

Application of a “Black Body” Like Reactor for Measurements of Quantum Yields of Photochemical Reactions in Heterogeneous Systems

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We report for the first time an experimental application of the concept of a “black body” like reactor to measure quantum yields (Φ) of photochemical reactions in liquid–solid heterogeneous systems. A major advantage of this new method is its simplicity since the fractions of reflected and transmitted light are negligible due to reactor geometry and high optical density of the heterogeneous systems. The average quantum yield of a test reaction (phenol photodegradation) over TiO_2 (Degussa P25) as determined by this method was 0.14, identical to the quantum yield measured earlier for this same reaction under similar conditions by Salinaro and Serpone [*Pure Appl. Chem.* **1999**, 71, 303]. We also report the quantum yield of phenol photodegradation over N-doped TiO_2 during photoexcitation at the fundamental absorption band ($\lambda = 365 \text{ nm}$; $\Phi = 0.12$) and at the N-doping induced extrinsic absorption band ($\lambda = 436 \text{ nm}$; $\Phi = 0.08$) of the photocatalyst.

Introduction

Experimental determination of the activity of photocatalysts in liquid–solid heterogeneous systems remains a significant challenge in the proper characterization of different photocatalysts. Despite the commonly accepted view that the quantum yield (Φ) of a heterogeneous photochemical reaction is a strong parameter in characterizing the activity of a photocatalyst, its practical application is seldom achieved. A major reason for this situation is the lack of a simple reliable experimental method to determine the quantum yield that can easily be used in any photocatalytic laboratory.

The quantum yield of a heterogeneous photochemical reaction is defined exactly in accordance with the definition of the quantum yield in general homogeneous photochemistry, i.e., the number of molecules of a given reactant consumed or of a given product formed per photon of light absorbed by the photocatalyst at a given wavelength (eq 1). This definition can also be used

$$\Phi = \frac{N_m}{N_{\text{hv}}} \quad (1)$$

for heterogeneous photocatalytic processes when the system has reached the stationary state. As recommended by Emeline and Serpone¹ and by Serpone and Salinaro,² for consistency, both quantities must be evaluated under otherwise identical conditions and preferably at the same time. In practice, the quantum yield is typically given in terms of “rates”. For instance, the numerator represents the rate of reaction and the denominator represents the rate of absorption of photons (eq 2). This

$$\Phi = \frac{N_m/\text{dt}}{N_{\text{hv}}/\text{dt}} \quad (2)$$

equation should also be used for heterogeneous photoreactions whether the photocatalytic nature of the process has been

demonstrated. In such cases, initial reaction rates are typically used to characterize the reproducible initial state of the photocatalyst. The major experimental obstacle in measuring quantum yields of heterogeneous photoreactions is how to estimate the number of photons actually absorbed by the solid photocatalyst. Equation 3 represents the

$$A + R + T = 1 \quad (3)$$

balance between the fractions of reflected (R), transmitted (T), and absorbed (A) light in the system following the conservation law. Consequently, determination of the fraction of absorbed light necessitates knowledge of the fractions of reflected and transmitted light, a feat that cannot be achieved by application of conventional spectroscopic methods because of the diffuse scattering of light in dispersed photocatalytic systems. More sophisticated means are required. This has caused many workers to report a so-called “quantum yield” estimated on the basis of the incident light rather than the light actually absorbed by the heterogeneous system.

Following the work of Sun and Bolton,³ Serpone and co-workers⁴ have suggested the application of an integrating sphere to estimate the fraction of absorbed light and developed a standard protocol to estimate the quantum yield of any heterogeneous photoreaction using the photodegradation of phenol over TiO_2 (Degussa P25) as a standard photoreaction based on the concept of a relative photonic efficiency (ξ_r ; eq 4).^{2,4}

$$\Phi = \xi_r \Phi_{\text{st}} \quad (4)$$

where Φ denotes the quantum yield of the photochemical process being examined and Φ_{st} is the quantum yield of the standard heterogeneous photochemical reaction. Application of this standard protocol should significantly simplify the procedure for determining the quantum yield of any photoreaction in liquid–solid heterogeneous systems, since with the known quantum yield of the standard reaction (used as a secondary actinometer) the experimental task of measuring the reaction

