Hydroxyl radical and free and shallowly trapped electron generation and electron/hole recombination rates in TiO₂ photocatalysis using different combinations of anatase and rutile

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Abstract

Hydroxyl radical (OH•) and electron (e⁻) generation in aqueous suspensions during TiO₂ photocatalysis was studied, varying the properties of the photocatalyst and using the molecular probes terephthalic acid (TA) for OH• and resazurin dye (Rz) for electrons. Overall photocatalytic activity was calculated from rhodamine B dye degradation. The percentage of e⁻ recombination was found as the difference between the results for aqueous Rz in the presence and absence of a hole scavenger (glycerol). The findings show that the properties of the TiO₂ particles affect e⁻ and OH• generation rates differently. The generation rates of these active species and their overall photocatalytic activity were observed to be heavily dependent upon the physical properties of the TiO₂ used and the recombination percentage.

Keywords: TiO₂; properties; hydroxyl radical; electron; recombination; photocatalytic activity.

1. Introduction

The mechanism governing TiO₂-mediated photocatalysis has been widely studied [1, 2]. The free carriers (e^- and h^+) generated have been shown to participate in the photocatalytic degradation of adsorbed pollutants, directly or via the formation of reactive oxygen species (ROS) [3, 4]. The identification of such species (charge carriers and ROS) and their generation and recombination rates are consequently of scientific and technological significance, for they may contribute to the design of new materials with practical applications.

This study analyzes the oxidative reaction induced by photogenerated OH• and the reductive potential of photogenerated e^- . The rates of e^- and OH• photocatalytic generation from TiO₂ powder obtained by calcining commercial anatase were respectively quantified with terephthalic acid (TA) [3-5] and resazurin dye (Rz) [6-9]. Despite the many reports on the use of Rz dye as an indicator of photocatalytic activity, its utility in that respect has been confined to research on the rate of change in properties such as the absorbance/color associated with photocatalytic reactions. Inasmuch as Rz can be specifically reduced by electrons, it may be deemed to be a suitable method for quantifying the rate of e^- formation in photocatalysis. To the authors' knowledge, this is the first study to quantify the e^- generation rate by measuring the decline in Rz concentration with UV-Vis spectrophotometry. The use of data gathered with this dye to calculate the electronic recombination rate also provides insight into the effect of e^-/h^+ recombination on reactions photocatalyzed by TiO₂ with different properties. Overall photocatalytic activity is measured as the rhodamine B (RhB) photodecomposition rate constant, for although part of the dye may be sensitized under visible light, RhB is often used to trace photocatalytic activity in construction materials (UNI 11259:2008). The relationships between the generation rates of the active species and their effect on overall photocatalytic performance are discussed.

2. Materials and methods

2.1 TiO₂ powder

Commercial titanium dioxide powder was used as supplied (Hombikat UV100 TiO₂; TiO₂-C). In addition, a number of blends of anatase/rutile TiO₂ were obtained by heating a crucible containing 1 g of powder in a muffle furnace for 4 h at temperatures ranging from 400 °C to 1000 °C.

2.2 TiO₂ characterization

TiO₂ crystallography was determined by X-ray diffraction (XRD) conducted on a Bruker Advance-D8 diffractometer. The specific surface of the powder was found with the Brunauer-Emmett-Teller (S_{BET}) method using a Micromeritics NOVA2000 nitrogen absorption analyzer. The optical properties of the compound were found with diffuse reflectance spectroscopy (DRS) conducted on a Shimadzu UV-2600 UV-Vis spectrophotometer.

2.3. Photocatalytic experiments

2.3.1 Hydroxyl radical (OH•) quantification: terephthalic acid (TA) fluorescence (FL)

The amount of $\text{OH}\cdot$ forming at the illuminated photocatalyst/water interface was quantified with terephthalic acid fluorescence (TA-FL) [3, 5]. Fluorescence was applied to detect the $\text{OH}\cdot$ forming on the irradiated sample with highly reactive TA as the chemical probe to speedily generate fluorescent 2-hydroxyterephthalic acid (TAOH) [5]. Earlier studies showed that this method reliably quantifies free $\text{OH}\cdot$ generation based on the h^+ photogenerated in photocatalytic materials [3, 4]. $\text{OH}\cdot$ formation was determined in a suspension of 0.0055 g of TiO_2 powder in 100 mL of a 2 mM TA aqueous solution containing 2 mM NaOH in an aerated Pyrex glass cell, experimental conditions under which TA hydroxylation has been shown to be attributable exclusively to $\text{OH}\cdot$ [3].

