by [25,26]:

$$R_{\mathrm{o},\lambda} = \frac{n_{\mathrm{B}}}{\Phi_{\mathrm{B}} t(1 - 10^{-A_\lambda^{\mathrm{Ac}}})} \quad \text{(photons/min)} \tag{9}$$

where n_B is the number of product molecules formed from the irradiated actinometer and t is the time(s) of irradiation. Thus, actinometry allows determination of the incident photon flow for a system of *specified geometry* and in a *well defined spectral domain* [26]. Typically, good stirring of the actinometric solution needs to be maintained during irradiation, and the photolysis cell should contain no particulate matter that might reflect or scatter light as this would have a detrimental effect on the precision and accuracy of the quantum yield data. Practical detailed procedures for determining quantum yields in homogeneous media are available elsewhere [9,25–27].

When polychromatic radiation is used there is an added complication in measurements of quantum yields since the action spectrum in the spectral region of interest (λ_1 to λ_2) to the reaction being examined must be known. In such case, we can define a wavelength averaged quantum yield from λ to $\lambda + d\lambda$ as:

$$\Phi_{\mathrm{poly}} = \frac{\int_{\lambda_1}^{\lambda_2} R_{o,\lambda}\Phi(\lambda)\,d\lambda}{\int_{\lambda_1}^{\lambda_2} R_{o,\lambda}\,d\lambda} \tag{10a}$$

When the action spectrum is unknown, Braun *et al*. [26] suggested usage of the term ***quantum efficiency***, η, to indicate:

$$\eta = \frac{\text{Amount of reactant consumed or product formed in the bulk phase}}{\text{Amount of photons absorbed over the spectral range } (\lambda_1 \text{ to } \lambda_2) \text{ used during the reaction period.}} \tag{10b}$$

In general $\eta \neq \Phi$; as well, note the different meaning that η takes as given by Braun *et al*. [26] from that given by a recent *IUPAC Glossary of Terms in Photochemistry* [9] which uses η to be the efficiency of a step. In the present context, η is best referred to as the *photo-efficiency* of a process over the spectral range (λ_1 to λ_2) of interest. When Φ_λ is independent of λ over the spectral range λ_1 to λ_2, then $\eta = \Phi_{\mathrm{poly}}$.

In any description of quantum yield in heterogeneous photocatalysis, it will be useful to employ simple methods (procedures) that use the most basic of instrumentation to define a parameter such that the heterogeneous photocatalytic data from various laboratories can be evaluated and compared [26a].

SUGGESTED PROTOCOL IN HETEROGENEOUS PHOTOCATALYSIS

General considerations

The heterogeneous photocatalysis literature reports *quantum yields* and in other cases *quantum efficiencies* incorrectly. It needs to be stressed that it is the number of photons absorbed and ***not incident*** that initiate and drive a photocatalytic process. Until the rate of absorption of photons has been adequately assessed, reference to ***quantum yield*** {or ***quantum efficiency***, also used by photochemists} in heterogeneous photocatalysis can only continue the confusion in the literature. The term quantum yield becomes useful only if it has the identical meaning to the photochemical quantum yield (symbolized by Φ) in homogeneous phase.

In measurements of photons absorbed by the semiconductor light harvester, the extent of light scattered or reflected by the particulate matter in the dispersion cannot be neglected. All molecules are both light absorbers and light scatterers depending on the nature of the medium. Light collecting particles having large refractive indices may not, in principle, absorb all the photons impinging on the dispersion. Such significant losses, too often of unkown quantity and too often neglected, should *a priori* preclude usage of the term ***quantum yield*** in a heterogeneous medium, unless scattering is adequately accounted for. Clearly, there is a need to explore simpler alternatives in heterogeneous photocatalysis to express process efficiencies that ultimately can be related to a parameter implicating the photons absorbed. Any proposed procedure must be simple and amenable to common instrumentation normally available in most (photo)catalysis laboratories [26a].

Quantum yields

In heterogeneous photocatalysis, *quantum yield* has heretofore been taken to describe the number of molecules converted relative to the total number of photons ***incident*** on the reactor walls for an undefined reactor geometry and for polychromatic radiation. In fact, the quantum yield, Φ_λ, as done above for homogeneous photochemistry must express the amount (mol) of reactant consumed or product formed in the bulk phase, n, to the amount (i.e. einstein) of photons at wavelength λ absorbed by the photocatalyst, n_{ph} (eqn 11) [25].

$$\Phi_{\lambda} = \frac{\text{Amount (mol) of reactant consumed or product formed in the bulk phase}}{\text{Amount (einstein) of photons absorbed by the photocatalyst at wavelength } \lambda} \tag{11a}$$

$$\Phi_{\lambda} = \frac{n}{n_{\mathrm{ph}}} \tag{11b}$$

Alternatively, we may define the quantum yield using the initial rate R^{in} of the reaction and the rate of photons *impinging on*, and *absorbed by* the reaction system as is common practice in homogeneous photochemistry. Thus:

$$\Phi_{\lambda} = \frac{R^{\mathrm{in}}}{R_{\mathrm{o},\lambda}} \tag{11c}$$

Analogous descriptions have been proposed for heterogeneous systems [26,28,29]. No particular difficulties are encountered in homogeneous media. In a heterogeneous system, the relationship in eqn 11 has been extended, modified and applied in an analogous fashion [18,30–32]. Because the number of absorbed photons, n_{ph}, is experimentally difficult to estimate owing to reflection, scattering (see below), transmission (for transparent colloidal sols) and absorption by the suspended particulates, usage of the term *quantum yield* referenced to ***incident*** photons in heterogeneous photocatalysis can and has only engendered confusion in the literature. Some methods to determine n_{ph} have appeared [30–33].