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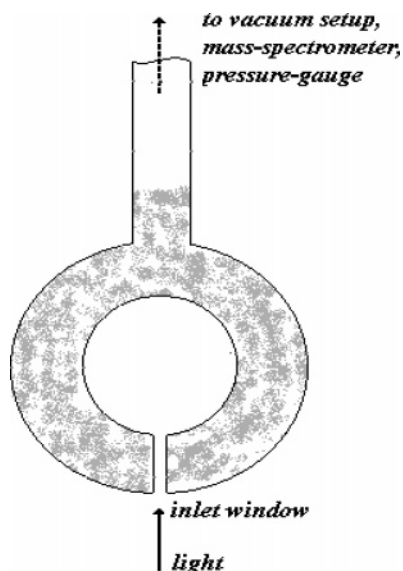


Figure 1. Sketch of the black body reactor for the measurement of the quantum yield in a gas–solid heterogeneous system.

rate of the photoreaction over the same photocatalyst is thereby simplified. The relative photonic efficiency is simply the ratio of the reaction rate of the photoreaction under examination to that of the standard photoreaction (eq 5). Thus,

$$\xi_r = \frac{\Phi}{\Phi_{st}} = \frac{dN/dt}{dN_{st}/dt} \quad (5)$$

Despite this simplicity, however, the suggested protocol does not find significant wide application in the photocatalytic community, with researchers continuing to report so-called “apparent quantum yields” (eventually the word “apparent” tends to be ignored in subsequent studies) based on the photon flow of the incident light that Serpone and co-workers^{1,2} have termed “photonic efficiency”.

In this article, we propose a relatively novel simple method for the “direct” experimental determination of quantum yields of photoreactions in liquid–solid heterogeneous systems with dispersed solid nano- or microparticles based on the application of the concept of the black body like reactor.

Concept of the Black Body Reactor. Application of the black body reactor for measuring the quantum yield of a photoreaction in gas–solid heterogeneous systems was first introduced by Solonitsyn and Basov⁵ in the early 1970s. Latter, this method was successfully used to measure the spectral dependences of the quantum yields of the photostimulated adsorption of oxygen, hydrogen, and methane on ZnO and TiO₂ as well as on other metal oxides.^{6–11} The design of the reactor is illustrated in Figure 1. The light beam is directed through the small area inlet window (diameter, ca. 2 mm) into the inner sphere (diameter about 25 mm). The space (thickness ca. 3–5 mm) between the inner and outer reactor walls is filled with the photocatalyst powder. Because of the high optical density, the transmittance of the powder layer can be assumed to be zero, (that is, $T \rightarrow 0$) over the whole spectral range. Also, because of the small area of the inlet window compared to the total area of the inner cavity of the reactor, the loss of light due to back reflection through the inlet window can also be assumed negligible (i.e., $R \rightarrow 0$). Accordingly, the light undergoes multiple reflection and scattering inside the reactor before it is eventually absorbed by the photocatalyst. We can therefore assume that all the light at any selected wavelength that entered

into the inner cavity of the reactor is absorbed by the photocatalyst. In other words, the absorption at the selected wavelength approaches unity (i.e., $A \rightarrow 1$). Accordingly, the experimental determination of the quantum yield is simplified to the measurement of the reaction rate and the light intensity at the inlet window of the reactor. It is clear that this type of black body reactor can be used only for gas–solid heterogeneous systems because of reagent transport problems.

Necessary Experimental Conditions to Measure the Quantum Yield. By definition, an additional necessity to determine the quantum yield correctly is for the surface of the photocatalyst to be irradiated uniformly. However, it is quite obvious that in the black body reactor (Figure 1) as well as in the majority of other types of reactors this condition cannot be fulfilled as the surfaces of the different particles of the photocatalyst are exposed to different intensities of the incident light. Nevertheless, Basov and co-workers^{6,12} have demonstrated that the experimentally measured quantum yield of a photochemical reaction in a nonuniformly irradiated heterogeneous system corresponds to the “true” quantum yield *provided* that the reaction rate scales linearly with light intensity. Indeed, the rate of a photochemical process on a unit of a uniformly irradiated surface can be represented as

$$dr = \varphi_\lambda \rho(S) dS \quad (6)$$

The total reaction rate is then given by eq 7.

$$r = \int_S \varphi_\lambda \rho(S) dS \quad (7)$$

where φ_λ is the “true” quantum yield on the uniformly irradiated elementary surface unit independent of photon flow, $\rho(S)$ is the irradiance on a given surface unit, and dS is an elementary surface unit. The quantum yield is then given by

$$\Phi = \frac{\int_S \varphi_\lambda \rho(S) dS}{\int_S \rho(S) dS} \quad (8)$$

If the rate of the photoprocess is directly proportional to the photon flow, then φ_λ is constant and the quantum yield is given by eq 9.