The suspension was stirred in a dark box until photocatalyst-TA adsorption-desorption equilibrium was reached, after which stirring continued and the powder sample was irradiated uninterruptedly for 20 min. The solution was subsequently centrifuged to remove the photocatalyst and FL intensity in the supernatant solution was measured at 425 nm after excitation at 315 nm. The amount of TAOH generated, determined from a calibration curve, was used to estimate the amount of free $\text{OH}\cdot$ formed, assuming a trapping factor of 35 % [3, 10].

2.3.2 Electron (e^-) reduction: resazurin (Rz) absorbance

The e^- formation rate at the illuminated photocatalyst/water interface was detected by UV-Vis absorbance using Rz as the probe molecule. Resazurin (Rz, blue) readily reacts with e^- to yield resorufin (Rf, pink) (Eq. 1).

Rz absorbance at 600 nm was measured for several standard concentrations and the absorbance – concentration values plotted to obtain a calibration curve. The concentration of the e^- generated in the photocatalytic reaction studied was found by extrapolating absorbance at 600 nm of the irradiated TiO₂ powder solution on the x-axis (Rz concentration). In addition to the aforementioned reaction mechanism ($\text{Rz} + 2e^- \rightarrow \text{Rf}$), electron calculations envisaged a trapping factor of 40 % to account for the direct or indirect competition between O₂ and Rz for the photogenerated e^- [11, 12].

Two ink formulations were used: (i) 3 g of glycerol and 0.04 g of resazurin dye in 1 L of aqueous solution as described by Mills et al. [13]; and (ii) the same formulation in the absence of glycerol. The glycerol-containing system is known as “intelligent ink” [7] for electron-hole (e^- - h^+) recombination is controlled by the hole scavenger (glycerol), affording the photogenerated electrons more time reduce the dye. The degree of electron recombination was calculated by comparing the values for the two formulations.

The experimental procedure involved magnetically stirring 0.0055 g of TiO₂ powder in 50 mL of Rz solution (with or without glycerol) in a Pyrex vial stored in the dark until photocatalyst-Rz adsorption–desorption equilibrium was reached. Stirring then continued as the suspensions were uninterruptedly irradiated. The TiO₂ powder was removed by centrifugation at different irradiation times and the degree of reduction measured in the supernatant solution. UV-Vis absorption spectra were collected on a Shimadzu UV-2600 spectrophotometer.

2.3.3 Photocatalytic degradation of rhodamine B

RhB discoloration was conducted under the same conditions as TA fluorescence and Rz absorbance, dissolving 0.05 g of TiO₂ powder in an aqueous solution containing 8 ppm of RhB. The solution was stored in the dark and stirred to saturate RhB adsorption prior to UV irradiation. The change in absorbance recorded by a spectrophotometer during irradiation at a wavelength of 550 nm was used to determine RhB concentration in the solution. As the relationship between the logarithm of the relative RhB concentration in the solution ($\ln(C/C_0)$) and irradiation time was approximately linear, the slope of the expression, i.e., the rate constant (k_{RhB}), was determined for each sample and used as the representative parameter for photocatalytic behavior.

2.3.4 Irradiation set up

The light source consisted of two Philips Actinic BL 15W/10 SLV fluorescent lamps emitting at 350 nm to 400 nm (optimally at 360 nm), with four additional narrow peaks at 406 nm, 435 nm, 545 nm and 576 nm. The light spectrum for the lamps is reproduced in Figure 1. The mean light intensity at the surface of the reaction solution was about 10 W/m².

