A New Perspective in the Use of FeOx-TiO₂ Photocatalytic Films: Insight into the Microstructure and Degradation Mechanism of Indole Occurring without Fe-Leaching

Sami Rtimi^{1*}, Cesar Pulgarin¹, Jean Claude Lavanchy², John Kiwi¹

¹Ecole Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-GPAO, Station 6, CH-1015 Lausanne, Switzerland

²IMG-Centre d'Analyse Minérale, Bât Geopolis, CH-1015, Lausanne, Switzerland

Corresponding author : sami.rtimi@epfl.ch

Abstract

The first evidence is reported for the degradation of Indole at the solid air interface under low intensity solar simulated light in a stable repetitive fashion. The co-sputtering of FeOx-TiO₂ on polyethylene (PE) lead to an accelerated Indole degradation kinetics compared to TiO₂-PE and FeOx-PE films. Indole degradation on TiO₂-PE, FeOx-PE and polyethylene (PE) supported photocatalysts is shown to proceed without Fe- or Ti-release as detected by inductively coupled plasma mass-spectrometry (ICP-MS). This opens a new perspective for the use of Fe-containing films in the degradation of pollutants. The mechanism of charge generation by TiO₂-FeOx-PE film under light irradiation as a function of the applied light intensity provides insight and is discussed in relation to Indole degradation. The photo-generated charges in the film give rise to highly oxidative radicals which were unambiguously identified by appropriate scavenging experiments. The most oxidative species was O-singlet presenting an estimated lifetime of ~20 microseconds and a mean-free path of ~140 nm. The probability of the Indole triplet deactivation was 0.01 and was much smaller compared to the probability of 0.99 for the Indole*-triplet reaction with O₂ dissolved in the aqueous solution. By attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), the systematic shift of $\nu_s(\text{NH})$ and the $\nu_s(\text{C}=\text{C})$ vibration-rotational peaks were followed during Indole degradation presenting the evidence for the increase in the inter-bond distance and molecular fluidity. The increase of the film hydrophilicity during the irradiation was evaluated and seems to be necessary for the Indole degradation. An average size of ~16.7 nm of the TiO₂-FeOx nanoparticles sputtered for 2 min on the PE was determined by atomic force microscopy (AFM) and remained invariable during the degradation of Indole. The topmost layers of the FeOx-TiO₂-PE film were characterized for their optical, crystallographic features and roughness (Rg) by adequate surface science methods. This study provides the evidence for a FeOx-TiO₂ heterojunction with a random distribution of TiO₂ and FeOx nanoparticles on PE leading to interfacial charge transfer (IFCT) from FeOx to lower-lying TiO₂ rapping states.

Keywords: Indole degradation, Photocatalysis, FeOx-TiO₂, ions release, Surface characterization, mechanism.

1. Introduction

Until now, Fe-based Fenton homogeneous or heterogeneous processes [1-5] and TiO_2 [6-9] photocatalysis have been extensively reported intervening in the degradation of recalcitrant compounds under UV-and solar light irradiation in solution. In Fenton and photo-Fenton systems, Fe-ions in the presence of H_2O_2 induce highly oxidative radicals leading to the pollutant abatement. During the last decade, many studies have been reported presenting supported TiO_2 and/or Fe_2O_3 films showing environmental remediation performance under band-gap irradiation [5]. More recently, innovative sputtered photocatalysts led to pollutant degradation with practically no release (ppb range) of photo-active species. This shows that the topmost layers of the sputtered film mediate pollutant degradation by way of a semiconductor effect and not by the intervention of the released ions within the photocatalytic process. This is a change in the perspective for the intervention of Fe-photocatalysts addressing the degradation of organic compounds.

Indole is an N-heterocyclic aromatic commonly found in cocking, livestock farming and pesticides/pharmaceuticals. It has also been reported during the treatment of municipal waste-waters as emerging pollutants [10-11]. Indole in small amounts is present in natural water bodies as a decomposition product of tryptophan. Its solubility is high (2g/L) binding by H-bonding to water and other compounds in solution [12]. The toxicity of Indole has been reported in many studies addressing its effect on bacteria and laboratory testing animals [13-14]. These toxicity reports have moved some laboratories to devise approaches to degrade Indole by TiO_2 dispersions under UV-light [15-16]. K. Ranjit and J. Moser et al., have reported Indole degradation and the degradation of other benzenic type compounds under UV-light mediated by doped- TiO_2 through Ti-complexes [17-18]. By using another approach, K. Schafer et al., have degraded Indole by acidification and oxidation [18]. Bacterial degradation of Indole has been recently reported [19] and direct photo-dissociation of this compound by a 206 nm excilamp induced degradation of Indole within 150 min [20].