$$\Phi = \frac{\varphi_\lambda \int_S \rho(S) dS}{\int_S \rho(S) dS} = \Phi_\lambda \quad (9)$$

Clearly then, the experimental quantum yield does not depend on the irradiated surface area regardless of the light irradiance impinging on a given particle and corresponds to the true quantum yield, Φ_λ , as long as the reaction rate scales linearly on light intensity. In any other case, the quantum yield will depend on the area of the irradiated surface, which in turn will be different at different wavelengths. In such other cases, it is tenuous, in fact impossible, to compare the activity of a photocatalyst at different wavelengths or to compare the activities of different photocatalysts.

The same condition is also essential to avoid a dependence of the quantum yield of a surface photochemical reaction on light irradiance.¹ The dependence of the reaction rate r on photon flow ρ can generally be represented by eq 10.

$$r = (\text{const})\rho^m \quad (10)$$

where m is the order of the reaction with respect to the photon

flow. In this case, the expression for the quantum yield is given by

$$\Phi = (\text{const})' \rho^{m-1} \quad (11)$$

Clearly, for $m < 1$, the quantum yield of a surface process decreases as the photon flow increases. If the order m of the reaction with respect to photon flow is unity, the quantum yield becomes independent of photon flow and yields the maximum value of Φ .

Another significant condition to characterize the activity of a photocatalyst is the independence of the reaction rate, and thus Φ , on reagent concentration, so that the efficiency of a heterogeneous system depends only on the activity of the photocatalyst. Where the reaction rate depends on both light irradiance and reagent concentration,^{13–16} the two conditions can be satisfied by varying only one parameter, that is, either the reagent concentration or light irradiance, to achieve the maximum activity for the same heterogeneous system in order to determine the true quantum yield.

Experimental Section

The photodegradation of phenol over TiO_2 was chosen as the test reaction. Distilled phenol (Aldrich; purity >99%) was used as the reagent and TiO_2 (Degussa P25) and N-doped TiO_2 (TP-S201, Sumitomo Chemical Ltd) were used as the photocatalysts dispersed in ultrapure water (Mili-Q). The pH of the system was adjusted to 3 with HCl. A 1000-W Xe–Hg lamp (Oriol) in combination with an IR water filter connected to a monochromator (Corner Stone, Oriol) was used as the light source. The half-width of the slits was chosen to give a band-pass of about 20 nm, which corresponds to the band-pass of the filter used previously.^{2,4} The optical fiber was connected to the output slit of the monochromator through a light-focusing adapter. A set of neutral density filters (Oriol) was used to vary the light intensity of the actinic light. Filters were placed between the output slit of the monochromator and the optical fiber. The concentration of phenol in the system was measured by HPLC methods (Shimadzu LC 2010) after filtering a 1-mL solution through an inorganic 0.02- μm membrane filter (Whatman). Transmittance spectra of the heterogeneous system were recorded with the UV–vis Shimadzu-2040 spectrophotometer equipped with an integrating sphere assembly. A detailed description of the reactor is given below.

Experimental Setup. As mentioned above, the black body like reactor used by Basov and Solonitsyn cannot be used for liquid–solid heterogeneous systems because of reagent transport issues. Consequently, we have built a new setup based on the same concept to measure quantum yields in liquid–solid heterogeneous systems. A schematic diagram and a photograph of the reactor setup are displayed in Figure 2a and b, respectively. The reactor consists of a beaker containing the liquid phase with a dispersed photocatalyst and a cavity with a quartz wall located in the center of the beaker. The solution is mechanically stirred to avoid mass transfer limitation problems. The optical fiber (diameter, 2 mm) is inserted into the cavity to direct the light inside the cavity. Since the area of the fiber cross section is much smaller than the total area of the cavity wall, we can assume that back reflection is negligible and that all the light (including the diffuse reflected light) is eventually directed inside the solution. Thus, in such a reactor, the reflected light will always be negligible; that is, $R \rightarrow 0$. A very high optical density of the heterogeneous system can always be achieved so that $T \rightarrow 0$ by increasing the loading of the