Figure 1. Light spectrum for Actinic BL 15W/10 SLV lamps

3. Results and discussion

3.1 Characterization of TiO₂ samples

The XRD- and BET-determined physical properties of the TiO₂ powder used are summarized in Table 1. Anatase was stable up to a temperature of 800 °C, with small amounts (1 %) of rutile first appearing in the 900 °C samples and rising to 51 % in the 950 °C and to 71 % in the 960 °C samples. Anatase disappeared altogether at 1000 °C. Entering the anatase (101) and rutile (110) reflection broadening values into the Scherrer equation [14] showed that the

anatase crystallites grew with rising temperature from 8 nm to 91 nm at 960 °C, the last at which they were detected. In contrast, rutile crystallinity and crystal size exhibited no particular temperature-dependent pattern. Sample surface area declined with rising calcination temperatures.

The diffuse reflectance spectroscopic (DRS) values for TiO₂ nanoparticles are represented in Figure 2, where the Tauc equation was used to plot the Kubelka-Munk optical absorption coefficients $[F(R)]$. The findings show a progressive red shift in the absorption edges of the TiO₂ samples with rising temperature. The slight changes observed in the absorption edges at temperatures of under 900 °C became more perceptible at 950 °C to 1000 °C due to the gradual transition from anatase to rutile. The progressive decline observed in UV light absorption region ($>4\text{eV}$), in turn, could be attributed to the greater light scattering characterizing larger crystallites [15]. These DRS findings were consistent with the XRD results discussed above.

The TiO₂ powder band gap (E_g) was found by using the Tauc equation [16] to plot the Kubelka–Munk optical absorption coefficients $[F(R)]$ (Figure 2). $(FRh\nu)^{1/b}$ ($b=2$ for indirect band gaps such as in TiO₂) vs. $h\nu$ curves are linear in the valence to conduction band transition region (VB-CB) (Figure 2). The E_g value was found by linear extrapolation to the x-axis. Table 1 also gives the band gap values for the samples.

Figure 2. Tauc plot: $(F(R) \cdot h\nu)^{1/2}$ [(absorption coefficient $\times$ Planck's constant $\times$ frequency) $^{1/2}$] vs. incident photon energy (eV).

Table 1. Physical-chemical and optical properties of TiO₂ samples (A: anatase; R: rutile)

Sample	Phase percentage (%) ^a		Crystallite size (nm) ^a		FWHM (°) ^a		BET surface area (m ² /g)	Band gap (eV)
	A	R	A	R	A	R		
TiO ₂ -C	100	-	8	-	0.99	-	310	3.32
TiO ₂ -400	100	-	11	-	0.65	-	109	3.30
TiO ₂ -500	100	-	16	-	0.51	-	79	3.29
TiO ₂ -600	100	-	32	-	0.37	-	49	3.26
TiO ₂ -700	100	-	49	-	0.26	-	27	3.25
TiO ₂ -800	100	-	69	-	0.18	-	13	3.22
TiO ₂ -900	99.1	1	75	163	0.17	0.074	9.5	3.22
TiO ₂ -950	44.9	51.1	90	138	0.18	0.075	3.4	2.94
TiO ₂ -960	28.5	71.5	91	136	0.21	0.076	3.2	2.91
TiO ₂ -1000	-	100	-	137	-	0.075	2.8	2.99

^aEstimated from the broadening of anatase (101) and rutile (110) XRD reflections

3.2 Rate of OH• formation in irradiated TiO₂ photocatalysts

FL intensity was observed to be linearly related to the duration of UV irradiation in the TiO₂ suspensions (Figure 3(a)). TAOH concentration was quantified from the calibration curve obtained by plotting FL intensity at 425 nm against previously reported standard TAOH concentrations ($FL(a.u.) = 143.66 \cdot [TAOH](\mu mol)$) [3] assuming a trapping factor of 35 % [3, 10]. The OH• formation rate (Figure 3(b)), $R_{OH\cdot}$ ($\mu mol/min$), was calculated from the slope of the FL intensity – irradiation time curve.

