Supporting information

Virtually Transparent TiO₂/Polyelectrolyte Thin Multilayer Films as High-Efficiency Nanoporous Photocatalytic Coatings for Breaking Down Formic Acid and for *Escherichia coli* Removal

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Substrate preparation

Silicon wafers (4.5 x 8 cm), glass (2.5 x 4.5 cm) and quartz slides (1.2 x 3.2 cm) were prepared as follows. The substrates were immersed in a 2 % v/v Hellmanex solution in distilled water and sonicated (ultrasound bath) for 15 min. The substrates were then rinsed with copious amounts of distilled water and then immersed in an ethanol-Milli Q water solution (50:50 v/v) and sonicated for 15 min. The substrates were then dried using compressed air and activated for 3 min using an oxygen plasma (Plasma Cleaner, Harick Plasma, New York, USA), with a power of 10,2 W applied to the radiofrequency coil. This process was repeated twice for quartz slides in order to activate both sides of the slides for UV-Visible spectroscopy characterisations. All substrates were used straight after plasma activation.

Gold coated quartz crystals for a quartz crystal microbalance with dissipation monitoring (QCM-D) were prepared by activating them with a UV/O_3 activator (UV/O_3 ProCleanerTM, BioForce NanoSciences, Ames, USA) for 20 min. Gold coated quartz crystals were used straight after activation.

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) measurement.

QCM-D measurements were carried out on the LbL films in a QCM-D E4 (Q-Sense AB, Sweden) using flow modules in parallel. In situ LbL assemblies of TiO₂ nanoparticles and polyelectrolytes were done in a similar manner to those on macroscopic silicon or glass/quartz substrates except that for QCM-D, the LbL assembly was done in parallel. The polyelectrolyte solutions and the TiO₂ suspensions were injected into the cell (600 μ l at a 300 μ l/min flow) and the solutions/suspensions were kept onto the substrates until stabilisation (full adsorption) was obtained. The substrates were rinsed by injecting 3 times Milli-Q water or acid Milli-Q water (according to the used solution or suspension) and the deposition steps were repeated for building the LbL film.

UV-Visible spectrophotometry in transmission mode

UV-Visible (UV-Vis) spectroscopy provides information on the absorption properties of a sample. It is based on the intensity of a monochromatic radiation once it passes through (transmission mode) or reflects (reflection mode) from the sample, compared to the initial intensity. In liquid media, the absorbance measured by UV-Vis spectroscopy is related to the amount of molecules in the media being passed through by the light according to the Beer-Lambert Law:

$$A = \log\left(\frac{l}{l_0}\right) = \varepsilon \times l \times c \tag{1}$$

where A is the absorbance or extinction of the molecules, c is the concentration of molecules in the media, l is the optical pathway corresponding to the cell length, ε is the extinction coefficient and I₀ and I are the intensity of the incident light and transmitted light respectively.

UV-visible spectroscopy in transmission mode was used in order to monitor the film construction on quartz slides. Here the optical pathway, l, corresponds to the thickness of the quartz slide. Since the film thicknesses are within the nanometric range, the film thickness is negligible in the optical pathway.

By neglecting the light scattering and assuming identical extinction values of TiO_2 in aqueous suspension and in LbL titania films deposited on quartz slide, the absorbance of the titania film can be correlated to the amount of titania per layer deposited using the following equation (Dontsova et al.):



here the m/S ratio corresponds to the mass of catalyst deposited per layer per surface area (g/m²). A₁ is the suspension absorbance and A is the absorbance of one layer of the deposited material (all absorbance measurements were made at 300 nm, see Figure 5 in the article). c_1 is the concentration of the titania suspension (g/m³), l_1 the width of the quartz slide.

The absorbance of the TiO₂ suspension (A₁) can be calculated through the establishment of a calibration curve of the TiO₂ suspension absorbance against the TiO₂ suspension concentration (*left*). The estimated amount of titania deposited per layer, derived from *right* graph, was found to be 47 ± 5 mg/m² ($4.7 \pm 0.5 \mu$ g/cm²).



(left) Absorbance of the TiO_2 suspension in regards to the TiO_2 concentration ; (right) amount of TiO_2 deposited per layer pairs calculated from Dontsova's equation.

$$m = V \times d \times f \tag{2}$$

with *m* the mass of TiO₂, *V* the volume of a monolayer with an apparent surface of 1 m², *f* the filling coefficient and *d* the density of TiO₂ at 4 x 10^{+6} g/m³.