The novelty presented in this study relates to: a) the presentation of a new supported composite film $\text{FeOx-TiO}_2\text{-PE}$ not leaching of the Fe and Ti-constituents

as detected by ICP-MS, b) the FeOx-TiO₂-PE film presents uniformity, good adhesion of the binary oxides on the PE support, mechanical strength and long-time photocatalytic performance, c) the unambiguous identification of the radical intermediates leading to Indole degradation, d) the application potential of these innovative FeOx-TiO₂-PE films inducing Indole degradation proceeding under low intensity solar simulated light within an acceptable time (min range), e) the hydrophobic super-hydrophilic conversion proceeds a far shorter time than the time necessary to degrade Indole, f) the evidence by AFM for the FeOx-TiO₂ nano-particulate conserving its size and morphology during the Indole self-cleaning process, g) the evidence is presented for the inter-bond Indole NH- and C=C bonds increase preceding bond lysis and complete Indole degradation by ATR-FTIR spectroscopy, and finally h) a new perspective for the use of Fe films without components leaching. This allows the prepared photocatalyst to be used in the manufacture of ultra-purity water required in the electronic and pharmaceutical industries.

2. Experimental

2.1. Sputtering details, determination of the sample loading by X-ray fluorescence (XRF), irradiation procedures, materials and ICP-MS determination of the Ti and Fe leached during the photocatalyst recycling.

The FeOx-TiO₂ binary oxide was sputtered on 4x4 cm PE fabrics from 5 cm diameter targets (Kurt Lesker, East Sussex, UK) by direct current magnetron sputtering (DCMS) in an Ar : O₂ gas mixture (90% : 10%). The PE-film was positioned at 10 cm from the target and rotating at 20 rpm to guarantee coating uniformity. The composite FeO_x-TiO₂-PE samples were co-sputtered simultaneously. The polyethylene (PE) film consisted of a highly branched semi-transparent film with the formula H(CH₂-CH₂)H. The (LDPE) 0.1 mm thick was obtained from Goodfellow (UK) had a density of 0.92 g/cm³.

The Fe- and Ti-content of sputtered on PE films were evaluated by X-ray fluorescence (XRF) in a PANalytical PW2400 spectrometer. The XRF analysis detects the content of the Fe/Ti layers on PE and the results are reported in Table 1.

The nominal calibration of the film thickness was carried out on the Si-wafers and the film thickness was determined with a profilometer (Alphastep500, TENCOR) and the results are shown in Table 2. The thicknesses of the FeO_x-TiO₂ layers sputtered for 2 min was of 54 nm as shown in Table 2. This was the most effective catalyst leading to Indole degradation within 180 min. Within 1 s, a layer of 0.45 nm thick was sputtered on PE. This is equivalent to 2.25 atomic layers of 0.2 nm each. An atomic layer consists of 10^{15} atoms/layer/cm². Being each layer 0.2 nm thick, a 54 nm sputtered thickness layer contains a total of 270 atomic layers with a total content of 2.7×10^{17} atoms/cm² and were deposited at a rate of 2.2×10^{15} atoms/cm²xs.

The irradiation of the samples was carried out in the cavity of a sunlight simulator from Atlas Metrial Testing Solutions (Harkingen, Switzerland) tuned at a light dose of 52 mW/cm² provided for with a filter blocking the light < 310 nm. The experimental set-up used during sample irradiation is shown in Figure 1. Indole aliquots of 750 microliters were irradiated each time and the Indole degradation was followed by absorbance at 270 nm in a ShimadzuUV-1800 spectrophotometer.

Inductively coupled plasma spectrometry (ICP-MS) was used to follow the Fe and Ti release during the Indole repetitive degradation on FeO_x-TiO₂-PE films. The FinniganTM ICP-MS used was equipped with a double focusing reverse geometry mass spectrometer presenting an extremely low background signal and high ion-transmission coefficient. The spectral signal resolution was 1.2×10^5 cps/ppb and the detection limit of 0.2 ng/L (ppb) and the results are presented in Table 3. The TiO₂ and FeO_x of the films were digested in nitric acid 69% (HNO₃ : H₂O = 1 : 1) to remove organics in solution and to insure that there were no remaining ions adhered to the flask wall. The samples droplets are introduced to the ICP-MS unit through a peristaltic pump to the nebulizer chamber allowing the sample components evaporation and ionization. The Ti, and Fe found in the nebulizer droplets were subsequently quantified by mass spectrometry (MS). Table 3 shows the results obtained after the 7th repetitive use of a FeO_x-TiO₂-PE film mediating Indole degradation.

2.2. Optical, crystallographic and roughness and size properties of the sputtered films active in Indole degradation.

Diffuse reflectance spectroscopy (DRS) of Cu sputtered films was carried out a Perkin Elmer Lambda 900 UV-VIS-NIR spectrometer within the wavelength range of 200–800 nm. The crystalline structure of the sputtered films was investigated by X-ray diffraction (XRD) and recorded on an X'Pert MPD PRO from PANalytical equipped with a secondary graphite (002) monochromator and an X'Celerator detector operated in Bragg-Brentano geometry. The wettability of the sputtered films was determined by the water droplet contact angle (CA) by the sessile drop method on a DataPhysics OCA 35 unit. Drop volumes of 0.5 microliter were chosen to avoid shape alteration due to gravitational forces and to diminish the evaporation effects. The measurements were performed at room temperature (65% controlled humidity).

