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Low irradiance photocatalytic degradation of toluene in air by screen-printed titanium dioxide layers

Thin Solid Films 545 (2013) 537–542

doi: [10.1016/j.tsf.2013.08.032](https://doi.org/10.1016/j.tsf.2013.08.032)

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Abstract

Screen-printed titania photocatalytic layers made from Degussa P25 were studied in order to assess the potential of this deposition technology for the production of catalytic surfaces for airborne pollutant degradation. The deposited catalytic TiO₂ layers were characterized by a low density (about 25% of the titania bulk crystal) typical of very porous films. The study was carried out using toluene at low concentration (12 ppb) as model pollutant and with a low UV-A irradiance level on the sample surface (200 $\mu\text{W cm}^{-2}$). The catalyst layers were deposited on alumina and quartz substrates demonstrating a good catalytic depollution activity. The relationship between the layer thickness and the catalytic activity was studied in the 1 to 6.8 μm range indicating an optimal 3–4 μm film thickness. Thicker layers do not show significant increases in the catalytic activity. The optical transmittance was studied using quartz substrate samples, showing a severely reduced photon flux for layers deeper than 5 μm . The effect of post-printing thermal treatment was studied in the 500–900 °C range, demonstrating good catalytic activity for processing temperatures ≤ 700 °C. These results indicate that the screen-printing process can be a promising technology for the realization of high efficiency photocatalytic materials for air depollution applications at low UV-A irradiance.

Keywords

photocatalysis; photocatalytic air depollution; toluene; screen-printing; TiO₂ layer; anatase-rutile conversion

1. Introduction

The photocatalytic oxidation of ambient air pollutants [1–3], such as the volatile aromatic compounds and NO_x found in urban and indoor air, is widely studied with many proposed applications for air depollution [4–6], both in passive [7] and active [8] implementations. Photocatalytic multifunctional

materials can be obtained by dispersion of the photocatalyst in the material matrix itself as in the case of cement [9], paint [10] and paper [11] or by surface coating of suitable substrates. Several technologies were proposed including sol-gel [12], chemical vapor deposition [13,14], sputtering [15,16], spray-pyrolysis [17] and related techniques for the coating of substrates such as glass [16], ceramic [13], and stainless steel [18] with a photocatalytic thin layer. In these processes the photocatalyst is directly synthesized as thin film (typically $<1\ \mu\text{m}$ thickness) on the substrate surface during the deposition.

The screen-printing process is a well-know technique to obtain controlled layers for several different applications including solar cells [19], fuel cells [20], sensors [21] and films for electronic applications in general. The screen-printing technology has several valuable characteristics for the production of photocatalytic surfaces, including the ability to produce layers with controlled porosity up to $10\ \mu\text{m}$ and more [22] and an easy process implementation and scale-up. Moreover, unlike other coating methods based on in-situ synthesis, screen-printing also allows to create thick layers made from a previously available inorganic powder, permitting the deposition of special catalysts produced in a separated process. In the latter case an ink constituted by the inorganic component(s) dispersed into an organic matrix is printed on the substrate in tightly controlled conditions through a mesh screen. A post-printing thermal treatment is used for the inorganic fraction sintering and the concurrent elimination of the organic matrix by degradation and vaporization. Screen-printed semiconductor photocatalysts were firstly studied by Tsoukleris *et al.* [22] and Labrincha *et al.* [23,24] for the degradation of organic dyes in aqueous solution. However to date there is a substantial lack of studies specifically addressing the potential of screen-printed photocatalysts in the degradation of airborne micropollutants. The only exception is the work of Yiu Liu *et al.* who developed a special heterojunctional-electrical layered device [25].

In this work the photocatalytic oxidation of toluene in air by screen-printed titania layers was studied in order to assess the potential of this deposition technology for the production of catalytic surfaces for airborne pollutant degradation. The study was carried out in typical ambient conditions with respect to the temperature, relative humidity (R.H.) and pollutant concentration [2] using a relatively low UV irradiance level on the sample surface ($200\ \mu\text{W cm}^{-2}$). The titania layer samples were made from a commercially available photocatalyst screen-printed onto alumina substrate. A series of auxiliary samples was also prepared onto quartz and soda-lime glass for optical measurement and method optimization purposes. A key parameter for layered photocatalysts is the optimal thickness that is strictly dependent on the physical properties of the catalytic layer and, ultimately, on the deposition process. The relationship between the layer thickness and the catalytic activity was studied using a series of screen printed titania layers prepared in the 1 to $6.8\ \mu\text{m}$ range with thickness-optimized ink formulations. The effect of the post-printing thermal treatment on the catalytic activity was studied using a series of samples processed at temperatures in the 500 – $900\ ^\circ\text{C}$ range.