To the extent that the numerator in eqn 11c expresses the rate of reaction, Φ_{λ} depends on the reactant concentration. However, as correctly noted by Braun and co-workers [26] and recently emphasized by Cabrera *et al*. [33], only for a zero-order reaction is Φ_{λ} uniquely defined at the given wavelength λ. In homogeneous photochemistry, the problem is normally overcome by determining Φ_{λ} at small (less than $\approx$ 10%) conversions of reactants, a point not often respected in heterogeneous photocatalysis where the focus is usually complete mineralization (100% transformation) of the substrate, at least in studies of environmental interest that focus on the total elimination of organic pollutants in water.

Additional considerations suggest that the photochemically defined *quantum yield* would be difficult to describe experimentally in heterogeneous media [33] particularly for complex reactor geometries. Consequently, so-called quantum yields thus far reported in the literature are but *apparent* or *lower limits* of the true quantum yield, since scattered light has not been accounted for [29]. In defining eqn 11, we must also recognize that semiconductor-assisted photooxidations take place on the surface of the solid catalyst (see Fig. 1), and thus the catalytic properties of the catalyst surface are important as the course of reactions depends highly on the characteristics of the surface on light activation. For example, usage of two TiO_2 photocatalysts obtained from different sources, or from different batches from the same source, can give different intermediate products and different distributions of intermediates under otherwise identical experimental conditions [34]. This calls attention to the necessity of reporting the characteristics of the photocatalyst [18,29,32]. Moreover, a distinction should be noted between (i) light-activated steps (from photon absorption to formation $^{\bullet}OH$ radicals on the particle surface) related to the quantum yield, and (ii) the ensuing catalytic steps in the photocatalyzed process (includes adsorption/desorption and reaction of the $^{\bullet}OH$ radicals with the adsorbed substrate) which depend highly on the surface properties of each photocatalyst. This distinction will be difficult to delineate experimentally when assessing process efficiencies. Quantum yields reported in this article do not delineate between the photochemical and catalytic processes.

The numerator in eqn 11c expresses the rate of a catalyzed heterogeneous reaction [34a] in heterogeneous photocatalysis which is related to the number of catalytically surface active sites [18]; unfortunately, these are also not experimentally attainable [8]. To bypass this difficulty, the number of active sites has often been replaced [35] by: (i) the surface area of the catalyst, (ii) the mass of the catalyst, or (iii) by the number of surface OH^- groups on the photocatalyst such as TiO_2 [30–32]. None of these suggestions, however, describe the actual heterogeneous rate since measuring the surface area for a somewhat porous catalyst (for example) comprises both the external and internal surfaces [33]; this internal surface may not be useful in some catalytic events. Also, not all the surface sites occupied by OH^- groups are necessarily catalytically active [8], especially since there may be different kinds of OH^-

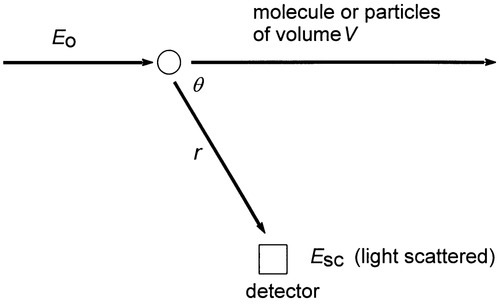
groups (two in titania). Finally, depending on the reactor geometry, particle aggregation, and stirring, not all the BET catalyst surface (Brunauer-Emmett-Teller measurements in the dry state) may be accessible to the substrate being photoconverted.

Therefore a simple alternative method of comparing process efficiencies for equal absorption of photons is desirable and is herein proposed for heterogeneous photocatalysis. But first the extent of light scattered in a heterogeneous medium, such as a TiO_2/water system, is worth consideration.

Scattering effects

The factor that most markedly complicates the measurements of the number (or rate) of absorbed quanta by a semiconductor photocatalyst is the non-negligible extent of light scattered by the particles in the dispersion. This can reach, according to some accounts, 13% to 76% of the total incident photon flow [30]. Using the photodegradation of trichloroethylene in a TiO_2 slurry, Cabrera *et al.* [33] confirmed some of these findings noting that only about 15% (Aldrich anatase TiO_2) of the radiation measured by homogeneous actinometry inside the reactor was effectively absorbed. They concluded that radiation flow measurements at the reactor entrance or homogeneous actinometry inside the reactor volume can be very misleading and scattering effects are important.

In this regard, a metal oxide material with a high refractive index (e.g. TiO_2 anatase and/or rutile) may not, in principle, absorb all the incident photon flow from a given source (however, see [36–38]) as the irradiance of light scattered, E_{sc}, by the suspension depends on the refractive indices of the scattering molecule/particle (n_1), the surrounding medium (n_o) and other factors. In Scheme 2 [39],



Scheme 2

where E_o is the incident light irradiance (W/m^2 or mW/cm^2).

$$\frac{E_{sc}}{E_o} \propto \frac{N_p\left(\frac{n_1}{n_o}\right)^4 P(\theta)V^2}{\lambda^4 r^2} \tag{12}$$

The ratio illustrates the difficulty. The fraction of scattered light (E_{sc}/E_o) by a molecule/particle scatterer depends on the number of particles (N_p), on the square of the volume V [hence on the sixth power of the radius] of the particle, on the factor $\{P(\theta)\}$ that accounts for the scattering from different parts of the same particle and on the fourth power of the ratio of the refractive indices (n_1/n_o), and finally depends inversely on the fourth power of the wavelength (λ) and on the square of the distance (r) of the detector from the scatterer.