Figure 3. (a) FL intensity vs. time (mean of two measurements); (b) OH• formation rate ($R_{OH\cdot}$) by photocatalyst

$R_{OH\cdot}$ rose with temperature up to values of 700 °C to 800 °C, began to decline with the appearance of the rutile phase at 800 °C and sharply thereafter. The effect of the intrinsic properties of TiO₂ samples on OH• formation is discussed in detail in section 3.5.

3.3 Rate of e^- formation in irradiated TiO₂ photocatalysts

As the calibration graph in Figure 4(a) shows, Rz concentration is linearly related to its absorbance at 600 nm (Abs_{600}). Given that Rz Abs_{600} in the TiO₂ suspensions declined at longer irradiation times, likewise linearly (Figures 4(b) and 4(c)), e^- formation at the TiO₂ surface could be inferred to be proportional to irradiation time. The formation rate (R_{e^-} , μmol/min) was consequently determined from the slope of the Abs_{600} - irradiation time curve

by extrapolating the experimental Abs₆₀₀ values on the calibration curve, assuming the reaction mechanism described in Eq. 1 and a trapping factor of 40 % (section 2.3.2.)

The linearity of Rz Abs₆₀₀ – irradiation time plots for all the TiO₂ suspensions is clearly visible in Figures 4(b) (with glycerol) and 4(c) (without glycerol). At irradiation times of over 10 min decline was non-linear in the most active TiO₂ suspensions, a finding attributed to Rz depletion. In this study, the e⁻ formation rates calculated from the data in Figures 4(b) and 4(c) for the two Rz formulations are shown in Figure 4(d), which also includes the recombination percentages found with Equation 2:

$$e^{-}_{recombination}(\%) = [(R_{e-g} - R_{e-})/R_{e-g}] \times 100 \quad (2)$$

where e⁻_{recombination} is the e⁻ recombination percentage; R_{e-g} is the e⁻ formation rate using Rz with, and R_{e-} the rate using Rz without glycerol.

The differences in the e⁻ formation rate with and without the scavenger (glycerol) were observed to vary widely depending on the temperature, as discussed in detail in section 3.5.

Figure 4. (a) Regression line for Rz absorbance; (b) absorbance (Abs₆₀₀) in Rz samples containing glycerol; (c) absorbance in Rz samples without glycerol; and (d) logarithm of the e⁻ formation rate (R_{e-}). The percentages of e⁻ recombination are also included.

3.4 Rhodamine B (RhB) test

The fluctuations in relative RhB concentration in water versus irradiation time are plotted for all the samples in Figure 5(a). The RhB degradation rate (K_{RhB} , min^{-1}) determined from the slopes of the lines in Figure 5(a) is graphed in Figure 5(b). The higher the calcination temperature, the higher was rate constant K_{RhB} up to around 700 °C to 800 °C, when it began to decline with the appearance of rutile, i.e., exhibiting the same pattern as observed for $\text{OH}^\bullet$ formation ($R_{\text{OH}^\bullet}$), discussed in section 3.2. The effect of the intrinsic properties of calcined TiO_2 samples on overall photocatalysis is discussed in detail in section 3.5.

Figure 5. (a) RhB photodegradation and (b) pseudo first order kinetic rate constant (K_{RhB}) for RhB degradation in the presence of TiO₂ samples (average of two measurements)

3.5 Factors affecting photocatalytic generation of active species and overall photocatalytic activity

Variations in the calcination temperature had a significant effect on the intrinsic properties of the photocatalyst, such as crystal size, type and content of phases present and surface area, all of which impacted its activity substantially, although the respective relationships were not straightforward. An earlier study of photocatalytic activity in 35 titania samples with different physical properties found the dependence of activity on each property to be ambiguous [17].

The graph in Figure 6 depicts the RhB photocatalytic degradation rate (K_{RhB}), the OH• formation rate ($R_{OH•}$), the e⁻ ($R_{e^{-}}$) formation rate before and after recombination and the

surface recombination percentage (e^- recombination) values found in this study versus calcination temperature, BET area, phase content and anatase crystal size.