Film roughness (R_g) and particle size were determined by atomic force microscopy. The AFM images were acquired in contact mode using a PSIA Xe-100 AFM. Silicon nitride cantilevers were used with feedback set points around 1.0 nN. The images originate from the Z-scanner and are not influenced by the non-linearity and the hysteresis of the z-scanner. The experimental error in the roughness was below 10% for the selected 300nmx300nm scanned area. The mean surface roughness values (R_g) involve an experimental error below 10%.

2.3. Infrared spectroscopy (ATR-FTIR) and XPS-spectroscopy of the atomic surface concentration on FeOx-TiO₂-PE during the degradation of Indole.

FTIR spectra were measured in a Portmann Instruments AG spectrophotometer equipped with a Specac attachment (45° one pass diamond crystal). Spectra were taken by 256 scans with a resolution of 2 cm⁻¹ in the range 900-4000 cm⁻¹. The position of the IR peaks was found by the second derivative of the spectra after Fourier deconvolution. The X-ray photoelectron spectroscopy (XPS) of the FeOx-TiO₂-PE films was measured using an AXIS NOVA photoelectron spectrometer (Kratos Analytical, Manchester, UK) provided for with monochromatic AlK_α ($h\nu=1486.6$ eV) anode. The carbon C1s line with position at 284.6 eV was used as a reference to correct the charging effect. The surface atomic concentration was determined from peak areas using the known sensitivity factors for each element [21-22]. Spectrum background was subtracted according to Shirley [23] and the XPS spectral peaks were deconvoluted with a CasaXPS-Vision 2, Kratos Analytical UK.

3. Results and discussions

3.1. Optimization of Binary-oxides Sputtering Parameters: Effect on the Degradation Kinetics of Indole leading to Stable Film Recycling.

Figure 2a, traces 1 and 2 show that the PE sputtered between 2 and 5 minutes containing the levels of TiO_2 and FeOx as shown in Table 1 lead within 180 min to Indole degradation. Figure 2a, traces 3 and 4 show that PE- TiO_2 by itself as well as FeOx-PE degraded Indole with a slower kinetics. Figure 2a, trace 5) shows that PE-films by themselves do not lead to Indole degradation. Finally, Figure 2a shows no degradation of Indole on co-sputtered FeOx- TiO_2 -PE films for 2 min in the dark. This implies that any Fe-Indole or/and TiO_2 -indole complex is only formed through Fe^{3+} or Ti^{4+} -complexes under light irradiation. Such complexes presenting low symmetry have been reported [15,17-18]. This is an important consideration since these complexes may also be involved in a mechanism proceeding by interfacial charge transfer mechanism leading to Indole degradation. Figure 2b shows the effect of an increasing Indole concentration mediated by FeOx- TiO_2 -PE co-sputtered films for 2 min slowing down the degradation kinetics under low intensity solar irradiation. Figure 2c shows the recycling up to the 7th cycle of a FeOx- TiO_2 -PE film under light leading to Indole degradation presenting a stable repetitive kinetics. By ICP-MS, Table 3 shows 0.5 ppb Fe was found for a 2 min FeOx- TiO_2 -PE co-sputtered film after degradation of Indole. The absence of Fe losses allows for the stable Indole degradation on FeOx- TiO_2 -PE films.

3.2. FeOx- TiO_2 -PE semiconductor behavior leading to the degradation of Indole: experimental evidence, scavenging of oxidative radicals and reaction mechanism

Figure 3 shows the effect of the light intensity on the Indole-degradation kinetics. Table 3 shows no TiO_2 leaching and only ppb Fe generation by the FeOx- TiO_2 -PE film under light irradiation. This proves the FeOx semiconductor behavior photo-generating surface charges as a function of the applied light dose [5-7]. No saturation effects in the FeOx- TiO_2 -PE film were observed for the kinetics of Indole degradation since this process accelerated step-wise as a function of the applied light intensity (Figure 3).

Evidence for Indole oxidative intermediates in aerobic conditions proceeds by highly oxidative radicals OH° , $\text{HO}_2^\circ/\text{O}_2^-$, $\text{vb}(\text{h}^+)$ and O-singlet is shown by the scavenging of these radicals in Figure 4. Indole degradation is slowed down by addition of these scavengers. Figure 4 presents the scavenging of the OH° -radical by methanol (trace 2), scavenging of $\text{vb}(\text{h}^+)$ by ethylene tetra-acetic acid di-sodium salt (EDTA-2Na, trace 3), scavenging of the HO_2 -radical by benzoquinone (trace 4), and finally scavenging of O-singlet by sodium azide (NaN_3 , trace 5). These radicals and O-singlet are generated by reactions (8-9). During Indole degradation the pH decreases from 6.2 to 4.7 consistent with eq.(10) as suggested below and the indole excited state reacting with O_2 leads to O-singlet by eq.(11) [15-18] as shown in Figure 4, trace 5) :

The FeOx-TiO₂-PE film upon sunlight irradiation leads to charge separation/Indole degradation as suggested in eqs.(1-7) and noted in Figure 5:

