

Quantum Yields of the Photocatalytic Oxidation of Formate in Aqueous TiO₂ Suspensions under Continuous and Periodic Illumination

Catherine J. G. Cornu, A. J. Colussi,* and Michael R. Hoffmann*,†

Environmental Engineering Science, W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125

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Quantum yields ϕ_F for the oxidation of formate in periodically illuminated TiO₂ suspensions are always smaller than, but approach, at sufficiently high intermittence, the ϕ_F 's measured under continuous exposure at equivalent average photon absorption rates $\langle I_a \rangle$. We find that $\phi_{F,\text{cont}} = (0.031 \pm 0.003) \times I_a^{-0.39 \pm 0.03}$ in the range $0.089 \leq I_a / \mu\text{einstein L}^{-1} \text{ s}^{-1} \leq 2.02$. Under periodic illumination, ϕ_F begins to rise from its minimum value: $\phi_{F,\text{long } \tau} = \phi_{F,\text{cont}}(I_{a,\text{max}}) = 0.021$, for light periods $\tau_L \leq 1$ s, regardless of the duty cycle γ . Thereafter, ϕ_F climbs to its upper limit: $\phi_{F,\text{short } \tau} = \phi_{F,\text{cont}}(\langle I_a \rangle = \gamma I_{a,\text{max}})$, after a single inflection at $\tau_L \sim 200$ ms for $\gamma = 0.35$, but only after a second inflection at $\tau_L \sim 10$ ms for $\gamma = 0.05$. Thus, the photocatalytic oxidation of formate in ~ 10 nm TiO₂ nanoparticle suspensions under periodic illumination behaves kinetically as a homogeneous photochemical system; i.e., ϕ_F 's are not limited by mass diffusion, or by adsorption/desorption, but by carrier recombination. The latter has a characteristic time of about 0.1 s under present conditions. Sparse carriers, such as those present in $\gamma = 0.05$ experiments at short τ_L 's, are deactivated within ~ 6 ms. Therefore, photocatalytic quantum yields on nanoparticle surfaces are actually insensitive to events in the sub-milliseconds domain.

Introduction

The low quantum yields for the oxidation of aqueous pollutants on illuminated TiO₂ interfaces currently prevent the application of photocatalysis for large scale water remediation.^{1,2} Much effort has been devoted to understanding the fundamental and engineering aspects of semiconductor photocatalysis with the goal of improving its efficiency.³ Remarkably, whereas quantum yields in dilute aqueous solutions typically remain below $\sim 10\%$, those measured for the oxidation of atmospheric organic species exceed 50% under very weak illumination.^{2,4,5} The presumed slowness of electron scavenging by O₂ at the aqueous semiconductor interfaces vs carrier trapping and/or recombination, as well as mass transfer control into and from the surrounding medium, have been invoked to account for these observations.^{6–8} Since many one-electron transfers are required to fully oxidize organic substrates into CO₂, the competition for the primary oxidizing species by any chemical intermediates will also result in inefficient reactant degradation.⁹

One of the approaches recently proposed to overcome dissipative effects in TiO₂ photocatalysts involves periodic illumination.^{10–15} The tacit assumption was that charge and concentration gradients developing during light exposure would eventually relax in the ensuing dark period, thereby removing the efficiency losses associated with irreversibility.⁸ The two-electron oxidation of formate into CO₂ seems to be particularly appropriate for testing this hypothesis, since the number of intermediates is kept to a minimum. In 1993, Sczechowski et al., reported a 5-fold increase in the photoefficiency of formate oxidation in concentrated TiO₂ aqueous slurries by using $\tau_L = 72$ ms, $\tau_{\text{D(ark)}} = 1.45$ s cycles, apparently confirming the above expectations.¹⁵ However, the average incident photon flux under

such conditions is 21 times smaller than in the continuous photolysis regime relative to which the comparison is based. A subsequent study by Buechler et al., also compares quantum efficiencies based on lamp output rather than on average photon flux.^{10,11} Stewart and Fox claim a 1.8-fold rate improvement for the photocatalytic oxidation of 1-octanol by decreasing the repetition rate of the applied laser pulses from 10 to 1 Hz, a procedure that effectively amounts to a 10-fold reduction in the average photon flux.¹⁶ Thus, it appears that the alleged performance enhancements induced by discontinuous illumination are actually based on quantum yields (or efficiencies, see below) determined under widely different average photon fluxes. The distinction between the quantum yields ϕ 's, i.e., the ratio of photochemical over photon absorption rates, reported in some experiments vs the quantum efficiencies η 's, i.e., the number (frequency) of photochemical events over the number (frequency) of incident photons, reported in other studies neither invalidates the preceding objection nor impairs the transferability of periodic illumination effects among different sets of data.¹⁷