Further to the figure, K_{RhB} and $R_{OH\cdot}$ followed the same pattern and each behaved fairly similarly in all the samples irrespective of their differing physical properties. Those data were consistent with the degradation pathway described in earlier studies, according to which RhB photocatalytic oxidation under UV light may proceed either by $OH\cdot$ or $OOH\cdot$ attack (or both) [18, 19]. The high correlation between these two parameters also suggested that RhB bleaching was related to the photocatalytic generation of this active species by the photocatalyst tested, for while dye sensitization cannot be ruled out completely, it may be deemed negligible in the cases studied here. In contrast, the e^- formation rate (R_{e^-}) detected by the molecular probes with and without glycerol did not follow the same pattern as $K_{RhB}/R_{OH\cdot}$. The surface recombination percentage was much lower in the rutile- than in the anatase-containing samples and taken separately appeared to have no effect on overall photocatalytic activity. Nonetheless, the highest recombination was observed for the pure anatase samples, while K_{RhB} and the e^- - h^+ recombination rate were inversely and linearly related, with the former declining when the latter rose.

Figure 6. $\text{OH}^\bullet$ formation rate ($R_{\text{OH}}^\bullet$, $\mu\text{mol/min}$), e^- formation rate with and without glycerol (R_e , $\mu\text{mol/min}$), e^- recombination (%) and RhB photodegradation (K_{RhB} , min^{-1}) vs. physical-chemical parameters

Figure 6 shows that in the anatase samples, larger crystal size in conjunction with a smaller surface area induced by rising calcination temperatures resulted in higher $R_{\text{OH}}^\bullet$ and K_{RhB} . As smaller particle size and larger surface area generally translate into higher catalyst efficiency due to the larger number of active sites per square meter, reactivity would have been expected to be lower under the conditions prevailing here [20]. Furthermore, $R_{\text{OH}}^\bullet$ and K_{RhB} photoactivity must also be related to the percentage of surface recombination taking place. In nanocrystalline semiconductor particles, e^-h^+ recombination is a more significant factor

at smaller particle sizes, due to the rise in recombination site density [21-23]. The findings described here therefore suggest that recombination prevailed over crystallographic and microstructural parameters in the anatase samples. In keeping with that reasoning, e^- formation with controlled e^- - h^+ recombination (Figure 6, R_{e^-} with glycerol) was higher at smaller particle sizes due to higher photonic efficiency.

In the rutile-containing (alone or in combination with anatase) samples, $R_{OH\bullet}$ and K_{RhB} were observed to decline with rising calcination temperature. That behavior appeared to be related to the increase in rutile phase content. Kim et al. suggested that as rutile adsorbs $OH\bullet$ more effectively than anatase, the amount of $OH\bullet$ generated on TiO_2 and diffusing to the bulk solution would be lower in rutile crystallites [24]. That difference in $OH\bullet$ adsorption might explain the present findings, whereby $R_{OH\bullet}$, as found with the TA-FL method, was higher in anatase than rutile. Other authors reported that although more $OH\bullet$ was found near the surface than in the bulk solution for the two types of crystals, both surface and bulk solution $OH\bullet$ yields were extremely small in rutile. Those data would support scant photocatalytic-mediated $OH\bullet$ formation in rutile [23-26]. The possible explanation would be that on the anatase surface, water oxidation would convert trapped h^+ to adsorbed $OH\bullet$, generating significant amounts of $OH\bullet$. In contrast, on the rutile surface water would be oxidized to H_2O_2 and subsequently to O_2 , generating a certain amount of $OH\bullet$ in the latter process [25-28]. That argument is consistent with the present findings.

These results conflict, however, with studies in which synergies were observed in the photoactivity induced by thoroughly blended anatase–rutile powders. The theoretical model to explain enhanced photocatalysis with such a combination is based on charge separation

