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Assessment of photocatalytic activity of Solaronix™ nanostructured anatase

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Abstract

The efficiency of photocatalytic materials can be investigated by several direct and indirect methods. In this study, photocatalytic materials are prepared from TiO_2 Solaronix™ nano-suspension by dip- and spin-coating methods. The photocatalytic activity of coatings is then assessed for several deposition and analysis parameters. An on-line indirect measure method is presented. This method is based on stearic acid degradation and allows the assessment of non-transparent photocatalytic films and displays a high sensitivity. The influences of nano-powder diameter and sintering temperature on film photocatalytic activity are discussed. The reproducibility of the assessment method is presented, and its dependency toward temperature and humidity is measured. Titanium dioxide films prepared from nano-powders are compared to similar coatings in order to illustrate the subject.

Keywords: Titanium dioxide; Anatase; Nanoparticles; Suspension; Dip-coating

1. Introduction

In heterogeneous semiconductor based photocatalysis, photonic energy from ultraviolet or visible radiation reaches the surface of semiconductor and excites the electrons on the surface of atoms, moving them from the valence band to the conductance band. The result of this energy change is the formation of holes in the surface of the photocatalytic material, and free electrons which are now available to form hydroxide, super-oxide or other radicals, which can in turn oxidise organic chemicals, or reduce metal species [1].

Semiconductor photocatalysis offers a convenient technology to help and accelerate chemical reactions under UV illumination. This subject has been increasingly attractive to many researchers in various fields of applications. Photocatalysis may provide environmental solutions to industrialisation and environmental pollution problems and can find applications in air treatment and building industry. Photocatalytic coatings may also be used in aeronautics, either inside of planes for their self-cleaning properties, or on outside surfaces for their super-hydrophilic properties, which may allow to reduce the cost of de-icing and cleaning operations.

Semiconductor photocatalysis has been able to accelerate the mineralising of toxic organic pollutants such as pesticides and insecticides. Among the many semiconductor photocatalysts such as ZnO, CdS, or WO_3, TiO_2 (titanium dioxide) has been most extensively studied in reason of its availability, low cost, inertness, chemical stability and band gap width [2]. Titanium dioxide can be deposited by several methods. In this work, coatings deposited by sol–gel and cold-gas spray methods will be presented and evaluated, while an important effort will be dedicated to the assessment of our experimental method for measuring photocatalytic activities.

The efficiency of photocatalytic reaction depends of several factors linked to energy and wavelength of incident radiation, exposed surface, and material properties governing ion-pair formation and recombining times [3–6]. The quantum yield Φ_λ is commonly defined as $\Phi_\lambda = n/n_{ph}$, with n, the amount of reac-

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tant consumed or product formed (mol), and n_{ph} the amount of photons at wavelength λ absorbed by the system (mol or Einstein).

For a given illumination source, a rate of photocatalytic activity R can be defined as the amount (mol) of reactant consumed or product formed per amount of time and per active and illuminated surface. In this work, assessment methods are based on the measure of initial rate R^{in}. The quantum yield can also be defined as $\Phi_\lambda = R^{\mathrm{in}}/\rho_\lambda$, using R^{in}, the initial rate of the reaction and ρ_λ, the absorbed photon flow defined at wavelength λ and per unit area. The rate at which occurs absorption of ultra-bandgap photons in the semiconductor is not directly accessible and depends on the photocatalyst's optical properties. The measure of Φ_λ is therefore complex and results are more commonly expressed in term of photonic efficiency ξ, defined as the amount of reactant consumed or product formed per amount of photons of monochromatic light incident on photocatalyst's surface. $\xi = R^{\mathrm{in}}/\rho_\lambda$, where ρ_λ is the incident photon flow defined at wavelength λ and per unit area. As pointed out in Ref. [9], the difference between Φ_λ and ξ may vary significantly due to optical properties of the photocatalyst, with reflection and scattering ranging from 13 to 76% [7]. ξ quantifies therefore the surface efficiency of the photocatalyst *and* its optical properties.

The photon flow ρ_λ is defined at wavelength λ in mol of photon (or Einstein) per unit area. Conversion from measured light irradiance (in $\mathrm{W\,m^{-2}}$) to photon flow can be made with Planck's equation, provided that the light wavelength is known. Experimentally, the reaction rate appears to vary proportionally to the square root of the irradiance [8].