The overall Indole degradation under sunlight can be suggested up in eq.(11):

The heterojunction of FeOx-TiO₂ in Figure 5 shows the charge transport and quasi-Fermi level equilibration at the FeOx-TiO₂ interface and allowing the FeOx electron injection to the lower-lying TiO₂ trapping states [24-25]. Under sunlight the FeOx-TiO₂ the electron pair separation will originate primarily from FeOx (mainly Fe₂O₃). A decrease in the FeOx electron-hole recombination rate occurs due to the e-injection into TiO₂ lower lying trapped states at $\sim(0.5-0.8)$ eV below the TiO₂cb [26-27]. This is the reason for the faster Indole degradation shown by the FeOx-TiO₂-PE film in (Figure 2, trace 1) with respect to the FeOx-PE film (Figure 2, trace 4). The Indole leads to a short-lived unstable cation Indole⁺ during the photocatalytic degradation process. This cation has been reported to have a reduction potential of 1.24 V in the reaction Indole⁺ + e⁻ → Indole [28]. Like many benzenic-ring cations, the Indole-cation⁺ is short-lived and unstable reacting with oxygen as noted above in eq.(4).

In eq(4) the concentration of O₂ in the dilute Indole solution is 0.5×10^{-3} M and the rate of reaction with Indole $k_1 \cong 9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. By way of $T = 1/[O_2] \times 1/k_1$, the triplet Indole lifetime was estimated to be close to 20 microseconds. To estimate the mean-free path of the O-singlet in solution we took into account the encounter lifetime of Indole and the O-singlet. Inserting the Indole concentration of 5 ppm (5×10^{-6} M) in the simplified Smoluchowski approximation $x^2 \cong DT$ (x mean free path of O-singlet) and taking the Indole diffusion coefficient $D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$, a value typical for small molecules, a value of 140nm can be estimated for the O-singlet mean free-path in solution. If the lifetime of the Indole triplet is 20 microseconds, k the diffusion control rate for the reaction of indole with O₂ ($\sim 9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and the O₂ concentration in the diluted Indole solution $[O_2] \approx 0.5 \times 10^{-3}$ M, the probability P_1 for the triplet Indole deactivation $P_1 = (t^{-1}) / [(t^{-1}) + k [O_2]] \approx 0.01$. The probability P_2 of reaction between Indole* + O₂ → Indole⁺ + O₂⁻ leading to the Indole cation can in this way be estimated by $k [O_2] / [(t^{-1}) + k[O_2]] \approx 0.99$ [29-30].

The hydroxy-Indole radical does not have a well-defined structure since the hydroxyl-indole heterocyclic-ring presents the -OH Π -electron distribution delocalized on different ring positions.

3.3. Changes followed by ATR-FTIR spectroscopy on Indole and by XPS on the FeOx-TiO₂-PE film.

ATR-FTIR spectroscopy was used to monitor the Indole peaks decrease under low intensity solar simulated light. The results are presented in Figure 6a. In Figure 6a, the signals were sensitive enough to follow the changes of amplitude during Indole degradation. This approach was used previously to quantify the degradation of the bacterial cell wall components [31]. Figure 6a shows the characteristic vibrational peaks of the amine N-H at 3406 cm⁻¹ and 3500.2 cm⁻¹ [31,32] at time zero, after 15 min and after 180 min. The stepwise band shifts noted in Figure 6a reflect an increased mobility/disorder in the Indole chain-packing. This introduces a change in the density of the amine N-H groups with concomitant increase in fluidity and stretching of the intermolecular N-H bond distance [32]. Figure 2a shows that after 180 min the N-H functional groups attain the fluidity/mobility necessary for Indole bond lysis [31-33].

Figure 6b shows that conjugated bonds in the Indole aromatic ring (C=C) decrease from time zero up to 180 min for peaks at 1497.6 cm⁻¹ and 1506.1 cm⁻¹ respectively. The shifts in the ATR-FTIR spectra reported in Figure 6b was due to an increase in the vibrational stretching of the aromatic ring (C=C) bond up to 180 min when bond lysis occurs due to over-stretched C-H inter-bond distance.

Table 4 shows the changes in the surface atomic percentage concentration on the FeOx-TiO₂-PE films during the sunlight induced Indole degradation. The Ti2p percentage is decreased after contacting with Indole as expected and increases again but not up to the initial value (time zero). This indicates that some residual intermediates remain after 180 min on the film. The same pattern is observed for the atomic percentages of Fe2p. The O1s peaks decrease continuously. The C1s increases significantly after the contact with Indole, decreasing afterwards slightly during the photocatalysis. This indicates that the Indole degradation occurs along a low percentage of mineralization. The N2p is seen to decrease due to Indole photocatalysis leading to the degradation of the N-heterocyclic compound.