For the materials making up a typical system in heterogeneous photocatalysis, n_o is 1.33 for H_2O and n_1 is 1.5–1.7 for glass, 3.87 for rutile TiO_2, and $\approx$ 2.5–3 for anatase TiO_2, all at 365 nm; [40,41]. If $n_1 >> n_o$, the extent of scattered light is negligible as commonly noted in absorption spectroscopy of dilute solutions relative to the case when $n_1 > n_o$ for which the light will be highly scattered. The percentage of photons absorbable by TiO_2 seems to be around $\approx$ 50–65% in some cases [40,42]. Evidence for this scattering effect is presented in the subsequent article [43].

Photonic efficiencies

One of the objectives of our work in the past decade has been to describe a protocol to standardize process efficiencies of degradation of various organic substrates for a given set of conditions. Any method proposed should circumvent the inherent difficulties encountered in the precise evaluation of the number of quanta absorbed by the photocatalyst (e.g. titania), difficulties with utilization of different light sources, different reactor geometries and other unspecified factors by referring all the results to an equivalent experiment carried out under identical conditions for a standard process.

Photonic efficiency (ξ) was used earlier [44] to describe the number or moles of reactant molecules transformed or product molecules n formed divided by the number (or einstein) of photons at a given wavelength incident on the reactor cell (flat parallel windows) n_{ph}. Alternatively, the photonic efficiency may be determined by relating the ***initial rate*** of substrate degradation to the ***rate of incident photons*** reaching the reactor as obtained by actinometry. **We do not recommend usage of ξ because it is basically what the literature has been incorrectly reporting as a *quantum yield* whose values have little, if any meaning** in describing process efficiencies (see above). We had suggested the term photonic efficiency earlier [34,44] simply to avoid the confusion between heterogeneous and homogeneous photochemistry; in the latter, quantum yield is defined precisely.

One final point is worth noting about photonic efficiencies. Experiments carried out to show the dependence of initial rates of disappearance of the organic substrate, R^{in}, as a function of the loading of the light harvesting photocatalyst TiO_2 typically show a functionality analogous to that of the Langmuir–Hinshelwood model; i.e. the dependence of R^{in} on $[TiO_2]$ can be described by:

$$R^{\mathrm{in}} = \frac{A\,[\mathrm{TiO_2}]}{(1 + B\,[\mathrm{TiO_2}])} \tag{13a}$$

where A and B are constants and $[TiO_2]$ denotes the concentration of TiO_2 in g/L. To the extent that the photon flow $R_{\mathrm{o},\lambda}$ remains constant for a given experiment, the functionality of the photonic efficiency ξ will follow a similar behavior; thus,

$$\xi = \frac{\xi_{\mathrm{lim}} C\,[\mathrm{TiO_2}]}{(\xi_{\mathrm{lim}} + C\,[\mathrm{TiO_2}])} = \frac{R^{\mathrm{in}}}{R_{\mathrm{o},\lambda}} \tag{13b}$$

where ξ_{lim} is the limiting photonic efficiency for large loadings of TiO_2 and C is a constant. This observation will have interesting consequences for heterogeneous dispersions (see below).

We now describe the steps needed to determine a photonic efficiency for a heterogeneous dispersion for later use (see below), even though in absolute terms ξ has little meaning:

1 Determine the photon flow $R_{\mathrm{o},\lambda}$ for the light source by actinometry using appropriate actinometric substances (see above) and the protocols in [25,26].

2 Determine the initial rates, R^{in}, of photoconversion of the organic substrate RH for a range of concentrations of RH at constant loading of the Degussa P-25 TiO_2 photocatalyst (initially, we suggest a loading of ≈ 2 g/L).

3 From the plot of R^{in} vs. [RH] for constant TiO_2 loading and for constant light irradiance E_{o} determine the concentration range of RH that defines the plateau of the relationship analogous to that of eqn 13a ($[TiO_2]$ is replaced by [RH]). Our experience with aromatic substrates suggests 20 mg/L may fall in this range. However, this may change depending on the substrate because of a connectivity between light irradiance of the lamp source used and the concentration of the substrate dependence of R^{in}. That is, a change in the concentration of the organic substrate changes the light irradiance dependence of R^{in} as noted in both solid/gas and solid/liquid systems [45].

4 Chose a concentration of RH in this plateau, then determine the range of the photocatalyst TiO_2 loading which also defines the plateau of the plot of R^{in} vs. $[TiO_2]$, eqn 13a, to ascertain that the loading of TiO_2 suggested in (**2**) indeed falls in the range.

5 Photonic efficiencies may then be calculated employing the relationship $\xi = R^{\mathrm{in}}/R_{\mathrm{o},\lambda}$ for which not all the photon flow $R_{\mathrm{o},\lambda}$ is absorbed because of scattering and other effects.

Relative photonic efficiency

To avoid unnecessary errors and the necessity of stipulating reactor geometry and light source, together with the properties (e.g. size, surface area) of the photocatalyst material used, the earlier suggested protocol [8,34,44] further defined an efficiency that could be used to compare experiments within the same laboratory or with other laboratories and that would be reactor-independent: the ***relative photonic efficiency***, symbolized as ξ_r and analogous to a relative quantum yield (*note*: we prefer usage of the former terminology in heterogeneous media) and thus related to an acceptable standard process, a standard photocatalyst material [34], and a standard 'secondary actinometer' in photocatalyzed processes. In the experimental description of a *relative photonic efficiency* [8,34,44], the effects of reactor geometry, light source, and photocatalyst properties remained constant in assessing ξ_r [44].