2. Experimental methods

2.1. Samples preparation

Titanium dioxide coatings were prepared by deposition of Solaronix$^{\mathrm{TM}}$ nano-powders on glass substrates. The nano-powders are provided in suspension in butanol, with a nominal particle size of 10 nm (Ti-Nanoxide HT-L) and 15–20 nm (Ti-Nanoxide T-L). Both suspensions appear similarly as a white, viscous cream. The suspensions were applied on silica glass (25 mm × 75 mm × 1 mm) and on polycarbonate substrates (50 mm × 60 mm × 3 mm) by dip- and spin-coating methods, respectively.

The films deposited on glass by dip-coating (samples 1–5) from Ti-Nanoxide HT-L were submitted to five thermal treatments in an oven Nabertherm LHT G8. First, all samples were dried in air at room temperature (20 °C). It represents the first thermal path (absence of thermal treatment, sample 1). Then, samples were submitted to a 120 °C heating curve. They were either withdrawn after 2 h (sample 2) or fully treated for 10 h with a slow decrease to room temperature (sample 3). Then, probes were submitted to a second 10-h thermal cycle at 300 or 500 °C (samples 4 and 5).

The films deposited by spin-coating on polycarbonate substrates were obtained by 1 min rotation at 2600 rpm and were dried at room temperature. Experiments 6–9 and 10–15 were carried out with two samples obtained by spin-coating from Ti-Nanoxide T-L. Sample for experiment 16 was obtained by spin-coating from Ti-Nanoxide HT-L.

The suspension deposited on glass substrates by dip-coating formed a solid and transparent/translucent film, 6.5 μm thick, with poor adhesive qualities (can be removed with nail) but which did not flake off. The suspension deposited on polycarbonate by spin-coating were thinner (3.9–4.1 μm), more transparent and displayed a correct adhesion.

Samples used for experiments 17–19 were obtained by cold-gas spray method, which is described into more detail in Ref. [9]. In this method, a powder (here a 99% anatase powder produced by EMPA laboratory) is sprayed at very high velocity against the substrate, which must be hard enough to sustain the process (here, aluminium). Particles bond together onto the substrate, which typically produces coatings with thickness of 10–15 μm.

2.2. Coating analysis techniques

The quality of deposited coatings was classically analyzed by several common methods. Coating thickness and roughness measurements were made with a "SLOAN Dektak^3 ST" surface profiler, produced by Veeco Instruments (USA). The coatings were observed by scanning electron microscopy (SEM) with a "LEO 1430" produced by Zeiss (Germany). Thickness of cold-gas spray samples were measured by optical microscopy.

2.3. Assessment method

The test method developed and presented here is derived from classical gas-phase and solid phase test methods described in [10]. It differs in two main points: this is an *on-line* assessment method, and it functions in *closed system*. Instead of repeating sequences of illumination and measure steps, the measure and the illumination are conducted simultaneously, as presented in Fig. 1, which allows continuous real-time curves to be obtained. The rate is obtained by observation of the gas-phase products of the photodegradation surface reaction, i.e. the reaction takes place in solid phase but the observation is conducted in gas-phase.

The system is composed of a quartz reactor (vol.: 0.43 L, transmittance 75% at 254 nm) containing the sample and placed under a CL-1000 ultraviolet Cross-linker produced by UPV (California, USA). The apparatus consist in a closed box equipped with five 8 W 254 nm UV lamps, which produce 45 $\mathrm{W\,m^{-2}}$ (source: manufacturer). The spectra were measured with a USB2000 Spectrometer produced by Ocean optics (Florida, USA). The samples receive then 3.9×10^{-3} Einstein $\mathrm{m^{-2}\,min^{-1}}$

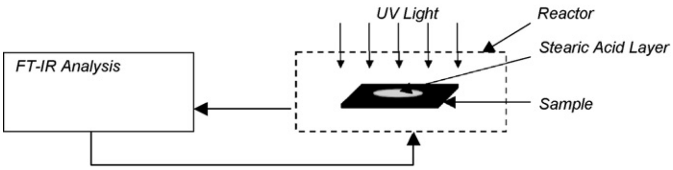

Fig. 1. Schematic of original assessment method: reaction in solid phase and measure is in gas-phase.