In this Letter we present the results of a quantitative study on the photocatalytic oxidation of formate in dilute (6 mg/L) suspensions of small ($\langle r \rangle \sim 10$ nm) TiO₂ particles that are fully consistent with the known kinetic behavior of a photochemical reaction occurring in a homogeneous (i.e., lacking kinetically relevant gradients) system under periodic illumination.¹⁸ More specifically, we find that the quantum yields measured under sufficiently high-frequency periodic illumination approach those measured under continuous illumination at the same average absorbed photon flux. Hence, no advantage accrues from the use of periodic illumination over the continuous regime. Buechler et al. have very recently reached a similar conclusion, which is at variance, however, with their previous analysis of these phenomena.¹⁹

* Corresponding authors.

† E-mail: mrh@its.caltech.edu.

Experimental Section

Titanium dioxide (Degussa P25), and formic acid (EM Science) were used as received. Suspensions were prepared by 20 min sonication of deionized water (MilliQ-UV-Plus, 18.2 MΩ·cm resistivity) loaded with 6 mg/L TiO₂, and later adjusted to 0.1 mM in formic acid at pH = 4.2. Solutions were sparged with neat oxygen at a flow rate of 20 mL min⁻¹ for 15 min prior to, and at 4 mL min⁻¹ during photolysis, while being magnetically stirred. The light source was an ozone-free 1000 W xenon arc lamp (Oriol). Its output traversed 10 cm of water to remove IR radiation, then a 320 nm high-pass filter, and finally a 340–380 nm band-pass filter. The light beam was subsequently focused onto the flat window of a jacketed, cylindrical fused silica reaction cell (26 mL, 2.5 cm optical path), whose temperature was maintained at 10 °C by means of a refrigerated circulating bath to prevent evaporative losses during prolonged sparging (see below).

Light pulses were generated by means of a mechanical shutter (Uniblitz VS14, 14 mm aperture, driven by a Uniblitz T132 controller) located at the focal point of two focusing lenses. The pulsed light beam fully illuminated the volume of the reaction cell. For the continuous photolyses, the shutter was left in place in the “open” position, and the light intensity was varied using neutral-density filters (Melles Griot). Sample aliquots (1 mL) were withdrawn at appropriate intervals, filtered through a 0.2 μm polysulfone syringe filter (Gelman), and analyzed for HCOO⁻ with a Dionex Bio-LC ion chromatograph (Dionex IonPac AS11/AG11 columns) equipped with a conductivity detector. Formate oxidation up to 80% conversions follows zero-order kinetics with respect to [HCOO⁻].

Photon absorption rate measurements were performed by chemical actinometry using (*E*)-α-(2,5-dimethyl-3-furylethylidene)isopropylidene)succinic anhydride (Aberchrome 540) as actinometer.²⁰ The photon rate incident on the cell in the absence of neutral-density filters was $I_0 = 7.59 \mu\text{einsteins L}^{-1} \text{ s}^{-1}$. At the low TiO₂ loads and the short (2.5 cm) optical path used, only a fraction of the incident light is absorbed. To determine the amount of scattered and transmitted vs absorbed radiation by TiO₂ suspensions, we performed an actinometry in which the cell was filled with the reaction solution, and the cell jacket with the actinometer. The jacket was externally shielded to exclude spurious light. In this configuration, I_0 photons L⁻¹ s⁻¹ enter the cell through the front window, of which I_b are scattered backward, I_a are actually absorbed by TiO₂, and the rest proceeds into the actinometer after being transmitted I_t , scattered forward I_f through the back window, or scattered through the cell side I_s . Therefore, the rate of photon absorption by the actinometer in the jacket I_j is given by $I_j = I_t + I_f + I_s = I_0 - I_b - I_a$. On the other hand, if T is the transmittance of these solutions measured with the UV spectrophotometer, $I_{t,UV} = T I_0 = I_0 - I_b - I_f - I_s - I_a$. Notice that I_f also represents a loss in this case, because only a negligible fraction of the diffuse radiation scattered forward is viewed by the collimated UV detector. Assuming Rayleigh scattering ($\lambda \gg$ average particle radius) and integrating over all scattering angles, we estimate that in our setup the geometric factor $I_b/(I_b + I_f + I_s) = 0.265$ applies.²¹ Furthermore, considering that, on average, the optical path lengths for scattered and transmitted photons inside the cell do not differ significantly, the coupling between absorption and scattering can be neglected. Therefore, from the experimental values of $I_j = 5.00 \mu\text{einsteins L}^{-1} \text{ s}^{-1}$, and $T = 0.449$ that apply to 6 mg L⁻¹ TiO₂ suspensions in the 2.5 cm length reaction cell, we obtain $I_{a,max} = 2.02 \mu\text{einsteins L}^{-1} \text{ s}^{-1} = 1.21 \times 10^{18} \text{ photons L}^{-1} \text{ s}^{-1}$. For spherical TiO₂