3.4. Optical and crystallographic properties found for the FeOx-TiO₂-PE films.

Figure 7 shows by DRS the significant enhancement of the optical absorption in the visible region of FeOx-TiO₂-PE films with respect to TiO₂-PE and FeOx-PE

films. This is partly due to the contribution of the plasmon resonance of the Fe-nanoparticles distributed at random on the sputtered binary oxide film [35-36]. The plasmon resonance of the FeOx nanoparticles interact with the random dispersed TiO₂ sputtered on PE described above during the discussion of the mechanism presented in Figure 5a,b. The spectrum amplitude of Fe₂O₃ between 250 and 500 nm has been reported to be a function of the film thickness and grain size [37]. In Figure 7 TiO₂-PE (traces 1) and FeOx-PE (trace 2) do not add up to trace 3 (FeOx-TiO₂-PE). Therefore, a new composite is formed during the co-sputtering showing a shift of trace 3 to longer wavelengths involving contact of Fe-oxides and TiO₂ with the formation of Fe-O-Ti transfer bands. The Fe-O-Ti bands lead to the formation of O-vacancies in the film with concomitant formation of the Ti³⁺-species absorbing in the visible region (blue color) [3-6,37]. The formation of Ti³⁺-ions on FeOx-TiO₂-PE allows the reduction of Ti⁴⁺ occurring along the back-reaction Fe²⁺ → Fe³⁺. The close radii of Fe³⁺ (0.68 Å) and Ti⁴⁺ (0.64 Å) enable the substitution of some Fe³⁺ by Ti⁴⁺ in the TiO₂-FeOx lattice [6-8]. The substitution of Ti⁴⁺ by Fe³⁺ introduces more O-vacancies in the TiO₂ with concomitant reduction of Ti⁴⁺ → Ti³⁺. The Ti³⁺-ions enhance the indirect transition of the TiO₂vbe- to the TiO₂cb. This increases the optical absorption of the FeOx-TiO₂-PE films (see Figure 7) [37]. The insert in Figure 7 shows the second derivative of the FeOx-TiO₂ spectrum with two absorption maxima at 382 nm and 526 nm.

The X-ray diffraction spectrogram (XRD) of the FeOx, TiO₂-PE and FeOx-TiO₂ films is shown next in Figure 8. Figure 8 (trace 1) shows for FeOx-PE hematite (2θ) peaks at 31.2° and 62.3°. The TiO₂ film in Figure 8 (trace 2) shows anatase and rutile peaks at 25.4° and 54.1° respectively. Finally, Figure 8 (trace 3) shows the hematite peak at 31.1° and TiO₂ peaks at 54.1° for rutile and 61.7° anatase. The fact that rutile and anatase peaks are observed on PE shows the structure forming function of the PE-substrate at temperatures 130-150°C as reported earlier by Kiwi et. al. [38]. Several additional peaks are observed in Figure 8 (trace 3) not found in traces 1 and 2. It is possible to suggest that the close radii of Fe³⁺ (0.68 Å) and Ti⁴⁺ (0.64 Å) induce crystal distortion in the TiO₂-FeOx composite lattice. This leads to an increase in the visible light absorption of the FeOx-TiO₂-PE film as shown in Figure 7.

3.5. Roughness, nanoparticle composite size and hydrophilicity build up on FeOx-TiO₂-PE during Indole degradation under light irradiation.

Figure 9 shows the AFM for the FeOx-TiO₂-PE 2 min co-sputtered films showing the mixed-phase TiO₂-FeOx nanoparticles with an average size of 16.7 nm and a roughness of 22.7 nm $\pm$ 10%. Three different magnifications are shown for these nanoparticles in Figure 3 revealing the morphology of these particles. During Indole degradation, the size of the particles remained invariable, showing the stability of the films used in Indole degradation. Figure 10 (trace 1) shows the hydrophobic to hydrophilic conversion kinetics under solar simulated light of FeOx-TiO₂-PE surfaces. This happens within the first 60 minutes of irradiation. Figure 10 (trace 2) shows the reverse reaction in the dark within much longer time (30 h) re-establishing the initial film hydrophobicity. This shows reversible photo-switching for these films. When a reverse reaction to the initial hydrophobic state is achieved, the repetitive kinetics reported in Figure 2c occur leading to repetitive Indole degradation. According to Young's theory, the " $\cos \Theta$ " of a liquid droplet on a solid surface is a function of the interfacial energy between the solid and the liquid [39]. Θ is a constant parameter in Young's equation, range from 0.6 to 1.1, depending on the nature of the film/surface. This point will not be discussed here since this is not the focus of the present work. Details have been widely reported [37,39,40].

4. Conclusions

This study presents the first evidence for Indole degradation on transparent FeOx-TiO₂-PE films under sunlight irradiation within acceptable times. The sputtered new composite films were uniform, adhesive, robust and present long-operational lifetime while degrading Indole without leaching oxide components. FeOx-TiO₂-PE films under low intensity sunlight irradiation leads to films with lower band-gap compared to PE-TiO₂ films since they shift the absorption into the visible region accelerating the Indole degradation. The probability for Indole triplet deactivation was estimated and is reported to be much lower compared to the probability for the reaction between Indole* + O₂ $\rightarrow$ Indole⁺. The IFCT going on between FeOx and TiO₂ was discussed and related to the random deposition of both oxides on PE. Evidence is presented for the specific oxidative intermediate species leading to Indole degradation and the properties of the most active oxidative intermediate

were described. Insight in the mechanism of the sunlight activated Indole degradation is provided consistent with the experimental results found in the course of this work. Our findings reveal important features related to the understanding of the degradation of heterocyclic aromatic pollutants like a) photo-redox induced reactions and b) the absence of Fe-ions during N-aromatic compound degradation.