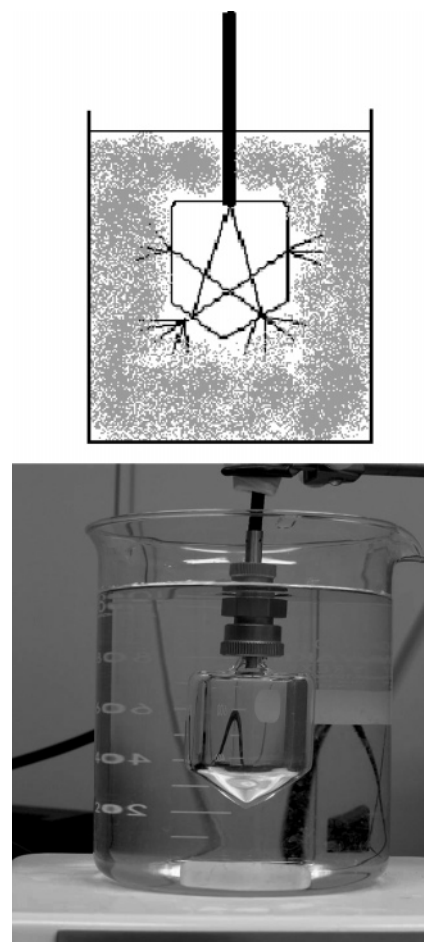


Figure 2. (a) Schematic sketch of the black body reactor for measurement of the quantum yield in liquid–solid heterogeneous system. (b) Photo of the black body reactor for measurement of the quantum yield in liquid–solid heterogeneous system.

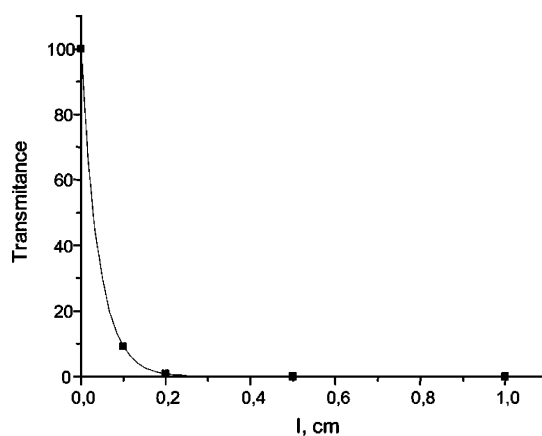


Figure 3. Dependence of the transmittance ($\lambda = 365$ nm) of the solution containing TiO_2 (Degussa P25; photocatalyst loading 1 g/L) measured with an integrating sphere on the light path length.

photocatalyst at a sufficient distance between the wall of the inner cavity and the wall of the beaker (in our experiments this distance was ca. 2.5 cm). As an example, Figure 3 represents a decay of the transmittance measured with the UV–vis spectrometer and integrating sphere assembly with increasing light path length in a solution containing TiO_2 (Degussa P25) at a photocatalyst loading of 1 g/L. As evident from the data, the loss of transmittance of light for a 1-cm path length does not exceed 1% in the spectral region of the fundamental absorption

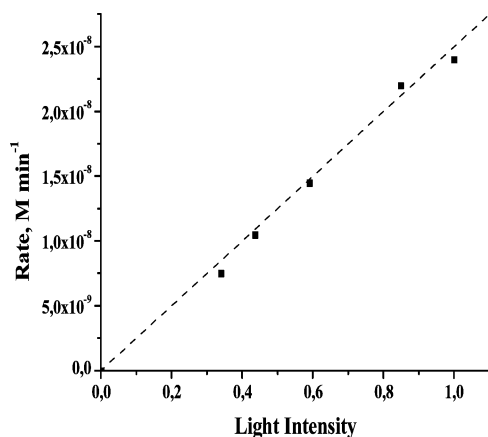


Figure 4. Dependence of the reaction rate of phenol photodegradation over TiO_2 (Degussa P25) on the light intensity.

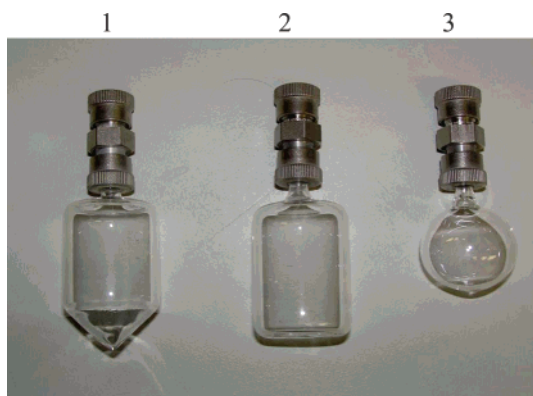


Figure 5. Photo of the inner cavities of the black body photoreactor used to measure the quantum yield of phenol photodegradation over TiO_2 (Degussa P25).

of the photocatalyst. Accordingly, we infer that all the light directed inside the cavity is eventually absorbed in our system so that $A \rightarrow 1$ in eq 3.