Here, with a monolayer thickness of 40 nm, the volume of a monolayer is $V = 1 \times 1 \times 40 \times 10^{-9} = 40 \times 10^{-9} \text{ m}^3$

Considering a TiO₂ amount *m* of 47 mg/m² derived from spectrophotometry (or of 70 mg/m² when derived from ICP-AES, see Figure S4), the filling coefficient *f* was calculated as 0.29 or 0.44, respectively. This corroborated the highly porous structure of the film.

 D. Dontsova, V. Keller, N. Keller, P. Steffanut, O. Félix, G. Decher, Photocatalytically Active Polyelectrolyte/Nanoparticle Films for the Elimination of a Model Odorous Gas, Macromol. Rapid Commun., 32(15) (2011) 1145–1149.

Time Resolved Microwave Conductivity (TRMC)

The charge-carrier lifetimes in the LbL films upon UV illumination were determined by microwave absorption experiments using the TRMC method ^{1,2}. The TRMC technique is based on the measurement of the change of the microwave power reflected by a sample, $\Delta P(t)$, induced by its laser pulsed illumination. The relative difference $\Delta P(t)/P$ can be correlated, for small perturbations of conductivity, to the difference of the conductivity $\Delta \sigma(t)$ considering the following equation:

$$\frac{\Delta P(t)}{P} = A\Delta\sigma(t) = Ae\sum_{i}\Delta n_{i}(t)\mu_{i}$$
(1)

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where $\Delta n_i(t)$ is the number of excess charge-carriers *i* at time *t* and μ_i their mobility. The sensitivity factor A is independent of time, but depends on different factors such as the microwave frequency or the dielectric constant. Considering that the trapped species have a small mobility, which can be neglected, Δn_i is reduced to mobile electrons in the conduction band and holes in the valence band. And in the specific case of TiO₂, the TRMC signal can be attributed to electrons because their mobility is much larger than that of the holes ³. The incident microwaves were generated by a Gunn diode of the K_{\alpha} band at 30 GHz. Pulsed light source was an OPO laser (EKSPLA, NT342B) tunable from 225 to 2000 nm. It delivers 8 ns fwmh pulses with a frequency of 10 Hz. The light energy density received by the sample was 1.3 mJ cm⁻² at 350 nm. The main data provided by TRMC are the maximum value of the signal (I_{max}), which indicates the number of the excess charge carriers created by the pulse, including decay processes during the excitation by the laser (10 ns), and the decay (*I(t)*) due to the decrease of the excess electrons, either by recombination or by trapping processes. Concerning the decay, i.e. the lifetime of charge carriers, a short and a long range is usually analysed. The shortrange decay, arbitrarily fixed up to 40 ns after the beginning of the pulse, represented by the I_{40ms}/I_{max} ratio, reflects fast processes, mainly recombination of charge carriers, a high value indicating a low recombination speed.

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EPR characterization of multilayer films

LbL film construction. Capillaries were cleaned with ethanol/water (50/50 v/v) in low density sonicating bath for 15 min. They were rinsed with water and dried upon airflow. The clean substrates were first dipped 20 min in a solution of polycation PEI followed by rinsing step (dipping 3 times of 3 min in 3 different containers of ultrapure water (18M Ω .cm, Milli-Qlab system). The next steps involved alternative stages of dipping capillaries of polyanion PSS solution (20 min in HNO₃ solution adjusted pH = 2.5) and in the TiO₂ suspension adjusted by HNO3 to pH 2.5 (20 min). After each dipping steps, a rinsing step, dipping 3 times of 3 min in 3 different containers of 3 min in 3 different containers of HNO₃ solution (pH = 2.5), was performed.

Except for PEI, which was only used as first deposit, all the dipping (PSS or TiO₂) and rinsing steps were repeated to reach the desired film configuration (PEI/PSS)/(TiO₂/PSS)_{n-1}-(TiO₂)_n with n = 1, 3, 5, 7, 10. Once films were constructed a final rinsing step in ultrapure water (3x5 min in 3 different containers) was performed. The last stage of the procedure was to clean the outside of the capillaries with an optical tissue soaked of ethanol in order to remove the films built.



(A) Open view of the irradiation chamber equipped with a cooling fan underneath (white arrow) and composed of 4 UV-A neon tubes surrounding a clear fused quartz tube (Wilmad, 705-PQ-6.25) positioned at 1 cm of each neon allowing to centered the capillary with respect to the light source. (B)

schematic top view of the closed irradiation chamber. **(C)** Irradiance spectra of the 4 UV-A neon tubes used for illumination of functionalized capillaries.