(2.33×10^{17} Photons cm^{-2} min^{-1}). This chamber is linked to the FT-IR cell by two pipes (vol.: 0.07 L), and atmosphere circulates between Reactor and FT-IR cell (vol.: 1.07 L) with help of a pump (4 L min^{-1}). The total volume of the system is 1.57 L. It allows a continuous monitoring of system atmosphere (up to one measure every 30 s) without manipulation of the sample. The samples are coated by a thin layer of stearic acid: 100 μL of a 8 g dm^{-3} solution of stearic acid in ethanol are deposited on the surface of the film, and dried in hot air. Photocatalyzed degradation of stearic acid occurs according to $CH_3(CH_2)_{16}CO_2H + 26O_2 \rightarrow 18CO_2 + 18H_2O$, and involves the transfer of 104 electrons [1,10]. Stearic acid is presumed to be mineralized by photocatalysis without any by-products or transitory species. However, according to Ref. [11], the reaction does not reach the complete degradation of stearic acid, which may be due to the blocking of titanium dioxide surface or to a lack of contact with the solid stearic acid layer.

The reactor is inert and transparent to UV light in the range 220–600 nm. The joins are silicon-free (protected with Teflon). A support allows the reactor to stay in place under the light, in horizontal position and prevent movements for the whole length of experiment. The reactor is easy to open, to manipulate, to clean and to put in place. This system gives results in an automated way and is adapted for samples up to 40 cm^2.

After calibration of FT-IR apparatus in nitrogen, the sample is introduced in reactor, and dry air is circulated into the system volume. Then, 100 μL of distilled water is introduced and the system is closed. The water concentration is monitored, and if necessary can be corrected by additional injection of distilled water. After 10–20 min, water and carbon dioxide concentration are stable and the UV illumination (in this case, nomochromatic at 254 nm) can be turned on. The growth of carbon dioxide concentration gives information on the photocatalytic activity of the sample.

As can be seen in the equation presented above, 18 molecules of CO_2 are generated for each degraded steric acid molecule. As result, the precision of this method allows the evaluation of samples which photoactivity is low. Initial rates are measured in mol min^{-1} m^{-2}.

3. Results

3.1. Dip-coatings on glass (samples 1–5)

Samples realised with Solaronix™ suspension of Ti-Nanoxide HT-L were photoactive. Rates of degradation were calculated from the measure of initial rate of CO_2 production in ppm/min. Obtained results are presented in Table 1: photonic efficiencies of Solaronix™ dip-coatings (particle size 10 nm) were found between 0.16 and 0.68%. Due to variation in humidity of atmosphere, all samples were not tested in identical conditions. The heat-treated samples did not show a systematic superior activity. The performed heat treatments do not seem to improve photocatalytic activity.

3.2. Spin-coating on polymer substrate: temperature effect (experiments 6–9)

The temperature at which the test is carried out has a minor effect on the measured photoactivity because of two competing phenomena. A temperature rise promotes the oxidation rate of an organic compound but it reduces the adsorption ability of the catalyst. In order to implement a reproducible test and gain comparable results, the influence of temperature over measured photocatalytic activity was evaluated as presented in Fig. 2 while all other experiments were carried out at room temperature. The variation of photoactivity due to the variations of room temperature does not exceed 0.2% per °C.

3.3. Spin-coating on polymer substrate: humidity effect (experiments 10–15)

Humidity can enhance or inhibit the photodegradation of organics depending on the nature of the compound and may have a huge effect on photoactivity of samples. In the case of Stearic acid degradation, an enhancement in the rate is frequently found in the presence of water vapour [8]. As pointed out by many authors, dissociative adsorption of water occurs on five-fold-coordinated sites, resulting in hydroxyl groups. Adsorbed water plays an important role in the initial steps of