The concept of relative photonic efficiency affords comparison of process efficiencies for the photodegradation of aromatic substrates and avoids unnecessary confusion with the terminology appropriately defined in homogeneous photochemistry. Moreover, ξ_r is applicable to whatever heterogeneous medium used: (i) for dispersions, (ii) for cases where the photocatalyst is immobilized on a support, and (iii) is also applicable to solid/gas as is for solid/solution media.

These relative process efficiencies are obtained by relating the ***initial rate*** of substrate degradation, R^{in}(substrate), to the ***initial rate of phenol degradation,*** R^{in} (phenol)**,** for constant incident photon flow $R_{o,\lambda}$ reaching the reactor (note that the same reactor and reactor geometry must be used for both the substrate and phenol). That is,

$$\xi_r = \frac{\dfrac{R^{\text{in}}\,(\text{substrate})}{R_{o,\lambda}}}{\dfrac{R^{\text{in}}\,(\text{phenol})}{R_{o,\lambda}}} \quad \frac{(\text{mol min}^{-1}/\text{einstein min}^{-1})}{(\text{mol min}^{-1}/\text{einstein min}^{-1})} \tag{14}$$

or

$$\xi_r = \frac{R^{\text{in}}\,(\text{substrate})}{R^{\text{in}}\,(\text{phenol})} \tag{15}$$

where both (initial) rates are obtained under otherwise ***exact identical conditions***.

Although there is no strict need to measure the photon flow, $R_{o,\lambda}$, of a given light source to estimate ξ_r as defined above, it should nevertheless be determined and reported when experimentally feasible (certain reactor geometries may preclude such measurements).

A preliminary report suggested the feasibility of this concept [44] using Degussa P-25 TiO_2. The results were encouraging even under broadband AM1 simulated sunlight radiation. More extensive studies [34,46] confirmed the usefulness of ξ_r. The initial photoconversion of phenol was chosen, and is herein recommended for aromatics as the standard process and Degussa P-25 TiO_2, a material used extensively by several workers, as the standard photocatalyst [34]. The choice of phenol is dictated by the recognition that the molecular structure of phenol is present in many organic pollutants and, like many of these, is degraded by an oxidative rather than a reductive pathway.

To be useful, ξ_r values should not depend on light irradiance and reactor geometry, and on such other parameters as pH, photocatalyst loading, substrate concentration, and temperature. Indeed in determining ξ_r, one must chose a concentration of the organic substrate RH being examined such that the initial rate of photodegradation of RH is no longer dependent on [RH] (for constant loading of photocatalyst); once this appropriate [RH] is chosen from the plateau of the plot of R^{in} vs. [RH] (see above protocol for ξ), an optimal concentration of TiO_2 at constant [RH] can also be assessed from the plateau of the plot of R^{in} vs. [TiO_2] (see above protocol and eqn 13a). Hence, experiments must be carried out to determine the conditions under which relative photonic efficiencies become independent of light irradiance E_o, or else the value(s) of ξ_r will depend on E_o and its usefulness becomes tenuous. In our earlier work [34] we used a loading of 2 g/L for TiO_2 and 20 mg/L for phenol and for other organic substrates.

The method of *relative photonic efficiencies* being proposed [34] presents the advantage of simplicity and affords a means by which other investigators can compare their results with those of others, and measurements of ξ_r require no added special instrumentations other than those already available in most photochemical and catalysis laboratories [26a].

In heterogeneous photocatalysis, the total mineralization or disposal of a pollutant, and the identification of the various intermediate species produced in their course to the ultimate oxidation product(s) CO_2 and H_2O is of primary concern. It would also be useful to assess the ξ_r for these processes, particularly the mineralization of total organic carbon, TOC [21]. A recent study [47] demonstrated that, at least for one case examined, the relative efficiency of the disappearance of phenol using two entirely different, industrially available titania photocatalysts is identical to the relative efficiency for the complete mineralization of phenol into carbon dioxide. That is, $\xi_r = 0.25 \pm 0.03$ for the (initial) disappearance of phenol with the Hombikat UV-100 TiO2 specimen (Degussa P-25 TiO2 was the standard photocatalyst); for the corresponding fundamentally more important TOC degradation process $\xi_r = 0.27 \pm 0.03$ [47].

The efficiencies ξ_r reported earlier [34] and in part reproduced here referred specifically to substrate disappearance and demonstrated the general applicability of the proposed method. Although ξ_r were given for substituted phenols, the concept of *relative photonic efficiencies* is by no means restricted to these species; ξ_r is also applicable to other aromatic substances with the only constraint being that phenol be the standard substrate against which all ξ_r are reported (experimental conditions should be reported for such efficiencies to be useful). The effects of variations in light irradiance (13–100% where 100% is 190 mW/cm^2), reactor geometry, pH (3–6), temperature (12–68 °C), concentration of organic substrate (40–800 μM), and loading of photocatalyst material TiO_2 (0.2–2 g/L) on the *relative photonic efficiency* were examined for 2-methylphenol, 2,4-dimethylphenol, and 4-chlorophenol [34]. Additionally, ξ_r of other organic substrates were determined at specified conditions. In the case of the photodegradation of aliphatic substrates, a different secondary actinometer may be needed and recommended; a good process and substance is the photodegradation of formic acid.