Electron Paramagnetic Resonance (EPR). The coated capillaries were filled with 50 μ L nondeoxygenated TEMPOL solution in water at 200 μ M and sealed. A first spectrum was recorded to reach the initial EPR intensity (I₀). For all measurements, the variations of the I₀ values are less than 3%. Then, successive illumination steps of 30 s were applied. Between each illumination step, one I(t) spectrum was recorded. All the intensities values, proportional to the TEMPOL concentration (I \propto [T•]), were obtained after baseline correction and double integrations. EPR data were plotted as I/I₀ vs. illumination time. Noteworthy, without the presence of paramagnetic probe, no EPR signal is detected.

Illumination of the capillaries was performed outside the EPR cavity with an UV neon-based labmade illumination chamber. Each neon presents a $\lambda_{max} = 365$ nm (hv = 3.4 eV) and E ≈ 1.5 mW.cm⁻² (at *ca.* 1 cm distance measured with a powermeter 1936-C and a 918D-UV-OD3 detector from Newport). The emission spectra of the neons and a schematic description of the experimental setup are depicted above. As TEMPOL does not absorb at this wavelength, there is no absorption variation during measurement. Electronic photo-generation processes occur only during the irradiation procedure and are assumed to stop as soon as light is off. All experiments were performed at room temperature (295 ± 1 K).

Schematic single-pass photocatalytic reactor used for the gas phase photocatalytic tests

The photocatalytic reactor was derived from that proposed in the ISO 22197 standard series. This reactor consisted of an aluminium chamber (260 mm in length x 50 mm in width x 40 mm in height) closed with a quartz window. A polytetrafluoroethylene (PTFE) support is located inside the aluminium chamber on which the pollutant flow passes. LbL films constructed on model surfaces (silicon wafers) and textiles were placed face-up in a cavity located at the centre of the PTFE support. LbL films built on 36 cm² silicon wafer were directly located in the cavity.



Schematic representation of the single-pass reactor containing a LbL film built on silicon wafer

A 8W UV-A lamp (Sylvania Blacklight Blue F8W/BLB T5) with a spectral peak centred at 365 nm was placed above the reactor (1.5 cm), parallel to the photocatalytic film. An irradiance of 2.5 mW/cm² was measured at the top of the sample surface. The photocalytic reactor was placed in a thermostated chamber for maintaining a constant temperature of 25°C during the test according to ISO standards, since heat generated by the lamp during the irradiation could not be neglected.



Irradiance spectrum of the UV-A lamp used in this work

The generation of the inlet polluted air flow was obtained by mixing three synthetic air flows: (i) dry air flow, (ii) humid air flow, (iii) gas-phase HCOOH containing air flow. Synthetic air was bubbled in a temperature-controlled saturator containing liquid phase formic acid (HCOOH, Sigma Aldrich, >95%) at 15°C and atmospheric pressure. Thus, the concentration of gas phase HCOOH was related to the vapour pressure of HCOOH at working temperature and pressure conditions. In the same way, synthetic air was bubbled in distilled water at 25°C and atmospheric pressure. Concentration in the gas phase was set by the vapour pressure in the working conditions. Water partial pressure was expressed in terms of relative humidity (RH): 100% of RH being defined as vapour pressure at 25°C and atmospheric pressure. These two air flows were then mixed with an additional synthetic air flow (dry air) to obtain the required pollutant-water-air ratio with a constant total air rate of 20 ml/min, corresponding to a velocity of 0.74 cm/s⁻¹ and a residence time of 10.8 s in the reaction zone of the reactor. Brooks 5850 massflow meters were used to control separately dry and humid air flows. Relative humidity was set at 50% (about 3% relative to the total atmospheric pressure). In-Flow Bronkhorst flow meter (Bronkhorst® High-Tech, the Netherlands) allowed the control of HCOOH containing air flow and the photocatalytic tests were implemented at a gas phase HCOOH concentration of 45 ppm_v.





XRD characterization of Aeroxide TiO₂ P25 suspensions and of multilayer films

Figure S1 : XRD analysis of (top) TiO_2 P25 as powder and from both the precipitate and the LbL suspension, (bottom) the titania and polyelectrolytes LbL films with 1 and 10 layer pairs, compared to the TiO_2 P25 powder from the Lbl suspension.

DLS characterization of the Aeroxide $TiO_2\ P25$ suspension used for the LbL film

construction



Figure S2 : Dynamic light scattering characterisation of the TiO_2 P25 suspension used for LbL film construction.