2. Experimental details

All air concentrations, volumetric flows and R.H. values in this work are given at $25\ ^\circ\text{C}$, $101.3\ \text{kPa}$ reference conditions.

2.1. Sample preparation

All photocatalytic samples were prepared at ISTE-CNR laboratories by screen-printing of TiO_2 (P25, Degussa) photocatalytic layer onto alumina, quartz (fused silica) and glass substrates. The titania P25 catalyst was drawn from a single batch with 80/20 anatase/rutile phase ratio (Section 3.4)

and, according to the manufacturer, $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ specific surface area (Brunauer-Emmett-Teller) and 21 nm average particle size. It is well known that the quality of screen printing deposition strongly depends on the properties and consequently on the formulation of the ink used [20,26]. Particularly, the area-specific mass of the obtained final sample layer (layer loading) is related to the inorganic solid amount in the printing ink (ink solid loading). In order to modulate the titania layer loading (and therefore the thickness) of the sample films a selection of printing inks formulations was considered with solid loadings in the 7–28 wt.% range.

All screen printing inks used in this work were based on terpineol (isomer mixture, Aldrich) as solvent. The inks were prepared adding to the solvent the TiO_2 powder and the proper amount of lauric acid ($\geq 99.5\%$, Aldrich), ethyl cellulose (45.0–46.5% w/w ethoxyl content, Fluka) and glycerol (85% reagent grade, Merk) used as deflocculant, binder and plasticizer respectively. A first ink (Ink 1) with the highest TiO_2 loading (27.8 wt.%) was prepared adjusting a formulation previously reported in literature [26] to the specific morphologic characteristics of the titania powder used (Table 1). Ink 1 was used both as is and diluted with terpineol for the preparation of a first series of samples as described hereafter. The other TiO_2 inks (Ink 2–5) were prepared by gradually decreasing the solid loading and keeping the solvent and the other organic components (binder and plasticizer) amounts constant. Only the deflocculant concentration was decreased according to the lowering of the TiO_2 amount, in order to satisfy the deflocculant/solid powder ratio of 0.017 (w/w) previously optimized for Ink 1. It was found that the reformulation of each ink was preferable rather than a direct dilution of the first ink because the latter approach, while leading to viable samples, demonstrates to cause severe rheological alterations in the resulting inks with consequent sub-optimal film generation. All the formulations reported in Table 1 were found to be suitable for printing. The decrease in solid loading was compensated by an increase of the organic components leading to small viscosity changes of the inks and, thus, good quality films.

After a preliminary manual mixing, each prepared ink suspension was ball-milled for 24 h and then a four-step fine milling was done with a three rolls grinding mill equipped with zirconia rollers of nanometric finishing (Exakt 80E, Exakt, Nordestedt, Germany) to improve homogeneity as previously reported [26].

Three substrate materials were selected for this work, namely commercial 96% alumina substrates (0.62 mm thickness, Aurel Automation S.p.A., Italy), quartz (1 mm thickness) for optical measurements and standard soda-lime glass microscope slides (Menzel, Germany) for method optimization. All the substrates were prepared in $26 \times 76 \text{ mm}$ pieces, washed with a NaOH saturated ethanol solution, HCl 1M aqueous solution and finally sonicated in ethanol for 15 min (Transsonic T460H Bath, Elma) to remove organic and inorganic impurities [27]. A suitable mask (165 mesh polyester printing screen) was used to print a $20 \times 50 \text{ mm}$ TiO_2 area onto the substrates. Thick films were screen printed (squeegee speed 90 mm s^{-1} , squeegee load 64 N, snap-off distance 0.7 mm) onto the pre-cleaned substrate by a single print step using a precision screen printing machine (Aurel 900, Aurel Automation S.p.A., Italy).