Ultimately, these ξ_r can be converted to the photochemically defined quantum yield Φ once the true quantum yield for phenol, Φ_{phenol}, for a given photocatalyst has been determined (see below): whence,

$$\Phi = \xi_r \, \Phi_{phenol} \tag{16}$$

Recent laser work from our laboratory noted that Φ is likely to be around 10% for the TiO_2 photocatalyst [3].

QUANTUM YIELDS IN HETEROGENEOUS PHOTOCATALYSIS

Earlier attempts

Apparent quantum yields (i.e. *photonic efficiencies*) based on the total number of photons incident on the reactor for the disappearance of various organic substrates have been reported at 365 nm for cresols and dimethylphenols [48]; they ranged from 0.0076 to 0.010 and from 0.0060 to 0.015, respectively (2 g/L TiO_2 and 20 mg/L of organic substrate). Analogous efficiencies were reported for phenol (0.006; 100 μM; 1 g/L TiO_2) [49], for 4-chlorophenol (0.015; 8 g/L TiO_2; $\lambda > 320$ nm) [37], for H_2 formation (0.01; reduction of water) [50], and hydrogenolysis of methylacetylene $CH_3C{=}CH$ (0.0012) [51]. The range in these values is rather general. By contrast, for the disappearance of 1-propanol and propanal [36,37] *apparent quantum yields* converged to unity for the pure substrates. The authors noted that these yields are true quantum yields and that there is efficient competition between substrate oxidation and electron/hole recombination. At the rather large concentrations of ≈ 0.10–0.12 M of 1-propanol, the reported quantum yield was ≈ 0.80. The inference was that charge carrier recombination had essentially been shut off. Taking phenol as an example substrate, it would be surprising that even at very high concentration formation of the oxygen-centered radicals ($O_2^{-\cdot}$, $HO_2^{\cdot}$ and $^{\cdot}OH$} and subsequent primary oxidation of phenol by these species, or directly by ‘holes’, would be so efficient (unitary efficiencies) as to totally preclude radiative and nonradiative recombination of the exciton and its dissociated conduction band electrons and valence band holes. The quantum yield of the primary oxidation of phenol to produce the corresponding cyclohexadienyl radical (or equivalent) and the subsequent intermediate products is more likely to be less than unity in dilute phenolic solutions.

In heterogeneous media, quantum yield is best described in a manner identical to that described in homogeneous photochemistry (see above). It suffices only to determine the number of absorbed photons or the fraction of light absorbed by the solid photocatalyst. Some attempts have been noted by Schiavello and coworkers [30–32], Cassano and co-workers [33], and by Valladares & Bolton [52]; the latter authors found $\Phi = 0.056$ for the photobleaching of methylene blue. The quantum yield of $^{\cdot}OH$ radical formation for an Aldrich TiO_2 anatase sample that was used to convert methanol to formaldehyde was 0.040 [42].

We have used a modified integrating sphere method (see [43]), otherwise identical to that used in [42], to determine the fraction of light absorbed by a Degussa P-25 TiO_2 sample (see above) later used as the standard photocatalyst sample to determine the quantum yield for the photooxidative conversion of phenol, Φ_{phenol}, taken as the standard process and test molecule, respectively. This Φ_{phenol} was then used to convert reported relative photonic efficiencies ξ_r [34] to quantum yields of photooxidation of other organic substrates (eqn 16 and Table 1).

Table 1 Experimental relative photonic efficiencies (ξ_r) and calculated quantum yields (Φ) for the initial photooxidative degradation of various organic substrates ($\approx$ 200 μM) in air-equilibrated aqueous TiO_2 (Degussa P-25 TiO_2; 2 g/L; pH $\approx$ 3) Dispersions

Substrate	Relative photonic efficiency (ξ_r)*	Quantum yields $\Phi_x = \xi_r\ \Phi_{phenol}$
Phenol†	1.0	0.14 ± 0.02
2-Methylphenol	1.2 ± 0.1	0.17 ± 0.02
3-Methylphenol	1.3 ± 0.1	0.18 ± 0.02
4-Methylphenol	1.6 ± 0.1	0.22 ± 0.02
2,3-Dimethylphenol	2.0 ± 0.2	0.28 ± 0.03
2,4-Dimethylphenol	2.7 ± 0.1	0.37 ± 0.03
2,5-Dimethylphenol	2.3 ± 0.1	0.32 ± 0.03
2,6-Dimethylphenol	3.0 ± 0.2	0.42 ± 0.04
3,4-Dimethylphenol	2.5 ± 0.2	0.35 ± 0.04
3,5-Dimethylphenol	1.6 ± 0.2	0.22 ± 0.02
2,3,5-Trimethylphenol	2.8 ± 0.4	0.39 ± 0.04
2-Chlorophenol	1.2 ± 0.1	0.17 ± 0.02
3-Chlorophenol	1.0 ± 0.1	0.14 ± 0.02
4-Chlorophenol	1.2 ± 0.1	0.17 ± 0.02
2,4-Dichlorophenol	1.0 ± 0.1	0.14 ± 0.02

* [56].

† Standard substrate.

Determination of quantum yields

Method of relative photonic efficiency

Given the relationship in eqn 16 and the relative photonic efficiency ξ_r of a given photocatalytic process, there remains to determine the actual quantum yield for the degradation of phenol Φ_{phenol} to obtain the quantum yields for other aromatic substrates RH. The quantum yield for the disappearance of phenol in an aqueous dispersion of Degussa P-25 TiO_2 at low loadings of titania upon irradiation at 365 ± 10 nm was Φ_{phenol} (365 nm) = 0.14 ± 0.02 [43]. The low TiO_2 loadings were necessitated in the determination of the photon flow actually absorbed by the photocatalyst (see Part II [43]).