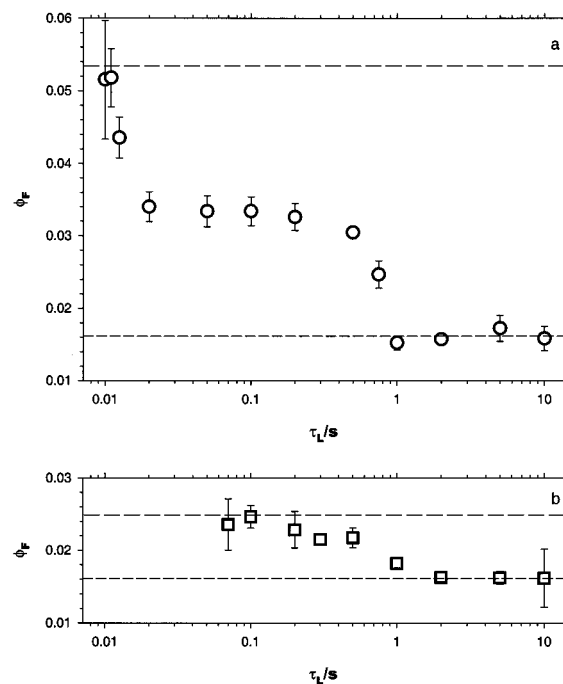


Figure 1. Quantum yields for formate photocatalytic oxidation under periodic illumination calculated from eq 1, at duty cycles γ : (a) 0.05, (b) 0.35. The upper dashed lines in each plot correspond to the quantum yields determined under continuous illumination at equivalent average photon absorption rates $\langle I_a \rangle = \gamma I_{a,max}$. The lower dashed lines in each plot correspond to the quantum yield measured under continuous illumination at $I_{a,max}$.

particles of radius $\langle r \rangle = 10 \text{ nm}$,²² and density $\delta = 3.7 \text{ g cm}^{-3}$, the number density in the suspension is $3.9 \times 10^{14} \text{ particles L}^{-1}$. Therefore, $I_{a,max}$ corresponds to the absorption of about 3100 photons particle⁻¹ s⁻¹. In contrast with laser photolysis, which delivers similar photon loads within nanoseconds, i.e., instantaneously in this context, the absorption of 3000 photons particle⁻¹ s⁻¹ does not imply the simultaneous presence of an equivalent number of carriers, because extensive recombination (as evidenced by the low quantum yields) takes place at comparable rates.

The effective photon absorption rate $\langle I_a \rangle$ in a particular pulsed experiment is given by the product of I_a times the fraction of the time the shutter is open [i.e., the duty cycle $\gamma = \tau_L/(\tau_L + \tau_D)$]: $\langle I_a \rangle = \gamma I_{a,max}$. For the continuous photolyses, the effective photon absorption rate is given instead by the product of $I_{a,max}$ times the transmittance of the interposed neutral-density filter: $\langle I_a \rangle = T_{\text{filter}} I_{a,max}$. The quantum yield for the photocatalytic degradation of formate, ϕ_F , was calculated in all cases as the degradation rate divided by the effective photon absorption rate, $\langle I_a \rangle$:

$$\phi_F = -\frac{1}{\langle I_a \rangle} \frac{d[\text{HCCO}^-]}{dt} \quad (1)$$