Unless otherwise stated the as-deposited films were dried in ambient conditions and thermally treated at $500 \text{ }^\circ\text{C}$ for 30 min with a heating rate of $100 \text{ }^\circ\text{C h}^{-1}$. The total amount of TiO_2 deposited on each sample was determined by weighting the sample substrate before the printing process and after the thermal treatment, allowing the calculation of the actual catalyst layer loading. The weighting repeatability was estimated by replicated weight measurements of selected samples, with resulting $\pm 0.01 \text{ mg cm}^{-2}$ layer loading error (1σ). The surface microstructure and the thickness of the titania films were evaluated using scanning electron microscopy (Leica Cambridge Stereoscan 360, Leica) operating at 15 and 25 kV. All the microscopy samples were metallized with gold.

A specific series of samples was prepared in order to study the post-printing process temperature, using 30 min thermal treatment at 500 °C, 700 °C and 900 °C respectively. A corresponding series of unsupported catalytic powders was processed in the same way and characterized by X-ray diffraction (D8 Advance with Linxeye detector, Bruker AXS, Germany) using Cu $K\alpha$ radiation in the 10–80° (2 θ) range, scan by 0.02° steps (92.5 s integration time per step). The quantitative phase analysis was performed following the reference intensity ratio technique.

The complete list of all samples used in this work is reported in Table 2.

2.2. Photocatalytic activity measurement

The photocatalytic activity measurements were carried out at ITC-CNR laboratories using toluene in air at ambient concentration as model pollutant. The photocatalytic activity was measured using a previously described dedicated experimental system [9] based on a continuous-flow stirred photoreactor. Briefly, the experimental apparatus comprises an artificial air generator, a 2 L photochemical reactor placed into an irradiation chamber and a gas chromatograph with photoionization detector for the measurement of the toluene concentration in the reactor effluent. Because of the reactor stirring, the toluene concentration in the effluent air stream is representative of the whole reactor internal atmosphere allowing the direct computation of the reaction rate (Section 3.3).

The photoreactor supply air was obtained by mixing and humidifying gas-chromatographic grade nitrogen and oxygen (Alphagaz 1, Air Liquide, Italy) with a 500 ppb toluene standard diluted cylinder (Sapio, Italy) using a computer controlled artificial air generator [9]. A 100 mL min⁻¹ total air supply flow (20.9% O₂ v/v) at 25 ± 0.2 °C, 50 ± 2% R.H. ambient conditions was used for all the measurements. The nominal operating toluene concentration was selected at 500 nmol m⁻³ (12.2 ppb) with 495 ± 25 nmol m⁻³ actual obtained value for all experiments. The nominal value of the toluene concentration inside the photochemical reactor was reached for each measurement by a two-step successive approximation method (Fig. 1) varying the flow from the standard toluene cylinder. The total air inlet flow was kept constant by compensation with the pure nitrogen flow. This approach was preferred instead of the operation with constant inlet concentration because the latter causes the internal reactor concentration to vary according to the catalytic activity of each sample, resulting in non-uniform measurement conditions across the whole study [9].

The reactor was operating with 1400 rpm mixing fan speed for all photocatalytic activity measurements. The velocity of the recirculating air inside the reactor was measured using a hot sphere anemometer (Testo 400, Testo AG, Germany) placed vertically to the sample position at 2.7 cm distance from the surface and integrating for 120 s. The measured air velocity was 0.34 ± 0.2 m s⁻¹.

Prior to the catalytic activity measurements, each sample was rinsed with deionised water (conductivity <1 μ S cm⁻¹), about 20 mL of reagent-grade ethanol (Carlo Erba, Italy) and again with deionised water immediately before the measurement. After a short drying period with hot air, the exposed surface of the photocatalyst layer was reduced to about 2.5–3 cm² by masking with aluminium foils in order to avoid excessive conversion in the photocatalytic reactor because of the high photocatalytic activity of the samples. The actual exposed surface of the layer was measured for each sample with an estimated accuracy of ±3% (Table 2).

The UV-A source was provided by two fluorescent lamps (PL-S/BLB, Philips). The resulting integrated irradiance in the 340–400 nm spectral band at the sample surface was 205 ± 10 μ W cm⁻² for all photocatalytic activity measurements. The irradiance was corrected for the radiometer spectral sensitivity and calculated for the previously indicated spectral region as previously described [9]. The

irradiance spectrum measured at the sample level is shown in Fig. 5. The components of the experimental system (synthetic air generator, irradiation chamber on-line radiometer and thermometer, gaschromatographic analyzer) were calibrated as previously described [9].