The quantum yields for the photooxidation of other organic substrates (Table 1) and of phenol using other photocatalyst materials (Table 2), experiments done under otherwise identical conditions, were subsequently estimated from $\Phi = \xi_r \Phi_{phenol}$ (Table 1) or from $\Phi_{TiO2} = \xi_r \Phi_{P25}$ (Table 2) using the appropriate relative photonic efficiencies reported (where Φ_{TiO2} is the quantum yield for the initial photodegradation of phenol using a different TiO_2 batch and Φ_{P25} is the quantum yield for the initial photodegradation of phenol using the standard Degussa P-25 TiO_2 specimen).

To obtain relative photonic efficiencies, the following is recommended:

6 Determine the initial rate of disappearance (or loss of or conversion of) of phenol, R^{in}(phenol), in mol/min. (A zero-order reaction).

7 Determine the initial rate of disappearance of (or loss of or conversion of) the substrate being examined, R^{in} (substrate), also in mol/min and obtained under otherwise exact identical conditions as the initial rate in (**6**).

Table 2 Experimental relative photonic efficiencies (ξ_r) and calculated quantum yields (Φ) for the initial photooxidative degradation of phenol ($\approx 200\,\mu$M) in air-equilibrated aqueous dispersions with various TiO_2 particulates (2 g/L; pH ≈ 3)

Titania, TiO_2	Relative photonic efficiency (ξ_r)*	Quantum yields $\Phi_{TiO2} = \xi_r\ \Phi_{P\text{-}25}$
Degussa P-25†‡	1.0 ± 0.1	0.14 ± 0.02
Baker & Adamson	0.38 ± 0.02	0.053 ± 0.002
Tioxide	1.9 ± 0.1	0.26 ± 0.03
Sargent–Welch	2.1 ± 0.1	0.29 ± 0.03
Fluka AG	2.2 ± 0.2	0.30 ± 0.03
Hombikat UV-100 ‡	0.25 ± 0.02	0.035 ± 0.003

* [56].

† Standard titania.

‡ Degussa P-25 TiO_2 was a gift from Degussa Canada Ltd. It consists of two crystalline phases ≈ 80% anatase and ≈ 20% rutile and contains traces of SiO_2, Al_2O_3, HCl and Fe. It is nonporous with a BET specific surface area of ≈ 55 m^2/g; crystallites range between 25 and 35 nm; in size (diam.). The Hombikat UV-100 TiO_2 was a gift from Sachtleben Chemie GmbH (Germany). It is 100% anatase with a particle size (diam.) less than 10 nm;. It is porous and has a BET specific surface area of ≈ 186 m^2/g.

8 The relative photonic efficiency ξ_r can subsequently be determined as indicated in eqn 15, namely $\xi_r = R^{in}$ (substrate)/R^{in} (phenol).

9 Given the quantum yield for the initial photodegradation of phenol $\Phi_{phenol} = 0.14 \pm 0.02$ (at 365 nm) calculate the quantum yield for the initial photodegradation of the organic substrate under examination (also at 365 nm irradiation) as indicated in eqn 16.

Method of photonic efficiency

We commented in the section on photonic efficiencies about the interesting consequence of the limiting photonic efficiency (see eqn 13b). Taking up eqn 13b again in the following form:

$$\xi = \frac{\xi_{lim} C\,[TiO_2]}{(\xi_{lim} + C\,[TiO_2])} = \frac{R^{in}}{R_{o,\lambda}} \tag{13b}$$

we note that for the case where $C\,[TiO_2] >> \xi_{lim}$, i.e. for high loading in photocatalyst TiO_2, we obtain $\xi_{lim} = R^{in}/R_{o,\lambda}$ which is exactly the definition of the quantum yield Φ (see eqn 11c) if the whole photon flow $R_{o,\lambda}$ impinging on the reactor system is totally absorbed by the photocatalyst TiO_2 at high loadings. Under these conditions, the limiting photonic efficiency for irradiation at a given wavelength λ will reflect the true quantum yield of the process at the same wavelength; that is $\xi_{lim} = \Phi_\lambda$. Note that if the R^{in} data are obtained under broadband radiation in the wavelength range λ_1 to λ_2 and the integrated photon flow is determined in the same wavelength range, then $\xi_{lim} = \Phi_{poly}$.

10 Determine the photonic efficiency as indicated in protocols (**1**) to (**5**) in the section on photonic efficiencies for various photocatalyst loadings at a given wavelength; we recommend obtaining several data points at the lowest loadings possible in the range 0.05–1 g/L with as much precision as possible in each of the data points, and subsequently an additional data set at loadings greater than 1 g/L (for Degussa P-25 TiO_2 we used up to 4 g/L) to describe a complete curve as per eqn 13b.