Hence, to measure the quantum yield of a heterogeneous photoreaction, one needs to know only the light irradiance at the outlet of the optical fiber and the rate of the heterogeneous photochemical reaction determined by any conventional method.

Results and Discussion

Experimental Verification of the Method Reliability. To verify the validity of the new method we measured the quantum yield of the photooxidation of phenol over TiO_2 (Degussa P25) at 365 nm to compare with that previously reported by Serpone and co-workers^{2,3} under very similar experimental conditions. As noted earlier, the necessary condition for the independence of the quantum yield of a heterogeneous photochemical reaction on light irradiance and on the irradiated surface area is that the reaction rate must scale linearly with the light irradiance. In previous studies,¹³ we established that the reaction rate of phenol photooxidation does not depend on the concentration and that it scales linearly on light irradiance at a phenol concentration of ca. 1 mM. As such, this concentration was chosen to measure the dependence of the reaction rate on light irradiance, as illustrated in Figure 4.

Cavities displaying three different shapes (see Figure 5) were used to confirm the independence of the quantum yield measured with the proposed method on the light distribution in solution and thus on the irradiated surface area of the photocatalyst. The

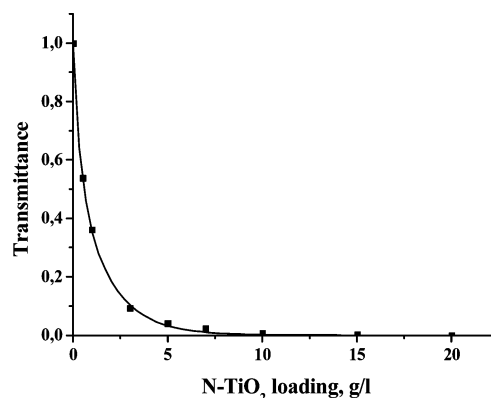


Figure 6. Decay of transmittance measured with the integrating sphere with increase of the photocatalyst loading at 436 nm (light path length, 1 cm).

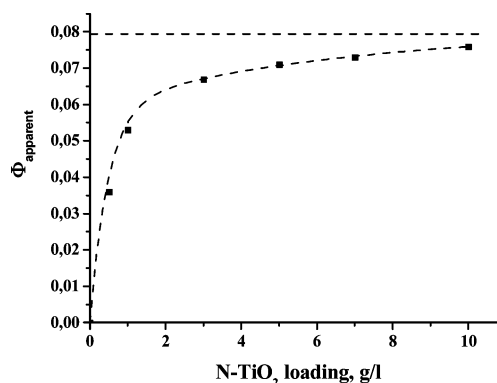


Figure 7. Increase of the apparent quantum yield with increase in the photocatalyst loading.

corresponding quantum yields were $\Phi = 0.14$ for cavity 1, $\Phi = 0.15$ for cavity 2, and $\Phi = 0.12$ for cavity 3. Therefore, all three values are within experimental error and in good accord with the quantum yield of phenol photodegradation ($\Phi = 0.14 \pm 0.02$) over TiO_2 (Degussa P25) reported earlier by Serpone and co-workers^{2,4} under similar conditions using an integrating sphere method. Thus, we conclude that our proposed new method for the experimental determination of quantum yields is valid and fairly reliable. A major advantage of the method is its simplicity so that it can easily be used in any photocatalytic laboratory.

Quantum Yield of Phenol Photodegradation over N-Doped TiO_2 . As a first application of our new method, we chose to measure the quantum yield of the photodegradation of phenol over N-doped TiO_2 at two different wavelengths, namely, 365 nm which corresponds to the fundamental absorption of TiO_2 and 436 nm corresponding to the N-doping induced visible absorption band.