2.3. Optical transmittance measurement

The optical spectral transmittance of titania films was measured for selected quartz samples. Because of the strong optical diffusivity, the measurements were carried out using an integrating sphere as transmitted light collector. The total transmittance was measured in the 300–450 nm spectral region using a 38 mm diameter integrating sphere (FOIS-1, Avantes) with 9.5 mm input port. The sample was placed directly on the integrating sphere input port and illuminated with a collimated light beam (4 mm diameter on the sample) from a deuterium lamp (Avalight DHS, Avantes) using a 600 μm fiber optics and a 6 mm collimating lens (Col UV-Vis, Avantes). The transmittance spectra were acquired by a fiber-optic spectrometer (Avaspec 2048L, Avantes) connected to the integrating sphere output port with a 600 μm fiber optics. For each measurement a reference spectrum was acquired measuring the transmittance of a prearranged clean area on the quartz substrate and five transmittance spectra at different places on the titania layer. The final transmittance spectra of each sample was computed as the mean of all the acquired spectra in order to lower the noise and compensate for local layer inhomogeneities.

3. Results and discussion

3.1. Morphological characterization

The scanning electron microscope (SEM) surface micrography of the 0.43 mg cm^{-2} layer loading sample on alumina is reported in Fig. 2. The SEM micrography shows a homogenous porous surface formed by well connected submicronic grains. The titania layer thickness of selected samples was estimated by analyzing SEM images of sample fractures (unpolished cross-sections). A single fracture was obtained for each sample and the titania layer thickness was directly measured with SEM at five positions along every fracture border (Fig. 3). The mean titania layer thickness of the measured samples versus the layer loading was reported in Fig. 4. The thickness error bar is the standard deviation estimated from the measurement along each fracture. While the fractures of the low loading samples demonstrate a quite uniform thickness value, the fractures of the samples at higher loading show a remarkable thickness variation. The availability of single fracture data does not, however, allow to evaluate the entire surface and to give more generalized conclusions on layer uniformity.

The mean titania layer density was found to be $1.0 \pm 0.04 \text{ g cm}^{-3}$ (error as standard deviation of unweighted fitting) from the origin-constrained linear fitting of the thickness data shown in Fig. 4. The crystal density of the P25 powder was estimated, from the crystalline phase composition (80/20 anatase/rutile) and the crystal density [28] of the anatase (3.83) and rutile (4.24) phase, to be 3.91 g cm^{-3} . The mean layer porosity (as void volume/total layer volume) for all the screen-printed titania samples was estimated from the previous density values to be $\sim 75\%$ (as reference the densest sphere packing has $\sim 26\%$ void volume). The presence of a high void volumes fraction in the bulk layer is in accordance with the porous characteristic evidenced by the SEM surface micrograph (Fig. 2).

3.2. Optical transmittance

The total optical transmittance of selected titania layers (quartz substrate) is reported in Fig. 5. The same figure reports the relative spectral irradiance of the UV-A light measured inside the photoreactor

at the sample surface according to a previously described procedure [9]. The transmittance in the UV region of the samples with layer loading $\geq 0.5 \text{ mg cm}^{-2}$ is quite low and with the lamp used it is appreciable only in the farthest tail of the irradiance spectrum. The total transmitted optical power can be calculated integrating the spectral transmittance with the spectral irradiance. The calculation gives 3.4% of the incident radiation for the 0.49 mg cm^{-2} sample ($4.8 \pm 0.2 \text{ }\mu\text{m}$ estimated thickness). This figure reduces to 2.6% for the 0.68 mg cm^{-2} sample ($6.7 \pm 0.3 \text{ }\mu\text{m}$ estimated thickness). The photon flux at titania catalytic layers deeper than $5 \text{ }\mu\text{m}$ from the film surface is therefore decreased by more than one order of magnitude in comparison to the flux available at the top.