[29-32]. Assuming the presence of well-defined rutile and anatase particles in the TiO₂ calcined samples analyzed, electronic contact between the two phases would efficiently separate the e⁻h⁺ pair, lowering carrier recombination. According to the findings of this study, however, separation efficiency expressed as surface recombination (%) did not enhance the photocatalytic efficiency parameters expressed as K_{RhB} photodegradation or R_{OH•}. Sun et al. [33] showed that the beneficial synergies of anatase-rutile blends are not observed consistently, but vary with the relative anatase and rutile Fermi levels and particle shape. The findings discussed hereunder are consistent with the model set out in [23, 28, 34]. As valence band edge energy is higher in rutile than in anatase [23, 28, 34, 35], when charge carriers are generated by UV excitation in the latter, h⁺ migrates toward the rutile phase. The outcome is longer conduction band e⁻ lifetime in anatase as well as a decline in the effective h⁺ concentration on its surface [23]. As discussed earlier, OH• formation via water oxidation is far less efficient in rutile than in anatase particles. Therefore, although the presence of rutile may render charge carrier separation more efficient, neither the R_{OH•} in aqueous photocatalytic reactions nor K_{RhB} photodegradation would be favored.

Moreover, while the surface recombination values were low in rutile-containing samples, a steep decline in R_{e-} (with and without glycerol) was also observed with rising calcination temperature due to the increase in rutile phase content. Such differences in behavior between the two phases may be the result of the proportion of free or shallowly trapped e⁻, which have a longer lifetime and are highly reactive. As the proportion is higher in anatase TiO₂, photocatalytic reduction capacity is greater in it than in rutile, where the deeply trapped free electrons are less reactive and reduction activity lower [36]. That reasoning is consistent with the present experimental results, in which the proportion of photogenerated electrons

declined with rising rutile content. The behavior of the three parameters analyzed ($\text{R}_{\text{OH}\cdot}$, K_{RhB} and $\text{R}_{\text{e-}}$) in rutile-containing samples can be said to be induced by crystallographic factors such as rutile phase content, and exhibit lower sensitivity to recombination.

In follow-up research these results are being compared to electrochemical findings to validate the above hypothesis.

4. Conclusions

The hydroxyl radicals ($\text{OH}\cdot$) and electrons (e^-) forming on photoirradiated TiO_2 powders were respectively quantified with terephthalic acid fluorescence (TA-FL) and resazurin (Rz). The generation of these two active species and their effect on the overall activity expressed as the rate of oxidative degradation of rhodamine B were studied in connection with the physical-chemical properties of TiO_2 . The findings showed that crystallite size and phase content play an important role in nanocrystalline TiO_2 -based photocatalysis primarily by affecting photonic efficiency and e^- - h^+ recombination dynamics. In anatase samples, recombination seems to prevail over the photonic efficiency governed by crystallographic and microstructural factors. In contrast, in mixed anatase-rutile samples, crystallography and microstructure appear to predominate.

The decline in $\text{OH}\cdot$ and e^- generation rates with the appearance of rutile is the outcome of inefficient $\text{OH}\cdot$ generation during water oxidation on the rutile particles, and the shorter lifetime and lower reactivity of the free e^- in rutile samples. These findings may suggest an answer to the long-unresolved question of why anatase is more active than rutile in many photocatalytic reactions. This study provides further support for the premise that the photocatalytic synergies attributed to anatase-rutile blends are not invariably present, but depend on the relationship between anatase and rutile particle Fermi levels as well as particle

characteristics. In addition to contributing to an understanding of TiO₂ photocatalytic mechanisms, these findings may prove useful for the development of highly active TiO₂ photocatalysts.

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References

- [1] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, Understanding TiO₂ photocatalysis: mechanisms and materials, *Chemical Reviews*, 114 (2014) 9919-9986.
- [2] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results, *Chemical Reviews*, 95 (1995) 735-758.
- [3] E. Jimenez-Relinque, M. Castellote, Quantification of hydroxyl radicals on cementitious materials by fluorescence spectrophotometry as a method to assess the photocatalytic activity, *Cement and Concrete Research*, 74 (2015) 108-115.