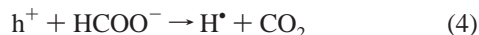
Results and Discussion

We measured ϕ_F 's under pulsed illumination conditions in which the incident photon rate was kept constant at $I_0 = 7.59 \mu\text{einsteins L}^{-1} \text{ s}^{-1}$, while the light times τ_L were varied over several orders of magnitude at fixed duty cycles of $\gamma = 0.05$ and 0.35. These correspond to average photon absorption rates $\langle I_a \rangle = \gamma I_{a,max}$ of 0.10 and 0.71 $\mu\text{einsteins L}^{-1} \text{ s}^{-1}$, respectively. The results are shown in Figure 1, in which error bars represent 95% confidence intervals. The error bars do not take into

account the accuracy of the assumptions made. Specifically, the possible systematic errors associated with our procedure for estimating light absorption rates (see above) are not included in the reported error bars, a shortcoming that would not affect, however, the relative quantum yield values on which most of the ensuing discussion is based. Quantum yields approach a common, minimum value of $\phi_{F, \text{long } \tau} = 0.021 \pm 0.003$ for both $\gamma = 0.05$ and 0.35 at $\tau_L \geq 2$ s. At shorter τ_L 's, ϕ_F jumps to constant values of 0.042 ($\gamma = 0.05$) and 0.031 ($\gamma = 0.35$), between 500 and 50 ms. For $\gamma = 0.05$, a second jump occurs at $\tau_L \leq 15$ ms. The experimental setup imposes lower limits of $\tau_L \sim 10$ and 70 ms for $\gamma = 0.05$ and 0.35 , respectively.

As a benchmark for quantum yield improvements over those merely due to a decrease in average photon absorption rate, we performed a series of continuous illumination photolyses with attenuated light beams. The results of these experiments are shown in Figure 2. ϕ_F increases monotonically with decreasing photon absorption rate from $\phi_{F, \text{short } \tau} = 0.021$ at $I_a = I_{a, \text{max}} = 2.02 \mu\text{Einsteins L}^{-1} \text{ s}^{-1}$ (without attenuation), to $\phi_{F, \text{short } \tau} = 0.074$ for $I_a = 0.089 \mu\text{Einsteins L}^{-1} \text{ s}^{-1}$ (95.6% attenuation). The solid line in Figure 2 corresponds to a power-law regression $\phi_F \propto a(I_a)^m$ to the data points. The best fit is obtained for $a = 0.031 \pm 0.003$, $m = -0.39 \pm 0.03$.

From these results one can evaluate the quantum yields that would be attained under continuous illumination at the average absorbed photon flux prevalent in the pulsed experiments at $\gamma = 0.05$ and 0.35 . These limits are indicated as dashed lines in Figure 1. Therefore, under present experimental conditions, the quantum yield for periodic illumination is smaller than or equal to the quantum yield for continuous illumination at the same average photon absorption rate, but larger than or equal to the quantum yield for continuous illumination at the maximum photon absorption rate $I_{a, \text{max}} = 2.02 \mu\text{Einsteins L}^{-1} \text{ s}^{-1}$. Additional experiments for light times of 5 s and 200 ms performed with duty cycles of $\gamma = 0.15$ and 0.25 (data not shown) confirm this conclusion. The quantum yields for any of the $\tau_L = 5$ s photolyses are the same within the experimental error: $\phi_{F, \text{long}} = 0.022$. The above results can be rationalized with reference to the following mechanism taking place in a homogeneous system:



where e^- and h^+ stand for photogenerated electrons and holes, respectively, and Ω_j for one of the j traps available per particle. This mechanism leads to reaction rates R_4 and quantum yields $\phi_F = R_4/I_a$ ($I_a \equiv R_2$).¹⁸

$$R_4 = \beta \langle I_a \rangle^n, \quad \phi_F = \beta \langle I_a \rangle^{n-1}, \quad 0.5 \leq n \leq 1 \quad (8)$$