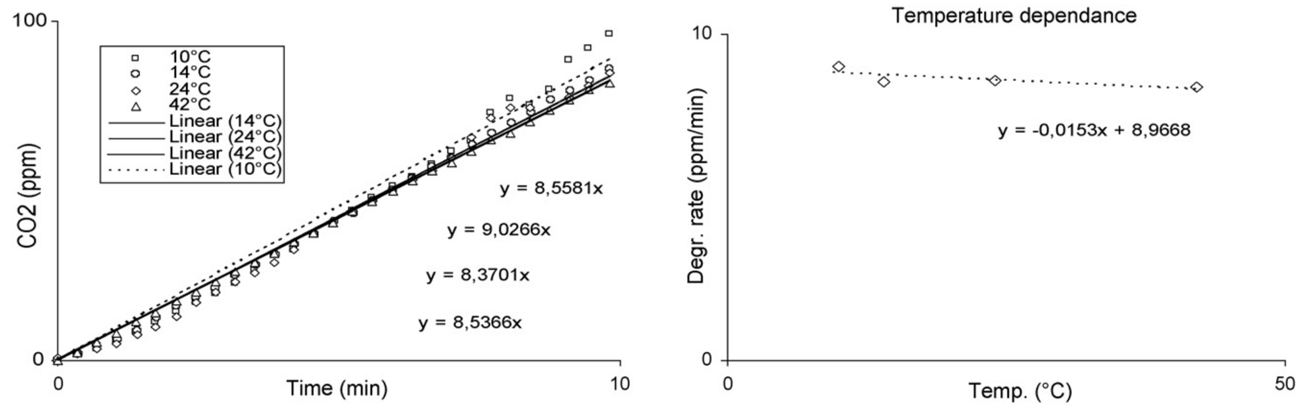

Fig. 2. CO_2 production rate for same sample at temperatures 10, 14, 24 and 42 °C (left) illustrate the influence of temperature over measured photocatalytic activity (right).

Table 1
Results for experiments 1–5

Experiment	Curing temperature (°C)	Curing time (h)	Measure temperature (°C)	$[H_2O]$ (mg/L)	Relative humidity (%)	Degradation rate (10^{-6} mol/s/m^2)	Photonic efficiency (%)
1	24	–	Room	4.2	21.7	27.6	0.553
2	120	4	Room	5.0	25.7	7.94	0.159
3	120	10	Room	2.5	12.7	10	0.201
4	300	20	Room	1.5	7.8	8.74	0.175
5	500	20	Room	6.7	32.6	34.1	0.684

Dip-coating of HT-L on glass substrates.

degradation reaction and a certain degree of humidity (usually exceeding the amount produced by the oxidation of the organic) is necessary for the photodegradation reaction and to avoid the blockage of the titanium dioxide surface by partially oxidized by-products. However, water adsorption favors electron–hole recombination, which may reduce the photocatalytic oxidation rate [6,8,12–15].

In the described assessment method, 10 μL of distilled water is injected inside the reactor, which is enough to create a water concentration of 3–10 mg/L during experiment. Thus, the water concentration is not fully controlled, but measured and recorded, contrary to other assessment methods such as classical solid phase methods carried out in room atmosphere with a high variability of its water content. Most of the unexplained variation in measured photoactivity can be attributed to variations in water vapour concentration in the atmosphere of reactor.

Experiments were carried out to investigate the effect of water concentration over photocatalytic activity and are presented in Fig. 3. Experiments 10–15 were carried out with diverse water concentrations inside the test reactor from 0 to 21 mg L^{-1}. Sitkiewitz and Heller observed a pronounced increase of reaction rate between 0 and 0.6% humidity and a less pronounced increase between 0.6 and 2.5% humidity [8]. The effect of water concentration in the evaluated range is important, as presented in Fig. 3, right.

3.4. Cold-gas spray coating (experiments 17–20)

Four cold-gas spray samples (deposited simultaneously, in identical conditions) were measured four times in 4 days, following the same procedure, in order to check the reproducibility of this assessment method. Such reproducibility tests are valuable to verify the absence of experimental error which may false the measures and reduce the results validity. The results of the measures are presented in Fig. 4 and Table 2. As can be seen, the absolute error grows with time. The relative error computed on the initial growth rate lies at 6.8%, while the error in concentration reaches 7.6% after 4 h. The assessment of photocatalytic efficiency computed from the increase rate of CO_2 concentration during the first minutes of the experiment can be considered reproducible with an error of ±7% or one digit. Thus, the average initial rate was 0.597 ppm min^{-1} ± 7%, and the degradation rate was 1.17.10^{-7} mol s^{-1} m^{-2} ± 7%.