- [4] T. Hirakawa, Y. Nosaka, Properties of $O_2^{\bullet-}$ and $OH^{\bullet}$ Formed in TiO_2 Aqueous Suspensions by Photocatalytic Reaction and the Influence of H_2O_2 and Some Ions, *Langmuir*, 18 (2002) 3247–3254
- [5] K.-i. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, Detection of active oxidative species in TiO_2 photocatalysis using the fluorescence technique, *Electrochemistry Communications*, 2 (2000) 207-210.
- [6] R. Mohan, K. Krishnamoorthy, S.-J. Kim, Enhanced photocatalytic activity of Cu-doped ZnO nanorods, *Solid State Communications*, 152 (2012) 375-380.
- [7] A. Mills, J. Wang, S.-K. Lee, M. Simonsen, An intelligence ink for photocatalytic films, *Chemical communications*, (2005) 2721-2723.
- [8] A. Mills, J. Wang, M. McGrady, Method of Rapid Assessment of Photocatalytic Activities of Self-Cleaning Films, *The Journal of Physical Chemistry B*, 110 (2006) 18324-18331.
- [9] A. Mills, J. Hepburn, D. Hazafy, C. O'Rourke, N. Wells, J. Krysa, M. Baudys, M. Zlamal, H. Bartkova, C.E. Hill, Photocatalytic activity indicator inks for probing a wide range of surfaces, *Journal of Photochemistry and Photobiology A: Chemistry*, 290 (2014) 63-71.
- [10] M. Sahni, B.R. Locke, Quantification of Hydroxyl Radicals Produced in Aqueous Phase Pulsed Electrical Discharge Reactors *Industrial & Engineering Chemistry Research*, 45 (2006).
- [11] A. Mills, N. Wells, J. MacKenzie, G. MacDonald, Kinetics of reduction of a resazurin-based photocatalytic activity ink, *Catalysis Today*, 281 (2017) 14-20.
- [12] A. Mills, N. Wells, C. O'Rourke, Probing the activities of UV and visible-light absorbing photocatalyst powders using a resazurin-based photocatalyst activity indicator ink (Rz Paii), *Journal of Photochemistry and Photobiology A: Chemistry*, 338 (2017) 123-133.

- [13] A. Mills, N. Wells, C. O'Rourke, Correlation between ΔAbs , ΔRGB (red) and stearic acid destruction rates using commercial self-cleaning glass as the photocatalyst, *Catalysis Today*, 230 (2014) 245-249.
- [14] P. Scherrer, Estimation of the Previous and Internal Structure of Colloidal Particles by means of Roentgen Rays, *Nach Ges Wiss Gottingen*, (1918) 96-100.
- [15] J.-G. Yu, H.-G. Yu, B. Cheng, X.-J. Zhao, J.C. Yu, W.-K. Ho, The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic Activity of TiO_2 Thin Films Prepared by Liquid Phase Deposition, *The Journal of Physical Chemistry B*, 107 (2003) 13871-13879.
- [16] E. Jimenez-Relinque, I. Llorente, M. Castellote, TiO_2 cement-based materials: Understanding optical properties and electronic band structure of complex matrices, *Catalysis Today*, (2016).
- [17] O.-O. Prieto-Mahaney, N. Murakami, R. Abe, B. Ohtani, Correlation between photocatalytic activities and structural and physical properties of titanium (IV) oxide powders, *Chemistry Letters*, 38 (2009) 238-239.
- [18] Folli A., Jakobsen U. H., Guerrini G. L., Macphee D. E., Rhodamine B Discolouration on TiO_2 in the Cement Environment: A Look at Fundamental Aspects of the Self-cleaning Effect in Concretes, *Journal of advanced oxidation Technology* 12 (2009) 1.
- [19] T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, Photoassisted Degradation of Dye Pollutants. V. Self-Photosensitized Oxidative Transformation of Rhodamine B under Visible Light Irradiation in Aqueous TiO_2 Dispersions, *The Journal of Physical Chemistry B*, 102 (1998) 5845-5851.
- [20] A. Ibadon, P. Fitzpatrick, Heterogeneous Photocatalysis: Recent Advances and Applications, *Catalysts*, 3 (2013) 189.