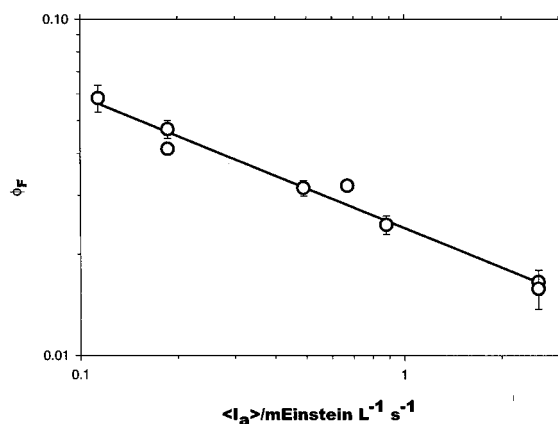


Figure 2. Quantum yields for formate photocatalytic oxidation under continuous illumination at $\langle I_a \rangle$. The solid line corresponds to a power-law regression to the data: $\phi_F = (0.031 \pm 0.003) \langle I_a \rangle^{-0.39 \pm 0.03}$ in the range investigated.

where β is a proportionality constant independent of I_a . The condition $0.5 \leq n \leq 1$ follows from the simultaneous occurrence of first- and second-order carrier recombination steps. At sufficiently long τ_L values the system reaches steady state during the illuminated periods, and the overall reaction rate under pulsed illumination is equivalent to that of having the reaction taking place under $I_{a, \text{max}}$ for γ of the time, i.e.

$$R_{4, \text{long } \tau} = \beta \gamma I_{a, \text{max}}^n \quad (9)$$

and $\phi_{F, \text{long } \tau} = \beta \gamma I_{a, \text{max}}^n / (\gamma I_{a, \text{max}}) = \beta I_{a, \text{max}}^{n-1}$, independent of γ , as observed. On the other hand, at very short τ_L 's the system cannot adjust to the modulated photon flux, and effectively behaves as irradiated under the average photon rate $\langle I_a \rangle = \gamma I_{a, \text{max}}$:

$$R_{4, \text{short } \tau} = \beta (\gamma I_{a, \text{max}})^n \quad (10)$$

and $\phi_{F, \text{short } \tau} = \beta (\gamma I_{a, \text{max}})^n / (\gamma I_{a, \text{max}}) = \beta (\gamma I_{a, \text{max}})^{n-1}$; i.e., the quantum yield under high-frequency pulsing is identical to that obtained at constant illumination at $\langle I_a \rangle = \gamma I_{a, \text{max}}$, in accord with present findings. Since $n < 1$, it follows that $\phi_{F, \text{short } \tau} > \phi_{F, \text{long } \tau}$. The kinetic response of photochemical systems to periodic light is such that, if first-order trapping, steps 6 and 7, were neglected, ϕ_F becomes roughly proportional to $[1 - \tanh(\alpha)]$, with $\alpha = (R_2 k_5)^{1/2} \tau_L$.¹⁸ Furthermore, the transition from long to short τ_L 's occurs at α values that are a weakly increasing function of γ , because second-order recombination decay times $[\propto (k_5 [\text{carrier}])^{-1}]$ and τ_D both decrease with γ . From literature tabulations,¹⁸ we infer that carrier lifetimes toward recombination are of the order of 0.1 s for $\gamma = 0.35$, and about 6 ms for those associated with the second inflection point in the plot ϕ_F vs. τ_L for $\gamma = 0.05$ (see below).

The fact that $\phi_{F, \text{short } \tau}$ is reached at $\tau_L \leq 200$ ms for $\gamma = 0.35$, but requires much shorter light intervals for $\gamma = 0.05$ deserves an explanation. Qualitatively, this finding implies the existence of a much faster decay channel for the charge carriers present under the specific regime supported by the shorter duty cycles.⁹ The presence of a small number j of carrier traps Ω per particle may account for this phenomenon. Note that about 63 carriers per particle are generated during a single 20 ms pulse, i.e., just before the onset of the second plateau in Figure 1a, followed by $\tau_D = 37$ or 380 ms dark intervals at $\gamma = 0.35$ or 0.05 , respectively. Traps would be eventually filled upon irradiation in both cases. However, empty traps would be available at the onset of every light period at $\gamma = 0.05$, since carriers decay more extensively during the ensuing long dark periods. In

contrast, traps would remain permanently occupied over experiments performed at $\gamma = 0.35$. Thus, in order to establish a steady-state carrier population for eq 10 to hold it is ultimately necessary to compete with fast trapping for $\gamma = 0.05$. A similar conclusion was recently arrived at in connection with experiments on metastable TiO_2 colloids at much lower I_a values.⁹