11 Plot these photonic efficiencies vs. TiO_2 loadings, in g/L, as indicated by eqn 13b (see Fig. 2 for an example).

12 Subsequently plot the linear transform ξ^{-1} vs. $[TiO_2]^{-1}$ (eqn 17); the ξ_{lim} is given by the intercept (as $\xi^{-1}{}_{lim}$; see eqn 17 and insert to Fig. 2 for an example). The precision in ξ_{lim} and thus in Φ_λ will be greatly improved and more consistent quantum yields achieved the greater the body of data obtained

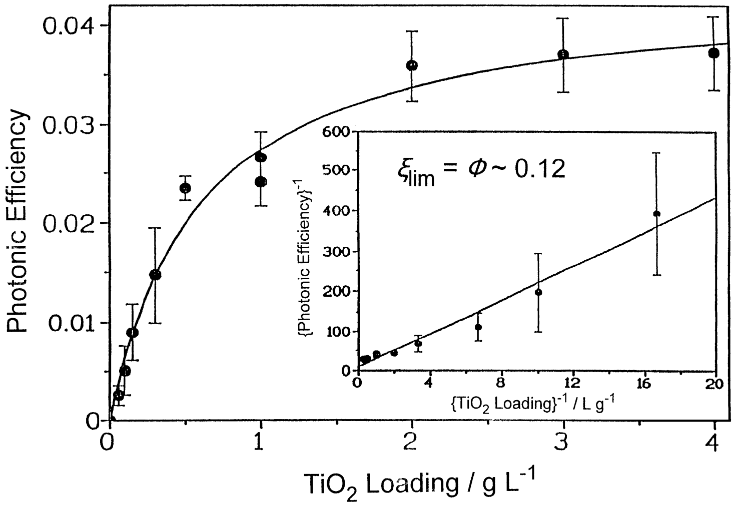


Fig. 2 Dependence of the photonic efficiencies ξ for for the initial photodegradation of phenol on the loading of Degussa P-25 titania $[TiO_2]$ for irradiation at the wavelength 365 ± 10 nm;; the insert depicts the linear transform plotted as ξ^{-1} vs. $[TiO_2]^{-1}$. The intercept from the linear transform gives the limiting photonic efficiency ξ_{lim}. For conditions, see text.

experimentally is

$$\frac{1}{\xi} = \frac{1}{\xi_{lim}} + \frac{1}{C\,[TiO_2]} \tag{17}$$

Figure 2 illustrates the photonic efficiencies as a function of various Degussa P-25 TiO_2 loadings for the initial photodegradation of phenol for a dispersion irradiated at 365 nm; the initial set of rate data between 0.05 and 0.50 g/L loading used to determine the quantum yield for phenol is that reported in Table 1 of the article Part II [43]. The insert illustrates the linear transform of the whole Langmuirian type curve; the intercept gives the limiting photonic efficiency at high titania loadings: $\xi_{lim} = 0.12 = \Phi$. This value is remarkably identical to the quantum yield assessed directly $\Phi = 0.14 \pm 0.02$ supporting the notion that at very high titania loadings all of the photon flow may be absorbed.

In an independent set of experiments we also determined R^{in} and then estimated the photonic efficiencies ($\xi = R^{in}/R_{o,\lambda 1-\lambda 2}$) for the photooxidation of 20 mg/L phenol with irradiated Degussa P-25 TiO_2 (0.050–4.0 g/L loading) in the wavelength range 300–400 nm at pH ≈ 2 in a pyrex reactor [43]. The limiting photonic efficiency at high titania loading under these conditions was $\xi_{lim} = 0.14 \pm 0.01$ identical to the calculated Φ_λ from eqn 16.

This lends credence to the possible usage of limiting photonic efficiencies at high photocatalyst loadings to assess quantum yields. Note, however, that because ξ_{lim} is determined by an extrapolation procedure in which the R^{in} at the lowest TiO_2 loadings bears the greatest relative error, the ξ_{lim} value will carry some uncertainty. This calls attention to obtaining good initial rate data if this method is chosen.

To further test the validity of the procedure advocated herein, i.e. $\xi_{lim} = \Phi$, we also assessed the limiting photonic efficiency for the photooxidation of 4-chlorophenol (P-25 TiO_2; 0.3 g/L; $\lambda = 365$ nm; $R_{o,365} = 1.9 \times 10^{-6}$ einstein/min; 20 mg/L of 4-ClPhOH): $\xi_{lim} = 0.19 \pm 0.02$, in good agreement with the estimated value (eqn 16) of $\Phi = 0.17 \pm 0.02$ in Table 1.

Additionally, we estimated the limiting photonic efficiency for the photooxidation of phenol using the Hombikat UV100 TiO_2 under conditions otherwise similar to those employed for the Degussa P-25 TiO_2 system (loading 0.10–5.0 g/L, pyrex reactor, pH ≈ 2, broadband radiation 300–400 nm): $\xi_{lim} = 0.052 \pm 0.009$ (correlation coefficient = 0.9899), a value in fair agreement with the estimated $\Phi = 0.035 \pm 0.003$ (see Table 2). Finally we note that the trend in the quantum yields for the photodegradation of phenol for three of the titania specimens follows the order: Fluka TiO_2 > Degussa P-25 TiO_2 > Hombikat UV-100 TiO_2, consistent with the greater light absorption at 365 nm of these systems in this order [53].

CONCLUDING REMARKS

In this article we have examined the common label ***photocatalysis*** that has been described in a variety of ways. No agreement appears possible on an acceptable description. We have proposed a simple, general and nonspecific definition. We have also presented a potentially useful protocol, noted as *Relative Photonic Efficiencies*, ξ_r, to correlate efficiencies of a given process with similar work from other laboratories in the active area of Heterogeneous Photocatalysis. The procedure is simple and requires no sophisticated instrumentation. These efficiencies can ultimately be converted to ***quantum yields*** for the photocatalyzed oxidation of a given substrate since the corresponding quantum yield for the photooxidative degradation of phenol was determined using an integrating sphere method [42,43] to determine the extent of light absorbed by the photocatalyst Degussa P-25 TiO_2 taken as the standard.