4. Discussion

The observed variation in the photoactivity of samples 1–5 does not appear to follow a clear pattern in connection with the intensity of calcinations process. As a result, a large part of this variation can be attributed to variations in water vapour concentration and deposition method (irregularities in film thickness obtained by dip-coating). It should be noted that anatase to rutile phase transformation temperature (≈630 °C) was not attained. As a result, the samples 1–5 most probably all remained anatase. The heat treatments may therefore have had an influence on crystallite size and surface area but did not change markedly the phase composition of samples. Variations in dip-coating process itself were in all probability responsible of most part of the observed variations in photocatalytic activity, the coating properties (thickness, porosity) varying in a large extend due to the

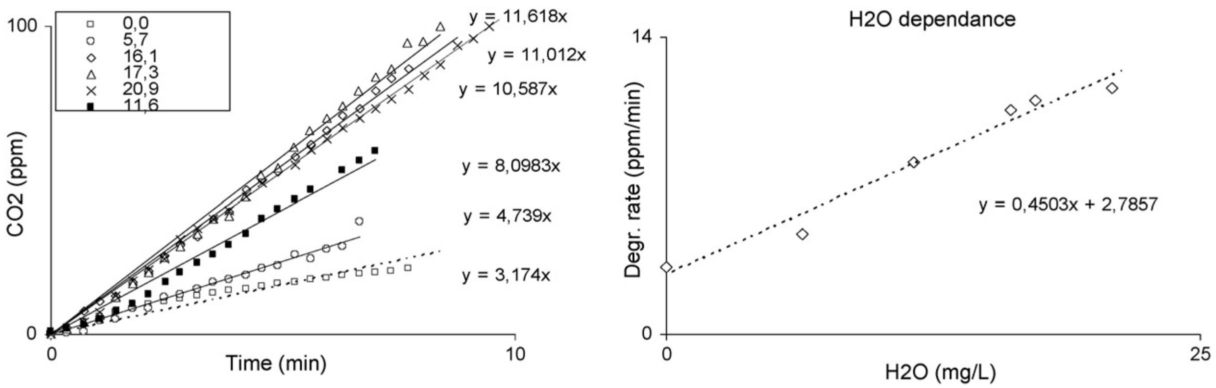

Fig. 3. CO_2 production rate for same sample and same temperatures with different water concentrations (left) illustrate the influence of humidity over measured photocatalytic activity (right).

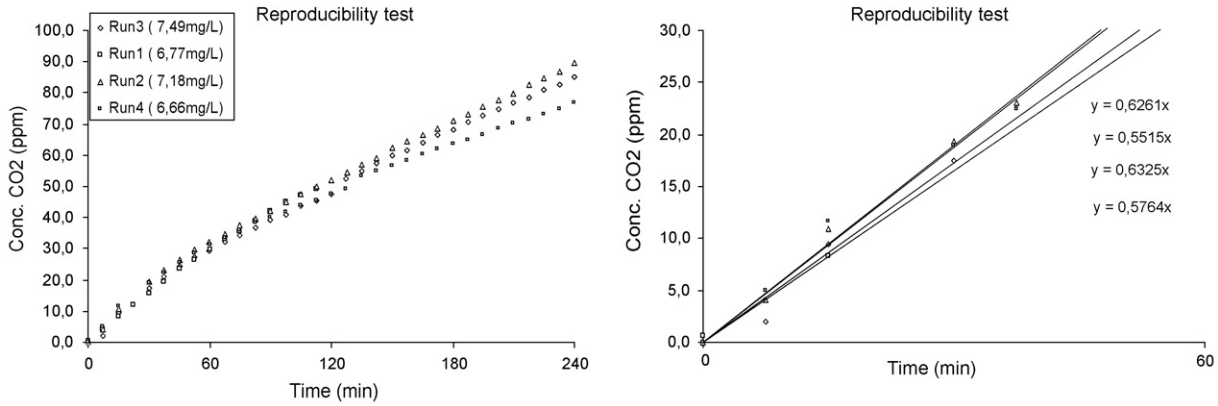

Fig. 4. Reproducibility test. Same sample was measured four times. The initial error is computed from the values of initial CO_2 concentration growth rate.