Superoxide steady-state yields and decay times on weakly illuminated ($1 \mu\text{W cm}^{-2}$) water– TiO_2 interfaces have been recently quantified.^{23,24} In contrast with the typically low photooxidation yields generally reported, and at variance with the contention that O_2 reduction, step 3, is rate-controlling, Ishibashi et al. measured $\phi_{\text{O}_2^-} \sim 0.8$. It was also found that O_2^- decay by a pseudo-first-order process with a half-life of about 70 s, probably via step 7 above. The shorter carrier decay times (~ 0.1 s) we measure are consistent with the 1.7 mW cm^{-2} irradiances [corresponding to illumination rates of 3100 (360 nm) photons particle⁻¹ s⁻¹] we use. In other words, carrier lifetimes determining photocatalytic quantum yields are compatible with each other, but are much longer than those (in the nanosecond–millisecond range) previously inferred from kinetic spectroscopy.^{2,25,26} A plausible, albeit tentative, interpretation of this observation is that at least one of the primary carriers produced photochemically in step 2 is rapidly localized and, hence, less prone to recombine, with a minimum loss of chemical potential. Efficient electron trapping as O_2^- , reaction 3, followed by interfacial recombination, reaction 7, would account for the reported large $\phi_{\text{O}_2^-}$ values, and for the O_2^- long decay lifetimes.²⁴ This is not a trivial result, because it implies that the characteristic times of all the chemically relevant processes in semiconductor photocatalysis are longer than a few milliseconds.

It is instructive to assess the importance of diffusional resistance in the photochemistry of colloidal suspensions. In our system, the Damköhler number, Da , which gives the ratio of kinetic to diffusional rates, is defined as²⁷

$$\text{Da} = \frac{R_{4,\text{max}}}{4\pi D r [\text{reactant}]} \quad (11)$$

where $R_{4,\text{max}} = 9.88 \times 10^{-23} \text{ mol s}^{-1} = 59.5 \text{ molecules s}^{-1}$, is the largest format decay rate per particle, $D = 1.45 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is the diffusion coefficient of formate in water at 300 K,²⁸ $[\text{HCOO}^-] = 0.1 \text{ mM}$, and $r = 10 \text{ nm}$, resulting in $\text{Da} = 5 \times 10^{-6}$. Similarly, for oxygen, $R_{4,\text{max}} = 4.94 \times 10^{-23} \text{ mol s}^{-1}$, $D = 2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $[\text{O}_2]_{\text{aq}} = 1.3 \text{ mM}$ at saturation, lead to $\text{Da} = 1 \times 10^{-7}$. Thus, throughout our experiments, even if sonication were not completely effective in breaking up particle aggregates, Da would be much smaller than the onset of diffusional control of chemical reactions ($\text{Da} \sim 0.01$). The fact that TiO_2 suspensions respond to light modulation as homogeneous media under present conditions implies that processes such as reactant adsorption and product desorption that, besides mass diffusion, could eventually generate concentration gradients do not contribute to the kinetics.⁸ We wish to emphasize that the preceding analysis and conclusions ultimately rest on the fundamental observation that ϕ_F values determined under periodic illumination are strictly bracketed by those calculated from the experimental $\phi_{F,\text{cont}}$ vs I_a dependence, and on the well-established theory of photochemical reactions driven by modulated light, rather than on mechanistic assumptions.

Conclusions

We verified that, in the absence of competing intermediates, and at the slow rates typical of most photocatalytic studies,

quantum yields under periodic illumination do not exceed those attained by continuous operation at equivalent average photon absorption rates. This conclusion is in accord with the theory of homogeneous photochemical reactions driven by intermittent illumination, and with estimates of the Damköhler number, which provides a measure of diffusional resistance in chemical processes, for nanoparticle suspensions. We found evidence for kinetically distinguishable carrier decay mechanisms at low and high duty cycles, and for carrier decay lifetimes that are much longer than previously estimated.