3.3. Photocatalytic activity

Using a continuous flow stirred photoreactor, the reaction rate per layer surface area (as mass of degraded pollutant per unit of catalytic layer surface and time) can be directly calculated with the following equation:

$$r = \frac{Q}{A} (C_0 - C) \quad (1)$$

where r is the reaction rate per surface area ($\text{mol s}^{-1} \text{ m}^{-2}$), Q is the volumetric flow rate ($\text{m}^3 \text{ s}^{-1}$), A is the geometric area of the titania layer surface (m^2), C_0 and C are respectively the inlet and the reactor internal concentration of the reacting specie (mol m^{-3}). The degradation rate r measured at constant toluene concentration for all the samples is reported in Fig. 6. The error indicated for the layer loading values was calculated from the repeatability of the sample weighting (Section 2.1). The reaction rate repeatability was calculated as error propagation in the (1) assuming $\pm 2\%$ error in the concentration C_0 and C , $\pm 1\%$ error in the supply air volumetric flow Q and $\pm 3\%$ error in the sample layer surface A . The estimated rate repeatability was verified by repeated analysis on a selected sample. The possible presence of mass transfer limitation due to the fluid dynamic conditions inside the reactor was verified by measuring the reaction rate at different mixing fan speeds (from 700 to 1800 rpm) using a highly active quartz sample (0.68 mg cm^{-2} layer loading). The measurements demonstrate a $\pm 10\%$ rate variation in dependence on the mixing fan speed, for actual air speed values ranging from 0.13 to 0.45 m s^{-1} (Section 2.2). The same test was repeated with a lower activity sample (0.16 mg cm^{-2} layer loading) demonstrating no detectable air speed dependence of the measured rate. This suggests that, for the high activity samples in this study, the photoreactor operates with a marginal mass transfer limitation and the measured reaction rates are subject to a slight influence from the reactor fluid dynamic conditions. This is not surprising considering that the alumina and quartz samples with high layer loading demonstrate a quite high catalytic activity (r/C ratio $> 3 \text{ mm s}^{-1}$). It is worth noting that the discussed mass transfer limitation can cause a slight underestimation of the maximum achievable reaction rate and, under complete kinetic control, an even higher activity for the high loading samples is to be expected.

The alumina and quartz samples show a comparable photocatalytic activity with differences within the experimental data dispersion. The sample activity was substantially proportional to the titania layer loading for loading $< 0.3 \text{ mg cm}^{-2}$. The sample activity appears, however, little sensitive to further layer loading increases, being fundamentally constant for loading $> 0.4 \text{ mg cm}^{-2}$. This suggests that for low film loadings the whole catalyst layer is active in the degradation process, while for loadings $> 0.4 \text{ mg cm}^{-2}$ (estimated thickness $> 4 \text{ }\mu\text{m}$) only the superficial layer is active, the deep catalyst being substantially inactive possibly because of both the UV extinction (Section 3.2) and the

layer internal diffusion limitations. A similar activity-film thickness relationship was observed by other authors in the oxidation of water dispersed organic compounds. A maximum $\sim 5\ \mu\text{m}$ useful catalyst layer thickness was observed [13] in the degradation of methylene blue in water for titania on alumina obtained by chemical vapor deposition (CVD) and a comparable 7–10 μm limit was found for thick titania layers on stainless-steel on the degradation of 4-chlorobenzoic acid in water [18]. A quite lower thickness limit ($\sim 50\ \text{nm}$) was observed by Mills *et al.* [14] in the mineralization of stearic acid in water using titania layers prepared by CVD. In this case, however, a short UV radiation ($\lambda = 256\ \text{nm}$) was used and the thickness limit was attributed to the high optical absorbance at this wavelength.

3.4. Post-printing thermal treatment

The X-ray diffraction patterns of the untreated P25 powder and thermally processed unsupported catalytic powders were reported in Fig. 7 and the respective calculated anatase phase fractions were reported in Fig. 8. The resulting anatase fraction for untreated P25 was $80 \pm 4\ \%$ matching the value reported in literature [29]. This value was identical (within experimental error) to the anatase fraction of the powder treated at $500\ ^\circ\text{C}$. The anatase fraction decreases in the sample treated at $700\ ^\circ\text{C}$ and disappears in the samples processed at $900\ ^\circ\text{C}$.