QCM-D measurements



Figure S3. Change of frequency overlaying of 3^{rd} , 5^{th} and 7^{th} overtones when a 4 layer pair PEI(PSS/TiO₂)₄ film is constructed on the QCM quartz slide.

ICP-AES chemical analysis of the multilayer films



Figure S4 : Mass of TiO_2 deposited investigated by chemical analysis ICP-AES. Error bars are too small to be clearly shown on the graph.



Figure S5: Number of adhered *E. coli* bacteria on control (silicon wafer) and reference films without TiO_2 (PEI, PEI/PSS, PEI/PSS/PDDA, PEI/PSS/PDDA/PSS) before (total population of bacteria) and after ("live" and "damaged" bacteria) 60 min UV-A irradiation (irradiance of 3 mW/cm². Films were built on 2 cm² silicon wafers. *: significant difference in live quantity compared to control (*p*-value < 0.05).

Bacterial assays were performed on control samples in order to remove any possibility of biocidal properties from the sample surface and polyelectrolyte. Reference samples were labelled as follow:

- Control: silicon wafer
- PEI
- PEI/PSS
- PEI/PSS/PDDA
- PEI/PSS/PDDA/PSS

Table	S1
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Layer deposited	Mass of material deposited (ng/cm ²)
PEI	119.6
PSS #1	201.1
TiO ₂ #1	6343.9
PSS #2	527.1
TiO ₂ #2	9514.4
PSS #3	1024.2
TiO ₂ #3	10857.8
PSS #4	1865.2
TiO ₂ #4	9989.3

Table S1. Amount of deposited materials on LbL film calculated with QCM-D data from the 3rd overtone.

Table S2

Evolution of the multilayer film thickness after being immerged in a 9 g/l NaCl solution, obtained by ellipsometry

Samples	Estimated thickness (nm)	Estimated thickness (nm)
	T = 0 h	T = 15 h
PEI/(PSS/TiO ₂) ₁	37.6 ± 2.8	47.3 ± 3.9
PEI/(PSS/TiO ₂) ₄	140.8 ± 6.2	154.6 ± 6.3
PEI/(PSS/TiO ₂) ₆	222.9 ± 8.3	246.3 ± 4.7
PEI/(PSS/TiO ₂) ₁₀	371.6 ± 9.0	380.6 ± 7.8

Table S2. Evolution of the multilayer film thickness after being immerged in a 9 g/l NaCl solution, obtained by ellipsometry. The stability of the titania LbL films for bacterial assay was assessed by being immerged in NaCl solution (9 g/l) for 15 h.

Table S3

HCOOH conversion obtained on specific architectures of films in comparison to that achieved on the PEI/(PSS/TiO₂) reference film with one single layer pair.

Table S3. HCOOH conversion obtained on specific architectures of films in comparison to that achieved on the PEI/(PSS/TiO₂) reference film with one single layer pair. Potentially active layer is visualized in italic format as *PSS/TiO₂*. Experimental parameters: [HCOOH] = 45 ppm_v, air flow = 20 mL/min, speed = 0.7 cm/s, UV-A irradiance = 2.5 mW.cm⁻², films built on 36 cm² Si wafers.

Film name	Architecture specification ^a	HCOOH conversion (%)
PEI/(PSS/TiO ₂)	Reference film. TiO ₂ as "final layer"	94
PEI/PSS/TiO ₂ /(PSS/PDDA) ₈	(PSS/PDDA) $_8$ built on the top of the first PSS/TiO ₂ layer pair	19
PEI/ <i>PSS/TiO</i> ₂ /(PSS/PDDA) ₈ / <i>PSS/TiO</i> ₂	(PSS/PDDA) ₈ deposited between two PSS/TiO ₂ layer pairs. TiO ₂ as "final layer"	32
PEI/(PSS/PDDA) ₈ / <i>PSS/TiO</i> ₂	PSS/TiO ₂ layer pair built on the top of the (PSS/PDDA) ₈ layer pairs. TiO ₂ as "final layer"	27

^a Additional (PSS/PDDA)₈ polyelectrolyte layer pairs were constructed using negativelycharged PSS (1 g/l at pH 2,5 adjusted by HNO₃) and positively-charged poly(diallyldimethyliammonium chloride) (PDDA, 1 g/l with 0.5M of sodium chloride) by the dipping LbL process, using the PEI/(PSS/TiO₂)_n film dipping parameters. The (PSS/PDDA)₈ layers had an average thickness of 20 nm determined by ellipsometry.