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References and Notes

- (1) Bahnmann, D. W.; Cunningham, J.; Fox, M. A.; Pelizzetti, E.; Pichat, P.; Serpone, N. In *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; Lewis Publishers: Boca Raton, FL, 1994; Chapter 21.
- (2) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnmann, D. W. *Chem. Rev.* **1995**, 95, 69.
- (3) *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier Science Publishers: Amsterdam, 1993, and references therein.
- (4) Linsebigler, A.; Lu, G.; Yates, J. T. *Chem. Rev.* **1995**, 95, 735.
- (5) (a) Ohko, Y.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. A* **1997**, 101, 8057. (b) Ohko, Y.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. B* **1998**, 102, 1724. (c) Ohko, Y.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. A* **1998**, 102, 2699.
- (6) Lewis, N. S. *J. Phys. Chem. B* **1998**, 102, 4843.
- (7) Gerischer, H. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: Amsterdam, 1993; p 1.
- (8) Upadhyay, S.; Ollis, D. F. *J. Phys. Chem. B* **1997**, 101, 2625.
- (9) Grela, M. A.; Colussi, A. J. *J. Phys. Chem. B* **1999**, 103, 2614.
- (10) Buechler, K. J.; Nam, C. H.; Zawistowski, T. M.; Noble, R. D.; Koval, C. A. *Ind. Eng. Chem. Res.* **1999**, 38, 1258.
- (11) Buechler, K. J.; Noble, R. D.; Koval, C. A.; Jacoby, W. A. *Ind. Eng. Chem. Res.* **1999**, 38, 892.
- (12) Foster, N. S.; Koval, C. A.; Sczechowski, J. G.; Noble, R. D. *J. Electroanal. Chem.* **1996**, 406, 213.
- (13) Sczechowski, J. G.; Koval, C. A.; Noble, R. D. *Chem. Eng. Sci.* **1995**, 50, 3163.
- (14) Sczechowski, J. G.; Koval, C. A.; Noble, R. D. In *Photocatalytic Purification and Treatment of Water and Air*; by Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: Amsterdam, 1993; p 121.
- (15) Sczechowski, J. G.; Koval, C. A.; Noble, R. D. *J. Photochem. Photobiol. A: Chem.* **1993**, 74, 273.
- (16) Stewart, G.; Fox, M. A. *Res. Chem. Intermed.* **1995**, 21, 933.
- (17) Serpone, N. *J. Photochem. Photobiol. A: Chem.* **1997**, 104, 1.
- (18) Burnett, G. M.; Melville, H. W. In *Technique of Organic Chemistry, Investigation of Rates and Mechanisms of Reactions*, 2nd ed.; Friess, S. L., Lewis, E. S., Weissberger, A., Eds.; Interscience Publishers: New York, 1963; Vol. VIII, Part II, Chapter 20.
- (19) Buechler, K. J.; Zawistowski, T. M.; Noble, R. D.; Koval, C. A. *Ind. Eng. Chem. Res.*, submitted for publication.
- (20) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 2, 341.
- (21) van de Hulst, H. C. *Light Scattering by Small Particles*; Dover: New York, 1981; p 65.
- (22) Product Information: Degussa Corp. Product: Titanium dioxide P25 (4/96).
- (23) Ishibashi, K.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Phys. Chem. B* **2000**, 104, 4934.
- (24) (a) Ishibashi, K.; Nosaka, Y.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. B* **1998**, 102, 2117. (b) Hirakawa, T.; Nakaoka, Y.; Nishino, J.; Nosaka, Y. *J. Phys. Chem. B* **1999**, 103, 4399. (c) Nosaka, Y.; Yamashita, Y.; Fukuyama, H. *J. Phys. Chem. B* **1997**, 101, 5822.
- (25) Serpone, N.; Lawless, D.; Khairutdinov, R.; Pelizzetti, E. *J. Phys. Chem.* **1995**, 99, 16655.
- (26) (a) Martin, S. T.; Herrmann, H.; Choi, W.; Hoffmann, M. R. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 3315. (b) Martin, S. T.; Herrmann, H.; Hoffmann, M. R. *J. Chem. Soc., Faraday Trans.* **1994**, 90, 3323.
- (27) Carberry, J. J. *Chemical and Catalytic Reaction Engineering*; McGraw-Hill: New York, 1976; Chapter 5.
- (28) *CRC Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, FL, 1998–99; p 5-95.