Acknowledgments

The authors wish to thank the EPFL and the Swiss National Science Foundation (SNF) Project (200021-143283/1) for financial support.

References

- [1] A. Sychev, V. Isak, Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O₂ and H₂O₂ and of the oxidation of organic substrates, *Russ Chem. Revs.* 64 (1995) 1105-1129.
- [2] P. Ciesla, P. Kocot, P. Mytych, Z. Stasicka, Homogeneous photocatalysis by transition metal complexes in the environment, *J. Molec. Catal. A* 224 (2004) 17-33.
- [3] J. Balzani, V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London 1970
- [4] J. Fernandez, J. Bandara, A. Lopez, Ph. Buffat and J. Kiwi, Photo-assisted Fenton Degradation of Non-biodegradable Azo-dye (Orange II) in Fe-free Solutions Mediated by Cation Transfer Membranes, *Langmuir* 15 (1999) 185-92.
- [5] M. Dhananjeyan, E. Mielczarski, K. Thampi, Ph. Buffat, M. Bensimon, A. Kulik, J. Mielczarski and J. Kiwi. Photodynamics and Surface Characterization of Immobilized TiO₂ and Fe₂O₃ Photocatalysts on Modified Polyethylene Films, *J. Phys. Chem. B* 105 (2000) 12046-12055.
- [6] A. Fujishima, X. Zhang, D. Tryk, TiO₂ photocatalysis and related surface phenomena, *Surf. Sci. Repts* 63 (2008) 515-546.
- [7] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D. Bahnemann, Understanding TiO₂ Photocatalysis: Mechanisms and Materials, *Chem. Rev.* 118 (2014) 9919-9986.
- [8] M. Pelaez, N. Nolan, S.C. Pillai, M. Seery, P. Falaras, A. Kontos, P.S.M. Dunlop, J. Hamilton, A-J Byrne, K. O'Shea, M. Entezari, A. D. Dionysiou, A review on the visible light active titanium dioxide photocatalysts for environmental applications, *Appl. Cat. B* 125 (2012) 331-345.
- [9] V. Etacheri, C. Di Valentin, J. Schneider, D. Bahnemann, S. Pillai, Visible-light activation of TiO₂ photocatalysts: Advances in theory and experiments, *J. Photochem. Photobiol. C* 25 (2015) 1-29.
- [10] O. Botalova, J. Schwarzbauer, T. Frauenrath, L. Dsikowitzky, Identification and chemical characterization of specific organic constituents of petrochemical effluents, *Water Research* 43 (2009) 3797-3812.
- [11] J. Lin, J. Aoll, Y. Niclass, M. I. Velasco, L. Wunche, J. Pika, C. Starkenmann, Qualitative and Quantitative Analysis of Volatile Constituents, *Environ. Sci Technol.* 47 (2013) 7876-7882.
- [12] J. R. Carney, F. C. Hagemeister, T. S. Zweier, The hydrogen-bonding topologies of indole-(water)_n clusters from resonant ion-dip infrared spectroscopy, *J. Chem. Phys.* 108 (1998) 3379-3382.
- [13] T. R. Garbe, M. Kobayashi, H. Yukawa, Indole-inducible proteins in bacteria suggest membrane and oxidant toxicity, *Archiv. Microb.* 173 (2000) 78-82.
- [14] M. Ibrahim, H. Ali, M. Abdullah, P. Hassandarvish, Acute Toxicity and Gastroprotective Effect of the Schiff Base Ligand 1H-Indole-3-ethylene, *Molecules* 17 (2012) 12449-12459.