The dependence of the transmittance of the heterogeneous system measured with the integrating sphere assembly on photocatalyst loading at 436 nm is reported in Figure 6. The results indicate that loss of transmittance of light for a 1-cm path length and photocatalyst loading greater than 7 g/L does not exceed 5%, which means that most of the light does not pass outside the reactor setup. We also measured the dependence of the apparent quantum yield on photocatalyst loading calculated with respect to the irradiance of the actinic light impinging on the reactor (Figure 7).

Here, we have used the term apparent quantum yield, instead of the otherwise more appropriate term photonic efficiency, to emphasize that regardless of the photocatalyst loading we can

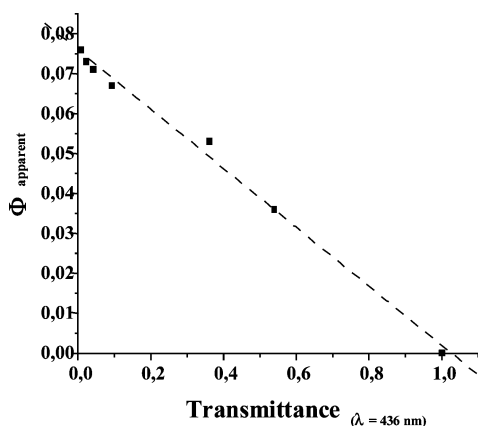


Figure 8. Decay of the apparent quantum yield with increase in transmittance.

always use eq 12 in our proposed method to calculate the parameter which at $A \rightarrow 1$ becomes the true Φ .

$$\Phi_{app} = \frac{dN_{molec}/dt}{dN_{hv(inc)}/dt} \quad (12)$$

This dependence is represented by a saturation curve that reaches the limit $\Phi_{app} = 0.08$ around a photocatalyst loading of about 12–14 g/L.

Taking into account that because of reactor geometry $R \rightarrow 0$ and that the reaction rate is directly proportional to the quantity of light absorbed, we can represent eq 12 as

$$\Phi_{app} = \frac{\Phi(1 - T) dN_{hv(inc)}/dt}{dN_{hv(inc)}/dt} \quad (13)$$

Clearly, the apparent quantum yield scales with the transmittance of the system (Figure 8), and when $T \rightarrow 0$ at sufficiently high photocatalyst loading, it approaches the limit of the true quantum yield.

The dependence of the photonic efficiency on photocatalyst loading similar to the one presented in Figure 7 was also observed and discussed in some detail by Serpone and co-workers.^{2,4} At sufficiently high loadings of the photocatalyst, the photonic efficiency approached the limit corresponding to the experimentally measured quantum yield of phenol photodegradation. The reason for such a coincidence is that at 365 nm (the wavelength used earlier²), corresponding to the fundamental strong light absorption, the fraction of reflected light, R , is quite small within the experimental error of the measurement of the quantum yield. In general, however, the fraction of reflected light may well be sufficiently large (particularly for extrinsic absorption in the visible spectral range) such that the limit of the photonic efficiency may not correspond to the true quantum yield. However, in the present proposed method, $R \rightarrow 0$ always, regardless of the wavelength of the actinic light so that, at sufficiently high loadings of the photocatalyst, one always measures true quantum yields.

The quantum yield determined at 436 nm for the photodegradation of phenol does not depend on light irradiance and therefore on the area of the irradiated surface of the photocata-

lyst. Accordingly, our system can also be applied to measure quantum yields in a spectral range corresponding to the extrinsic absorption caused by impurities or defects, provided that one uses a sufficiently high photocatalyst loading to satisfy the condition $T \rightarrow 0$. Under such conditions, then, the quantum yield for the photodegradation of phenol in N-doped TiO₂ aqueous dispersions under irradiation at 365 nm (intrinsic absorption of TiO₂) is $\Phi = 0.12$, whereas under irradiation in the extrinsic absorption at 436 nm induced by the N-doping Φ is 0.08.

Concluding Remarks

The concept of the black body like reactor has been applied for the first time to measure the quantum yield of photochemical reactions in liquid–solid heterogeneous systems. The major advantage of the new system compared to the previously used method is its simplicity. Owing to reactor geometry, the loss of reflectance of light, R , can always be taken to be 0, and at sufficiently high loadings of photocatalyst, which prevent transmittance loss of light ($T \rightarrow 0$), all the actinic light directed inside the heterogeneous system is eventually absorbed; that is, $A \rightarrow 1$. Thus, the experimental determination of the quantum yield requires only measurements of reaction rates and the irradiance of the actinic light, which can easily be done in any photochemical laboratory.

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