The photocatalytic activity of samples processed at temperature in the $500\text{--}900\ ^\circ\text{C}$ range was studied using the previously described experimental conditions (Section 2.2). The resulting degradation rates r were reported in Fig. 8. The degradation rate of the sample treated at $700\ ^\circ\text{C}$ was 77% of those demonstrated by the sample treated at $500\ ^\circ\text{C}$. The activity of the sample treated at $900\ ^\circ\text{C}$ was below the measurable level in the adopted experimental conditions (*i.e.* it was about one order of magnitude smaller than the activity measured for the sample treated at $500\ ^\circ\text{C}$).

The measured catalytic activity decreases in the samples treated at different temperatures according to the depletion of the anatase phase. This was an expected result, because the rutile crystalline form is characterized by a lower photocatalytic activity than anatase [30,31]. The thermal treatment however can also cause a reduction of the specific surface of the catalyst. This effect was specifically studied for Degussa P25 free powder by Mills and Morris [32] who found out a severe reduction of the specific surface area with treatments at temperatures higher than $600\ ^\circ\text{C}$, considered by the authors as the main reason for the concomitant decrease of the catalytic activity. In the studied system, the two effects operate in the same direction and it is not possible, with the available data, to quantify their relative importance.

These results demonstrate that the adjustment of the post-printing thermal treatment is a critical step in the realization of titania photocatalytic layers by screen-printing.

4. Conclusions

The screen-printed titania photocatalyst demonstrated a good catalytic activity on the depollution of toluene in air at ambient concentration level using a low irradiance source. The deposited catalytic layer is characterized by a low density (about 25% of the titania bulk crystal) typical of very porous films. This is congruent with the SEM surface micrography that shows a complex structure of sintered grains with rough surface dominated by irregular cavities. The dependence of the reaction rate on the catalytic layer loading indicates an optimum value in the $0.3\text{--}0.4\ \text{mg cm}^{-2}$ range, corresponding to 3–4 μm thickness. Thicker layers do not demonstrate significant increases in the catalytic activity. This is consistent with the measured total optical transmittance that shows a high photon extinction beyond 5 μm of screen-printed catalytic layer. The post-printing thermal processing has a critical

impact on the activity of the final catalytic layer and a quite good catalytic activity was demonstrated for 30 min thermal treatment up to 700 °C. These results indicate that the screen-printing deposition is a very interesting technology for the manufacturing of photocatalytic layers for air depollution applications.

Acknowledgements

This work was supported by ITC-CNR, Production Systems Department, project SP.P04 “Instruments and methods for the technological, energy and environmentally sustainable innovation and management in civil and building construction”, sub-project SP.P04.005 and ISTECCNR project ET.P06.010. We thank Mr P. Cardillo for revising the English usage in the manuscript.

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Sample		Ink 1 (wt.%)	Ink 2 (wt.%)	Ink 3 (wt.%)	Ink 4 (wt.%)	Ink 5 (wt.%)	Ink 5 (wt.%)	Ink 5 (wt.%)
Titania powder (P25)		27.82	19.99	11.75	8.72	6.97	6.97	6.97
Terpyneol	[8000-41-7]	68.63	76.26	84.28	87.24	88.94	88.94	88.94
Lauric acid	[143-07-7]	0.48	0.35	0.20	0.15	0.12	0.12	0.12
Ethyl cellulose	[9004-57-3]	1.21	1.34	1.48	1.53	1.56	1.56	1.56
Glycerol	[56-81-5]	1.86	2.06	2.28	2.36	2.40	2.40	2.40

Table 1. Screen-printing ink formulations (weight percent). Formulation components are identified also by CAS Number.