The quantum yield can be calculated from photonic efficiencies using $\Phi = \xi_r\ \Phi_{phenol.}$ The procedure of limiting photonic efficiencies for high loadings of photocatalyst TiO_2 may provide an alternative method to assess quantum yields in heterogeneous photocatalysis, *albeit limited* to heterogeneous dispersions and one which does carry some uncertainty (see above). The latter procedure is precluded, for example, when the photocatalyst TiO_2 is immobilized on a support since no limiting photonic efficiency can be determined under these conditions.

Examination of the quantum yields and relative photonic efficiencies for different photocatalyst materials (Table 2) shows a nine-fold variation between the lowest value (Hombikat UV-100 TiO_2) and the highest (Fluka) as expected from the lower extent of light absorbed by the former (see [53]). Such variations may also be due to several other nonphotonic factors: (i) differences in the crystalline phase of the titania (anatase vs. rutile—the latter is known to be relatively inactive in photodegradations); (ii) differences in the size and shapes of the particles, thereby affecting the extent of light scattered; (iii) differences in the density of OH^- groups on the particle surface and in the number of water molecules hydrating the surface, particularly for particles for which the hydrophilic/hydrophobic properties vary; (iv) differences in the number and nature of trap sites both in the lattice and at the surface; and finally (v) the adsorption/desorption characteristics of each surface that may vary according to the nature of the photocatalyst material but also on the nature of the organic substrate. Such adsorption/desorption variations may also affect the efficiency of the photocathodic reduction of molecular oxygen which is thought to control the efficiency of the photoanodic process, not to mention the possibility, as suggested by Fox [54], that active sites switch identity with inactive sites during the photocatalytic sequence. Taking all these factors into consideration precludes a definition [33] for a *heterogeneous quantum yield* (defined as a function of a heterogeneous rate in terms of amount (mol) of species converted per unit time per surface area of the catalyst ($mol/min/cm^2$) divided by the amount (einstein) of photons absorbed per unit time and unit volume of suspension ($einstein/min/cm^3$)). The treatment of quantum yields presented herein has assumed a pseudo-homogeneous treatment.

Finally, the congruence between the quantum yield of photooxidation of phenol by illuminated Degussa P-25 TiO_2 of 0.14 (Table 1) with the value of 0.11 reported by Augugliaro and co-workers [55] for the photooxidation of phenol using ‘home prepared’ polycrystalline TiO_2 specimens in the size range 44–250 μm and using an entirely different approach is indeed noteworthy. It would be of interest to confirm this alternative approach by assessing the quantum yield of some other substrate(s).

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APPENDIX

Glossary of proposed terms in heterogeneous photocatalysis

Photocatalysis: a label that refers simply to a reaction or process that is **photon-driven** and that is **catalytic** as established by assessing the *turnover number* of the reaction or process.

Φ_λ quantum yield of a process at wavelength λ defined as:
(1) number of events which occur per photon ***absorbed*** by the system at wavelength λ.

	(2) amount (mol) of reactant consumed or product formed per amount (einstein) of photons ***absorbed*** at wavelength λ. (3) initial rate of reactant consumed or product formed (R^{in}) per photon flow ($R_{o,\lambda}$) ***absorbed*** at wavelength λ.
R^{in}	***initial rate*** of reactant consumed or product formed (mol/min).
$R_{o,\lambda}$	***incident*** photon flow of the irradiation source at a given wavelength λ (einstein/min).
$R_{o,\lambda 1-\lambda 2}$	integrated ***incident*** photon flow of the irradiation source in the wavelength range λ_1 to λ_2 (einstein/min).
$\mathrm{R}_{\mathrm{Ac},\lambda}$	rate at which photons are ***absorbed*** by the actinometric substance Ac at the wavelength λ (einstein/min).
η	photo-efficiency of a process, defined as: amount (mol) of reactant consumed or product formed in the bulk phase per amount (einstein) of photons ***absorbed*** under polychromatic radiation over the spectral range λ_1 to λ_2 used during the reaction period and where the action spectrum of the light harvester or photocatalyst is unknown.
Φ_{poly}	quantum yield of a process under polychromatic radiation in the wavelength range λ_1 to λ_2 if the action spectrum of the light harvester or photocatalyst over this wavelength range is known.
n	amount (mol) of reactant consumed or product formed in the bulk phase.
n_{ph}	amount (einstein) of incident photons from the radiation source.
n_1	Refractive index of the solvent medium.
n_o	Refractive index of the TiO_2 particles.
E_o	irradiance of the light source (W/m^2 or mW/cm^2)
E_{sc}	irradiance of the light scattered by a molecule or a particle (W/m^2 or mW/cm^2)
ξ	photonic efficency of a process defined as: amount (mol) of reactant consumed or product formed per amount (einstein) of ***incident*** photons on the reaction system either at a given wavelength or under broadband irradiation (**usage is not recommended**). (Values of photonic efficiencies are *apparent* quantum yields or *lower limits* of the quantum yield).
ξ_r	relative photonic efficiency of a process given by the initial rate of reactant consumed (or CO_2 product formed from substrate) divided by the initial rate of phenol consumed (or CO_2 product formed from phenol). (both reactions of the substrate and phenol are carried out under exact identical conditions).
ξ_{lim}	limiting photonic efficiency of a process at high loading of the light harvester or photocatalyst.
V	Volume of particle or molecule.
r	Distance between the particle or molecule and the detector in light scattering experiments.
E_g	Bandgap energy between the valence and conduction bands of a semiconductor, in this case TiO_2.
N_p	Number of particles in light scattering for a solid/liquid system.