- [21] H. Lin, C. Huang, W. Li, C. Ni, S.I. Shah, Y.-H. Tseng, Size dependency of nanocrystalline TiO₂ on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol, *Applied Catalysis B: Environmental*, 68 (2006) 1-11.
- [22] Z. Zhang, C.-C. Wang, R. Zakaria, J.Y. Ying, Role of particle size in nanocrystalline TiO₂-based photocatalysts, *The Journal of Physical Chemistry B*, 102 (1998) 10871-10878.
- [23] J.T. Carneiro, T.J. Savenije, J.A. Moulijn, G. Mul, How phase composition influences optoelectronic and photocatalytic properties of TiO₂, *The Journal of Physical Chemistry C*, 115 (2011) 2211-2217.
- [24] T. Kim, M. Lee, S. Lee, Y. Park, C. Jung, J.-H. Boo, Development of surface coating technology of TiO₂ powder and improvement of photocatalytic activity by surface modification, *Thin Solid Films*, 475 (2005) 171-177.
- [25] T. Hirakawa, K. Yawata, Y. Nosaka, Photocatalytic reactivity for O₂⁻ and OH radical formation in anatase and rutile TiO₂ suspension as the effect of H₂O₂ addition, *Applied Catalysis A: General*, 325 (2007) 105-111.
- [26] J. Zhang, Y. Nosaka, Mechanism of the OH radical generation in photocatalysis with TiO₂ of different crystalline types, *The Journal of Physical Chemistry C*, 118 (2014) 10824-10832.
- [27] R. Nakamura, Y. Nakato, Primary intermediates of oxygen photoevolution reaction on TiO₂ (rutile) particles, revealed by in situ FTIR absorption and photoluminescence measurements, *Journal of the American Chemical Society*, 126 (2004) 1290-1298.
- [28] M. Buchalska, M. Kobielski, A. Matuszek, M. Pacia, S. Wojtyła, W. Macyk, On oxygen activation at rutile-and anatase-TiO₂, *ACS Catalysis*, 5 (2015) 7424-7431.

- [29] H. Hou, M. Shang, L. Wang, W. Li, B. Tang, W. Yang, Efficient Photocatalytic Activities of TiO₂ Hollow Fibers with Mixed Phases and Mesoporous Walls, *Scientific Reports*, 5 (2015) 15228.
- [30] T. Kawahara, Y. Konishi, H. Tada, N. Tohge, J. Nishii, S. Ito, A patterned TiO₂ (anatase)/TiO₂ (rutile) bilayer-type photocatalyst: effect of the anatase/rutile junction on the photocatalytic activity, *Angewandte Chemie*, 114 (2002) 2935-2937.
- [31] X. Zhang, Y. Lin, D. He, J. Zhang, Z. Fan, T. Xie, Interface junction at anatase/rutile in mixed-phase TiO₂: formation and photo-generated charge carriers properties, *Chemical physics letters*, 504 (2011) 71-75.
- [32] J. Yan, G. Wu, N. Guan, L. Li, Z. Li, X. Cao, Understanding the effect of surface/bulk defects on the photocatalytic activity of TiO₂: anatase versus rutile, *Physical Chemistry Chemical Physics*, 15 (2013) 10978-10988.
- [33] B. Sun, P.G. Smirniotis, Interaction of anatase and rutile TiO₂ particles in aqueous photooxidation, *Catalysis Today*, 88 (2003) 49-59.
- [34] D.O. Scanlon, C.W. Dunnill, J. Buckeridge, S.A. Shevlin, A.J. Logsdail, S.M. Woodley, C.R.A. Catlow, M.J. Powell, R.G. Palgrave, I.P. Parkin, Band alignment of rutile and anatase TiO₂, *Nature materials*, 12 (2013) 798-801.
- [35] X. Sun, W. Dai, G. Wu, L. Li, N. Guan, M. Hunger, Evidence of rutile-to-anatase photo-induced electron transfer in mixed-phase TiO₂ by solid-state NMR spectroscopy, *Chemical Communications*, 51 (2015) 13779-13782.
- [36] A. Yamakata, J.J.M. Vequizo, H. Matsunaga, Distinctive Behavior of Photogenerated Electrons and Holes in Anatase and Rutile TiO₂ Powders, *The Journal of Physical Chemistry C*, 119 (2015) 24538-24545.