Sample	Substrate	Ink	Layer Loading (mg cm ⁻²)	Deposit. Area (cm ²)	Masked Area (cm ²)	Figure	Notes
1	Alumina	Ink 4	0.11	10.0	4.0	6	
2	Alumina	Ink 4	0.12	10.0	3.7	6	
3	Glass	Ink 4	0.15	10.0	---	4	
4	Quartz	Ink 4	0.15	10.0	3.1	6	
5	Quartz	Ink 4	0.16	10.0	3.4	5,6	
6	Alumina	Ink 3	0.16	10.0	2.7	6	
7	Quartz	Ink 3	0.18	10.0	3.6	6	
8	Quartz	Ink 3	0.18	10.0	3.5	6	
9	Alumina	Ink 1 Diluted 1÷3	0.22	14.0	3.7	6	
10	Alumina	Ink 2	0.24	10.0	4.0	6	
11	Quartz	Ink 2	0.25	10.0	---	4	
12	Alumina	Ink 2	0.28	10.0	3.8	6	
13	Alumina	Ink 1 Diluted 1÷2	0.36	14.0	3.8	6	
14	Alumina	Ink 5	0.43	10.0	4.0	6	
15	Glass	Ink 1 Diluted 1÷1.5	0.43	14.0	---	4	
16	Alumina	Ink 5	0.43	10.0	---	2	
17	Glass	Ink 1 Diluted 1÷1.5	0.45	14.0	---	3a	
18	Quartz	Ink 5	0.49	10.0	3.4	1,5,6	
19	Alumina	Ink 1 Diluted 1÷1.5	0.49	14.0	3.8	6	
20	Quartz	Ink 5	0.50	10.0	3.3	6	
21	Quartz	Ink 1	0.66	10.0	3.4	6	
22	Alumina	Ink 1	0.66	14.0	3.7	6	
23	Glass	Ink 1	0.67	14.0	---	3b,4	
24	Quartz	Ink 1	0.68	10.0	3.4	5,6	
25	Alumina	Ink 1 Reformulated	0.69	3.0	Unmasked	8	
26	Alumina	Ink 1 Reformulated	0.69	3.0	Unmasked	8	Therm. treat. 700 °C
27	Alumina	Ink 1 Reformulated	0.69	3.0	Unmasked	8	Therm. treat. 900 °C

Table 2. List of all samples mentioned in the paper enumerated in layer loading order. The samples are reported in the indicated Figures. Layer loading estimated measurement repeatability ± 0.01 mg cm⁻² (1 σ). The deposition area is the geometric area on the substrate of the printed layer. The masked area refers to the exposed geometric area of the sample after masking with aluminium foils with estimated measurement error $\pm 3\%$ (1 σ). All samples were thermally treated at 500 °C for 30 min unless otherwise specified.

Figure 1. Experimental run with a two-step successive approximation method (0.49 mg cm^{-2} layer loading sample on quartz). UV-Lamp activation and the standard cylinder flow are reported for the different steps. The inlet concentration is actually measured at the outlet port with the irradiation source switched off. The figure shows both the stabilization verification measurements (white circles) and the actual concentration measurements (black circles) with the corresponding mean value.

Figure 2. SEM surface micrograph of 0.43 mg cm^{-2} layer loading sample on alumina (25 kV, gold coating).

Figure 3. Fracture (unpolished cross-section) SEM image of two selected samples on glass substrate with 0.45 mg cm^{-2} layer loading (a) and 0.67 mg cm^{-2} layer loading (b) respectively (15 kV, gold coating). The actual layer thickness is evaluated as the mean of five measurements along each fracture.

Figure 4. Measured layer thickness versus layer loading for selected samples. Error bars (1σ) computed as described in the text (Section 3.1).

Figure 5. Total optical transmittance for selected samples with quartz substrate (solid lines) and relative spectral irradiance at the sample surface (dashed line).

Figure 6. Toluene degradation rate r for samples with quartz (white squares) and alumina (black squares) substrate. Integrated irradiance (340–400 nm) $205 \pm 10 \mu\text{W cm}^{-2}$, toluene concentration $495 \pm 25 \text{ nmol m}^{-3}$. Error bars (1σ) computed as described in the text (Section 2.1 and 3.3). Linear fitting is intended to provide eye guidance and is calculated for samples with $<0.3 \text{ mg cm}^{-2}$ (a) and $>0.3 \text{ mg cm}^{-2}$ (b) layer loading respectively. The fitting (a) is forced to the origin.

Figure 7. X-Ray diffraction patterns ($\text{Cu } K\alpha$) for the unsupported catalyst powder thermally treated (30 min) at the indicated temperatures.

Figure 8. Toluene degradation rate r for the samples thermally treated at different temperatures and anatase phase fraction of the corresponding catalyst powder. Integrated irradiance (340–400 nm) $198 \pm 5 \mu\text{W cm}^{-2}$, toluene concentration $485 \pm 30 \text{ nmol m}^{-3}$ (1σ error bars).