Table 2
Results for experiments 6–16 (spin-coating on polycarbonate substrates, cured at room temperature) and 17–20 (cold-gas spray)

Experiment	Suspension	Measure temperature (°C)	$[H_2O]$ (mg/L)	Relative humidity (%)	Degradation rate (10^{-6} mol/s/m^2)	Photonic efficiency (%)
6	T-L	10	4.5	47	17.4	0.349
7	T-L	14	5.5	45	16.5	0.33
8	T-L	24	4.6	21	16.5	0.331
9	T-L	42	5.0	8.8	16.1	0.323
10	T-L	Room	0.0	0	6.12	0.123
11	T-L	Room	6.3	30.7	9.14	0.183
12	T-L	Room	11.6	53	15.6	0.313
13	T-L	Room	16.1	75.7	20.4	0.409
14	T-L	Room	17.3	83.7	21.2	0.425
15	T-L	Room	20.9	100	22.4	0.449
16	HT-L	Room	6.1	34	26.1	0.524
17	–	Room	6.8	34	0.11	0.136
18	–	Room	7.2	36	0.12	0.149
19	–	Room	7.5	37	0.11	0.13
20	–	Room	6.7	34	0.12	0.148

high viscosity of the nano-suspension. If it exists, the influence of calcination temperature on photocatalytic activity is low and did not appear in this investigation.

More experiments were carried out to investigate the effect of temperature and humidity inside test reactor and reproducibility of the assessment method. Assessment temperature appeared to have a slight negative influence on the measured photocatalytic activity. The effect of humidity was important, and almost linear in the investigated range (from 0 to 21 mg L^{-1}). It was taken care, in the next experiments, to use identical water concentration in order to obtain comparable results.

Photonic efficiencies of dip-coatings (particle size 10 nm) were found between 0.16 and 0.68%. Comparing experiments 11 and 16 (similar temperature and humidity conditions), the photonic efficiencies of spin-coatings were lower with T-L powder (0.33%) than with HT-L powder (0.52%), which can be explained by differences in particle size (15–20 and 10 nm, respectively) and therefore in maximal crystal size. It is generally recognized that anatase films with a lower crystal size typically display a higher photocatalytic activity [16].

The obtained photonic efficiencies are slightly below sol–gel coatings degradation, which have presented efficiencies up to 0.2% (Mills et al. reported efficiency of 0.158% at 254 nm for a coating obtained by a comparable sol–gel method [10]), and slightly above CVD coatings, which presented efficiencies of 0.028–0.035% (Mills et al. report the value of 0.034% for a similar CVD coating [10]). Obtained results are comparable with other cold-gas sprayed titanium dioxide coatings, which present photonic efficiencies ranging from 0.15 to 0.96%, as will be presented in Ref. [17].

The samples obtained by dip- and spin-coating of nano-suspension were generally found more active than most titanium dioxide coatings obtained by cold-gas spray method and presented a good adhesion when deposited on polymers substrate.

5. Conclusion

Photoactive samples prepared by deposition of Solaronix^{TM} titanium dioxide nano-powders by several methods have been investigated for their photocatalytic activity. The samples all exhibited photoactivity at various levels, which was to an extend influenced by water vapour concentration during experimentation.

The concentration of water vapour was found to affect the photocatalytic activity in a large degree, while temperature was found to have little or no effect.

Some samples were submitted to various temperature treatments below phase-transition temperature. Partly due to variation in water vapour concentration, it was not possible to observe any systematic effect of temperature treatment over photocatalytic activity.

The effect of particle size was investigated and the films prepared with HT-L suspension (particle size 10 nm) displayed a higher efficiency than those prepared with T-L suspension (particle size 15–20 nm). Smaller particle size may improve the surface contact of titanium dioxide or limit crystal size, which is beneficial in term of photocatalytic activity.

The photoactivity was compared to a thermal-spray coating produced in EADS and was comparatively good. The Solaronix^{TM} titanium dioxide nano-powder is a practical mean of obtaining photoactive films. The obtained films display a moderate but sufficient adhesion, and a good photoactivity.

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