- [15] S. Merabet, A. Bouzaza, D. Wolbert, photocatalytic degradation of indole in a circulating reactor by UV/TiO₂ process-influence of some operating parameters, J. Hazard. Mater. 166 (2009) 1244-1249.
- [16] S. Merabet, M. Schneider, D. Robert, S. Benkhanouche, M. Bohuelassa, J. Weber, Optimization of the Indole photodegradation on supported TiO₂, Influence of temperature, concentration of TiO₂ and flow rate, Water Sci. Technol, 58 (2008) 549-554.
- [17] K. Ranjit, I. Willner, S. Bossmann, A. Braun, Modified TiO₂ Photocatalysis for the Enhanced Photodegradation of Organic Substrates, Res. Chem, Intern. 25 (1999) 733-756.
- [18] J. Moser, S. Punishhewa, P. Infelta, M. Grätzel, Surface Complexation of Colloidal Semiconductors Strongly Enhances Interfacial Electron-Transfer Rates, Langmuir 7 (1991) 3012-3018.
- [19] P. Arora, A. Sharma, H. Bac, Microbial Degradation of Indole, J. Chem. 2015, ID129159 /<http://dx.org/10.1155/2015/129159>.
- [20] Z-L. Ye, B. Wang, J.J. Lu, F. Li, R.X. Zhang, New type of electrodeless excilamp for advanced treatment on N-heterocyclic NHCs compounds in aqueous solutions, Environmental Science (Huanjing Kexue) 33 (2012) 849-856.
- [21] C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, G. E. Mullenberg, *Handbook of X-ray Photoelectron Spectroscopy*, 2nd Ed, Minn, USA, 1979.
- [22] J. Nogier, M. Delamar, P. Ruiz, P. Albers, J. Kiwi, XPS and SIMS characterization, Cat. Today 56 (2000) 403-413.
- [23] D. A. Shirley, (1972) High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. Phys. Revs. B5, 1972, 4709-4714.
- [24] S. Pendlebury, S. Wang, F. Le Formal, M. Cornuz, M. Kafizas, S. Tilley, S. M. Gratzel, J. Durrant, J. Am. Chem. Soc. Ultrafast charge carrier recombination and trapping in hematite photoanodes under applied bias 136 (2014) 9854-9857.
- [25] D. Wheeler, G. Wang, Y. Ling, Y. Li, J. Zhang, Nanostructured hematite: synthesis, characterization, charge carrier dynamics, and photoelectrochemical properties, En. Environ. Sci. 5 (2012) 6682-6691.
- [26] J. Cherepy, P. Moore, A. Mathies, Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin Dye-Sensitized TiO₂ Nanocrystalline Electrode, J. Phys. Chem. B 101 (1997) 3250-3257.
- [27] A. Joly, J. Williams, A. Chambers, G. Xiong, W. Hess, D. Laman, Carrier dynamics in Alfa-Fe₂O₃ thin films and single crystal probed by femtosecond transient absorption and reflectivity, J. Appl. Phys. 99 (2006) 05352.
- [28] T. D. Pham, B.K. Lee C. H. Lee, The advanced removal of benzene from aerosols by photocatalytic oxidation and adsorption of Cu-TiO₂/PU under visible light irradiation, Appl. Catal. B 182 (2016) 172-183.
- [29] J. Bandara and J. Kiwi, Fast Kinetic Spectroscopy, Decoloration and Production of H₂O₂ Induced by Visible Light in Oxygenated Solutions of Azo-dye Orange II, New J. Chem. 23 (1999) 717-724.
- [30] S. Kolakkandy, S. Pratihari, A. J. Aquino, H. Wang, W. L. Hase, A unified model for simulating liquid and gas phase intermolecular gas collisions, J. Phys. Chem A 40 (2014) 9500-9511.
- [31] J. Kiwi and V. Nadtochenko, New evidence for TiO₂ photocatalysis during

- bilayer lipid peroxidation. *J. Phys. Chem. B.* 108 (2004) 17675-17684.
- [32] J. G. Graselli and W. M. Ritchey, *Atlas of Spectral Data and Physical Constants for Organic Compounds*, CRC Press 1975, Cranwood Park Ohio, USA.
- [33] D. Naumann, C. Schultz, A. Sabich, M. Kkasrowsky, H. Labishinski, New insights into the phase behaviour of a complex anionic amphiphile: architecture and dynamics of bacterial deep rough lipopolysaccharide membranes as seen by FTIR, X-ray, and molecular modelling techniques, *J. Molec. Struct.* 214 (1989) 213-246.
- [34] J. Pitha and N. Jones, A comparison of optimization methods for fitting curves to infrared band envelope 44 (1966) 3031-3050.
- [35] H. Gao, C. Liu, H. Jeong, P. Yang, Plasma Enhanced Photocatalytic Activity of Iron Oxide on Gold-Nanopillars, *ACS Nano* 6 (2012) 234-240.
- [36] M. Mishra, D. Chun, Alfa-Fe₂O₃ as photocatalyst material a review, *Appl. Cat A* 498 (2015) 126-141
- [37] S. Rtimi, R. Sanjines, J. Kiwi, C. Pulgarin, M. Bensimon, I. Kmehl, V. Nadtchenko, Innovative photocatalyst (FeOx-TiO₂): transients induced by Femtosecond laser leading to bacterial inactivation under visible light, *RSC Advances* 5 (2015) 101751-101759.
- [38] A. Bozzi, T. Yuranova and J. Kiwi, Self-cleaning of Wool-polyamide and Polyester Textiles Due to Surface TiO₂-rutile Modification under Daylight Irradiation. *J. Photochem. Photobiol. A.* 172 (2005) 27-34.
- [39] N. Sakai, A. Fujishima, T. Watanabe, K. Hashimoto, Enhancement of the photoinduced hydrophilic conversion rate of TiO₂ film electrode surfaces by anodic polarization *J. Phys. Chem. B* 105 (2001) 3023-3028.
- [40] K. Hashimoto, H. Irie, A. Fujishima, TiO₂ photocatalysis: an overview and future prospects, *AAPPS Bull.* 17 (2005) 12-28.

Table 1. Fe and Ti-oxide surface loadings sputtered and co-sputtered on FeOx-TiO₂-PE films detected by X-ray fluorescence (XRF)

	Species	Wt%/wt PE (Error%=0.006)
FeOx-TiO ₂ (co-sputtered for 5 min)	TiO ₂	0.059
	FeOx	0.082
FeOx-TiO ₂ (co-sputtered for 2 min)	TiO ₂	0.033
	FeOx	0.045
FeOx (sputtered for 1 min)	FeOx	0.05
FeOx (sputtered for 2 min)	FeOx	0.08
TiO ₂ (sputtered for 8 min)	TiO ₂	0.09

Table 2. Sputtered film thicknesses as determined with a profilometer (AlphaStep500, TENCOR) with an error margin of $\pm 10\%$.

Sample	Thickness (nm)
TiO ₂ (8 min)	38
FeOx (1 min)	40
FeOx-TiO ₂ - (2 min)	54
FeOx-TiO ₂ (5 min)	130

Table 3. Ions-release after the 7th washing cycle from TiO₂-PE, FeOx-PE and FeOx-TiO₂-PE as detected by ICP-MS.

	Ti (ppb)	Fe (ppb)
TiO ₂ -PE (sputtered for 8 min)		--
FeOx-PE (sputtered for 60 s)	--	9.0
TiO ₂ -FeOx-PE (co-sputtered for 1 min)	n.d.	0.2
TiO ₂ -FeOx-PE (co-sputtered for 2 min)	n.d.	0.5

Table 4. XPS surface atomic percentage concentration on FeOx-TiO₂-PE before, during and after Indole degradation (180 min) under low intensity solar simulated light (52 mW/cm²).

	Time zero	Contacted with Indole for 15 min under irradiation (dried before analysis)	After Indole degradation (180 min) (dried before analysis)
Ti2p	39.21	28.04	29.99
Fe2p	29.81	16.76	17.39
O1s	23.31	22.08	21.27
C1s	7.55	31.39	30.34
N2p	0.09	1.69	1.01

Figure 1. Set-up used to evaluate the Indole kinetics under light low intensity simulated solar irradiation.

Figure 2a. Degradation of Indole (10 ppm) on: (1) FeOx-TiO₂-PE co-sputtered for 5 min under light irradiation, (2) FeOx-TiO₂-PE co-sputtered for 2 min under light irradiation, (3) TiO₂-PE sputtered for 8 min under light irradiation, (4) FeOx-PE sputtered for 2 min under light irradiation, (5) PE under light irradiation and (6) FeOx-TiO₂-PE co-sputtered for 2 min in the dark. Used light: solar simulated light 52 mW/cm².

Figure 2b. Photocatalytic degradation on FeOx-TiO₂-PE co-sputtered for 2 min as a function of the indole concentration: (1) 5 ppm, (2) 10 ppm, (3) 20 ppm and (4) 25 ppm under low intensity solar simulated light (52 mW/cm²).

Figure 2c. Recycling of the photocatalytic degradation of Indole on FeOx-TiO₂-PE co-sputtered for 2 min under low intensity solar simulated light (52 mW/cm²).

Figure 3. Indole degradation on FeOx-TiO₂-PE co-sputtered for 2 min under different solar simulated light at intensities of: (1) 75 mW/cm², (2) 52 mW/cm², (3) 20 mW/cm², (4) 10 mW/cm² and (5) 5 mW/cm².

Figure 4. Indole degradation on FeOx-TiO₂-PE under low intensity solar simulated light (52 mW/cm²): (1) without adding radical scavenger, (2) adding methanol (0.2mM) (3) adding EDTA-2Na (0.2mM), (4) adding benzoquinone (0.2mM) and (5) adding sodium azide NaN₃ (0.2mM).

Figure 5. Mechanism suggested for the Indole degradation under sunlight on FeOx-TiO₂-PE films.

Figure 6a. Solar simulated light Indole degradation on FeOx-TiO₂-PE (co-sputtered for 2 min) as followed by FTIR of the N-H group peaks at: (1) time zero, (2) after 15 min irradiation and (3) after total indole degradation (180 min).

Figure 6b. Solar simulated light Indole degradation on FeOx-TiO₂-PE (co-sputtered for 2 min) as followed by FTIR C=C group changes at: (1) time zero, (2) after 15 min irradiation and (3) after 60 min irradiation and (4) after total indole degradation (180 min).

Figure 7. Diffuse reflectance spectroscopy (DRS) of: (1) TiO_2 -PE, (2) FeOx -PE and (3) co-sputtered FeOx-TiO_2 -PE (2 min).

Figure 8. XRD pattern of: (1) FeOx -PE, (2) TiO_2 -PE and (3) FeOx-TiO_2 -PE co-sputtered for 2 min.

Figure 9. AFM imaging of FeOx-TiO₂-PE films co-sputtered for 2 min.

Figure 10. Kinetics of FeOx-TiO₂-PE wettability: (1) hydrophobic-hydrophilic transformation under low intensity solar simulated light (1 hour) and (2) dark reverse reaction to the initial hydrophobic state (30 hours).

Graphical abstract: