coatings

Supplementary Materials: Photocatalytic Activity in the In-Flow Degradation of NO on Porous TiO_2–Coated Glasses from Hybrid Inorganic–Organic Thin Films Prepared by a Combined ALD/MLD Deposition Strategy

Ramón Azpiroz [1], Marina Borraz [2], Aida González [1,3], Catalina Mansilla [2,*], Manuel Iglesias, [1,*] and Jesús J. Pérez-Torrente [1,*]

[1] Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain; rayazp2@gmail.com (R.A.); a.gonzalez@duglass.es (A.G.)
[2] Ctechnano, Av. de Tolosa 76, 20018 Donostia – San Sebastian, Spain; m.borraz@ctechnano.com
[3] Ariño Duglass, Pol. Ind. Royales Bajos s/n, Puebla de Alfindén (la), 50171 Zaragoza, Spain
* Correspondence: c.mansilla@ctechnano.com (C.M.); miglesia@unizar.es (M.I.); perez@unizar.es (J.J.P.-T.)

Table of contents

Citation: Azpiroz, R.; Borraz, M.; González, A.; Mansilla, C.; Iglesias, M.; Pérez-Torrente, J.J. Photocatalytic Activity in the In-Flow Degradation of NO on Porous TiO_2–Coated Glasses from Hybrid Inorganic–Organic Thin Films Prepared by a Combined ALD/MLD Deposition Strategy. *Coatings* **2022**, *12*, 488. https://doi.org/10.3390/coatings12040488

Academic Editor: Joaquim Carneiro

Received: 1 March 2022
Accepted: 1 April 2022
Published: 5 April 2022

1. ALD/MLD thin film deposition on glass. Deposition and annealing conditions.

1.1. $TiCl_4$-ethylene glycol (EG) precursors.

Table S1. $TiCl_4$-EG. Standard deposition conditions. Annealing conditions: 2 h at 400 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1000	15	90	70	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S2. $TiCl_4$-EG. Standard deposition conditions. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1000	15	90	70	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S3. $TiCl_4$-EG. Deposition conditions: 80 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1000	15	90	80	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S4. $TiCl_4$-EG. Deposition conditions: EG Pulse 1500ms. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1500	15	90	80	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S5. $TiCl_4$-EG. Deposition conditions: EG Pulse 1500ms. Annealing conditions: RT to 250 °C (1 min), 250 °C to 550 °C (90 min), 3 h at 550 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1500	15	90	80	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S6. $TiCl_4$-EG. Deposition conditions: EG Pulse 1500ms. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 5 h at 450 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	1500	15	90	80	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S7. $TiCl_4$-EG. Deposition conditions: EG Pulse 4000ms. Cycles: 260. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Precursors							
	$TiCl_4$			Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	4000	15	90	80	260

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

Table S8. $TiCl_4$-EG/EG. Deposition conditions: EG Pulse 4000 ms. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Precursors											
	$TiCl_4$			Ethylene glycol				Ethylene glycol				
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
40	300	15	80	4000	20	90	80	4000	20	90	80	200

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
110	110	110	120

1.2. $TiCl_4$-H_2O precursors.

Table S9. $TiCl_4/H_2O$. Deposition temperature: 180 °C. Annealing conditions: 3 h at 400 °C.

	Precursors						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
100	200	0	40	200	0	45	600

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
120	180	180	120

1.3. $TiCl_4$-hydroquinone (HQ) precursors.

Table S10. $TiCl_4/H_2O$ (20 cycles)-$TiCl_4$/HQ (500 cycles). Deposition temperature: 210 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Layer 1: TiO_2						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
40	300	15	80	4000	20	90	20

Layer 2: Ti-HQ							
$TiCl_4$			Hydroquinone				
Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles
200	0	60	12	0	80	120	500

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
120	210	210	120

Table S11. $TiCl_4/H_2O$ (2 cycles)-$TiCl_4$/HQ (4 cycles). Global cycles 120. Deposition temperature: 210 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Layer 1: TiO_2						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
65	200	0	60	200	0	65	2

Layer 2: Ti-HQ								
$TiCl_4$			Hydroquinone					
Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles	Cycles Global
200	0	60	12	0	70	120	4	120

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet

120	210	210	120

Table S12. $TiCl_4/H_2O$ (2 cycles)-$TiCl_4$/HQ (8 cycles). Global cycles 120. Deposition temperature: 210 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Layer 1: TiO_2						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
65	200	0	60	200	0	65	2

Layer 2: Ti-HQ								
$TiCl_4$			Hydroquinone					
Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles	Cycles Global
200	0	60	12	0	70	120	8	120

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
120	210	210	120

Table S13. $TiCl_4/H_2O$ (4 cycles)-$TiCl_4$/HQ (2 cycles). Global cycles 120. Deposition temperature: 210 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 3 h at 450 °C.

	Layer 1: TiO_2						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
65	200	0	60	200	0	65	4

Layer 2: Ti-HQ								
$TiCl_4$			Hydroquinone					
Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles	Cycles Global
200	0	60	12	0	70	120	2	120

Temperature (°C)			
Inlet	Bottom Chamber	Lid Chamber	Outlet
120	210	210	120

Table S14. $TiCl_4/H_2O$ (2 cycles)-$TiCl_4$/HQ (8 cycles). Global cycles 120. Deposition temperature: 210 °C. Annealing conditions: RT to 250 °C (1 min), 250 °C to 450 °C (90 min), 5 h at 450 °C.

	Layer 1: TiO_2						
	$TiCl_4$			H_2O			
N_2 (sccm)	Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Cycles
65	200	0	60	200	0	65	2

Layer 2: Ti-HQ								
$TiCl_4$			Hydroquinone					
Pulse (ms)	Residence (s)	Purge (s)	Pulse (ms)	Residence (s)	Purge (s)	Temperature (°C)	Cycles	Cycles Global

200	0	60	12	0	70	120	8	120

Temperature (°C)			
Inlet	**Bottom Chamber**	**Lid Chamber**	**Outlet**
120	210	210	120

2. Online monitoring of the photocatalytic degradation of NO(g).

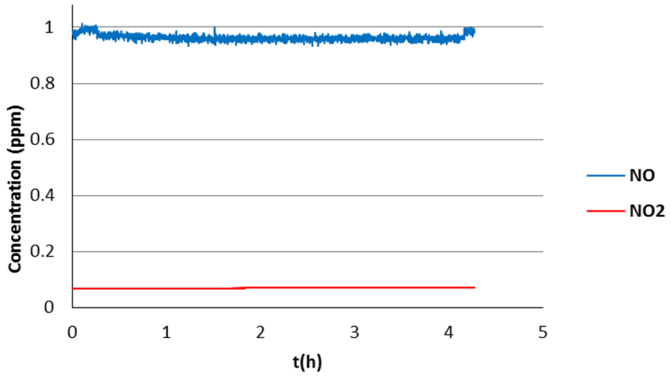


Figure S1. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S1.

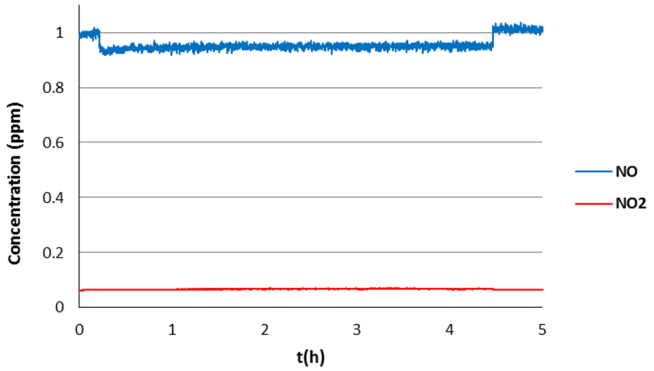


Figure S2. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S2.

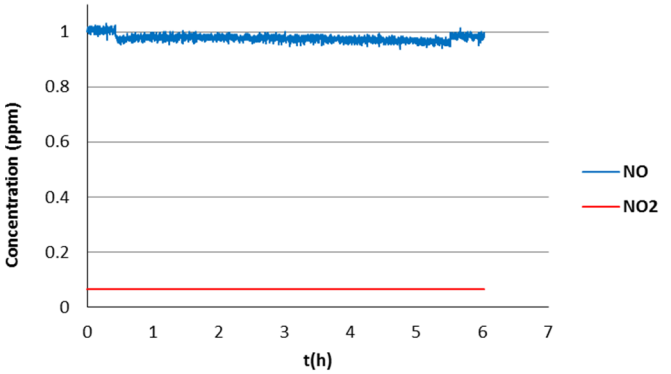


Figure S3. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S3.

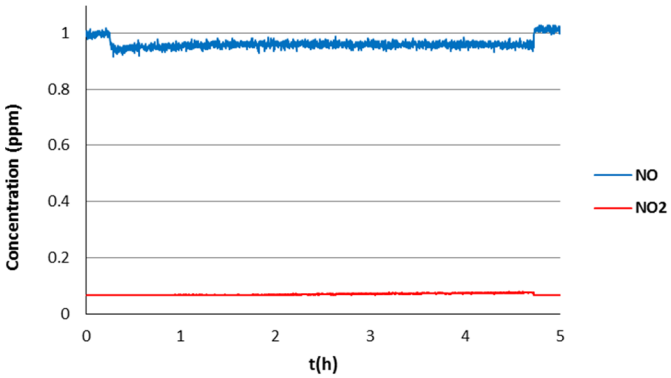


Figure S4. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S4.

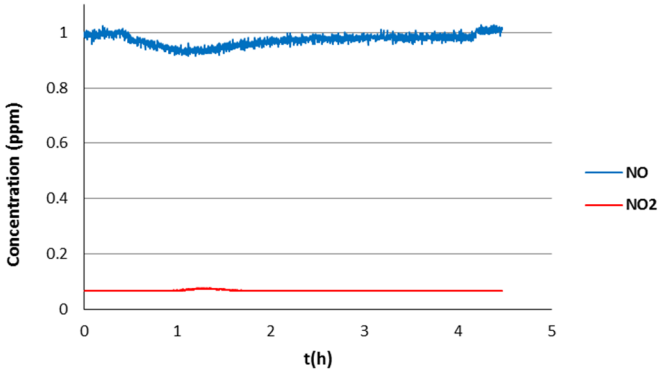


Figure S5. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S5.

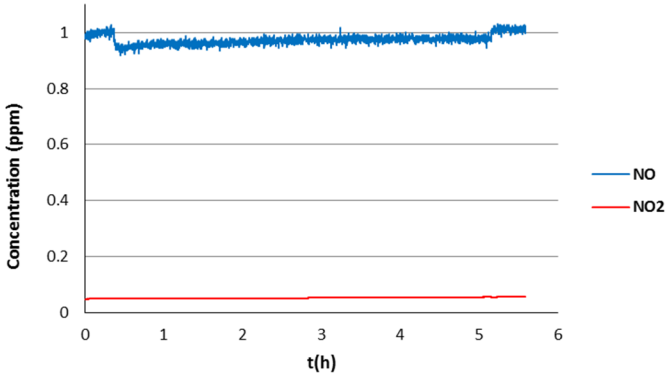


Figure S6. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S6.

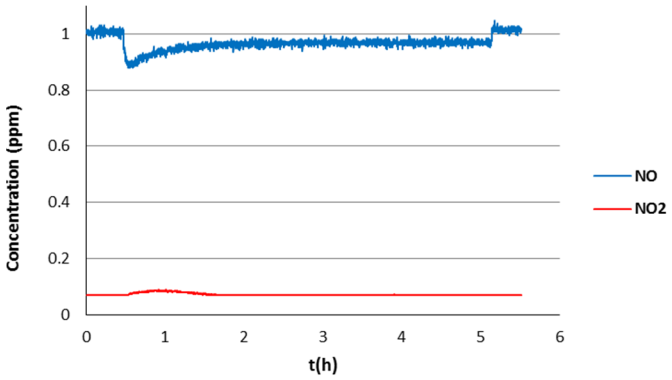


Figure S7. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S7.

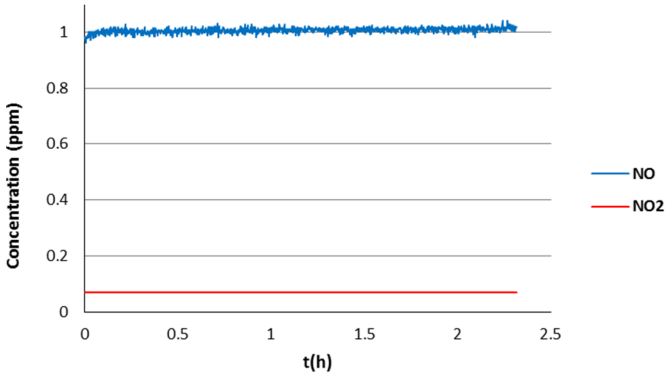


Figure S8. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S8.

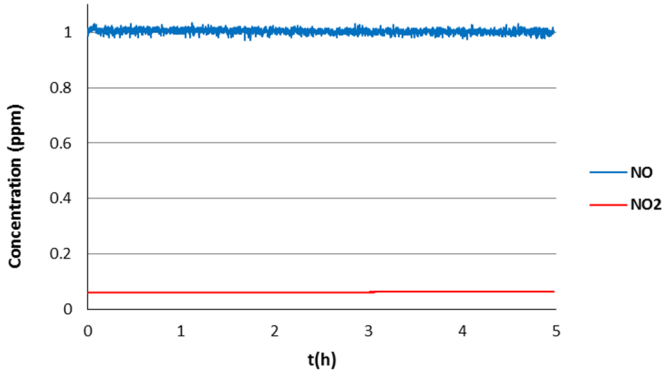


Figure S9. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a ALD TiO_2 thin film ($TiCl_4$/H_2O) with deposition and annealing conditions according to Table S9.

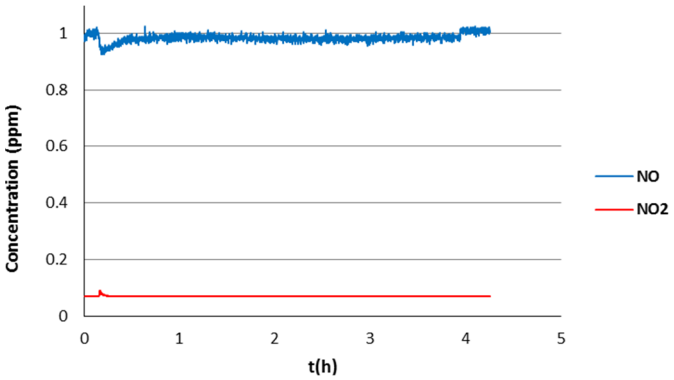


Figure S10. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a titanicone thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S10.

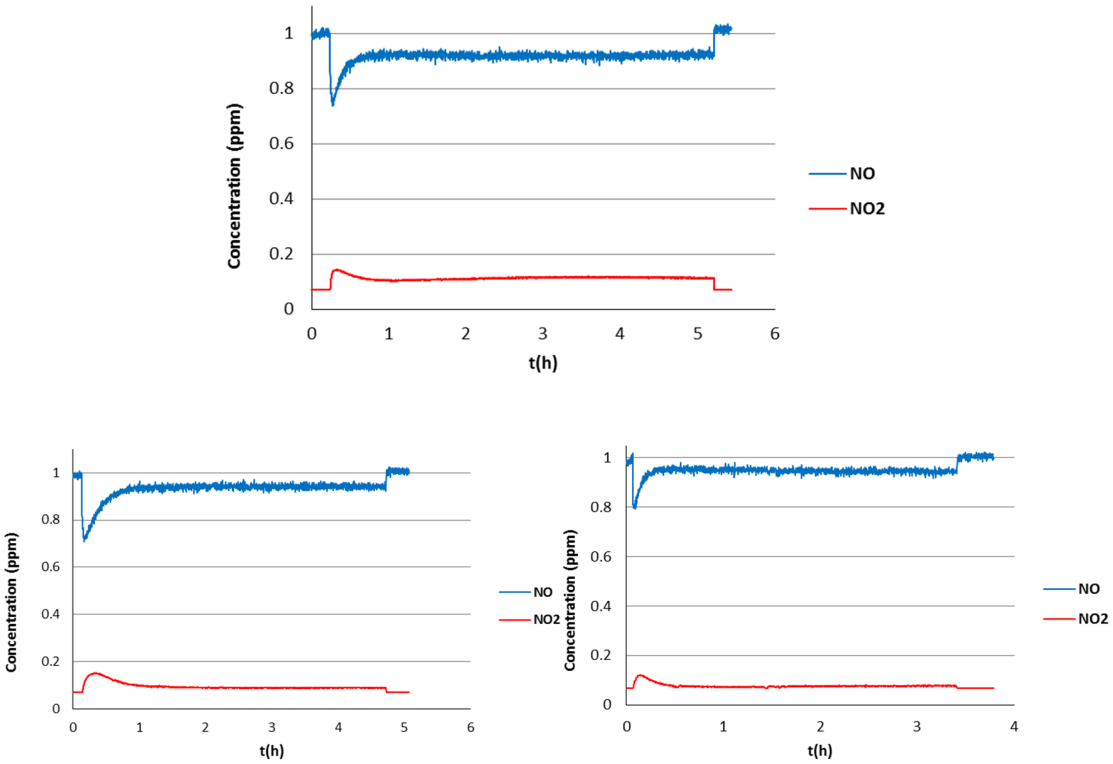
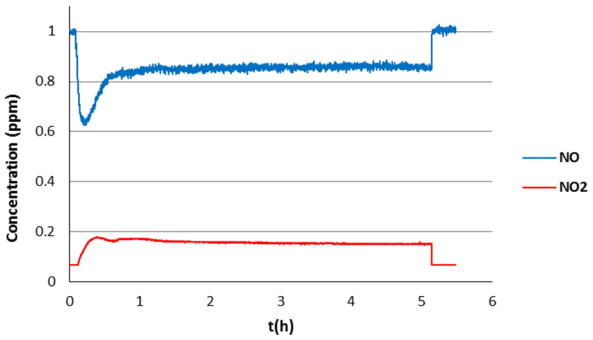


Figure S11. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a titanicone thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S11: first photocatalytic cycle (top), second photocatalytic cycle (bottom left), third photocatalytic cycle (bottom right).



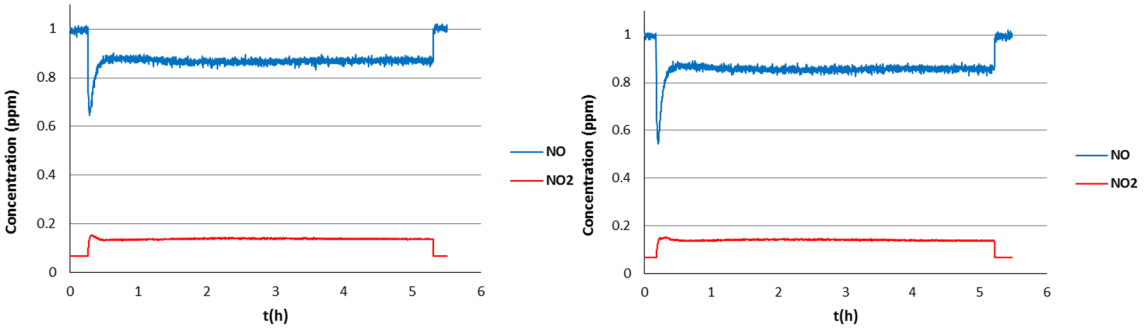


Figure S12. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a titanicone thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S12: first photocatalytic cycle (top), second photocatalytic cycle (bottom left), third photocatalytic cycle (bottom right).

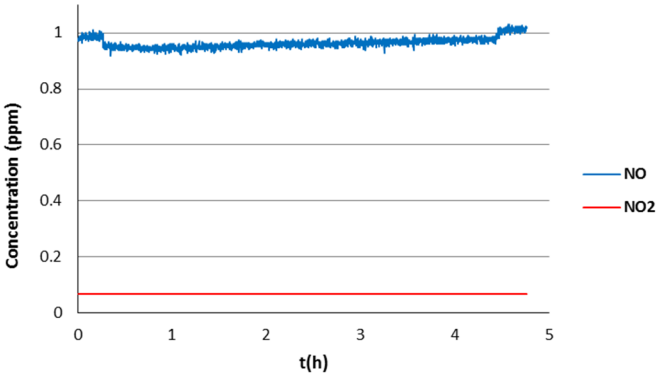


Figure S13. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a titanicone thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S13.

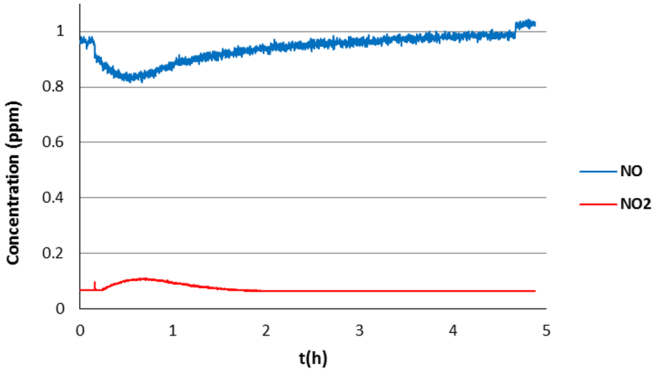


Figure S14. Monitoring of the photocatalytic degradation of NO(g) by a coated-glass fabricated from a titanicone thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S14.

3. Experimental setup for the measurement of the photocatalytic activity.

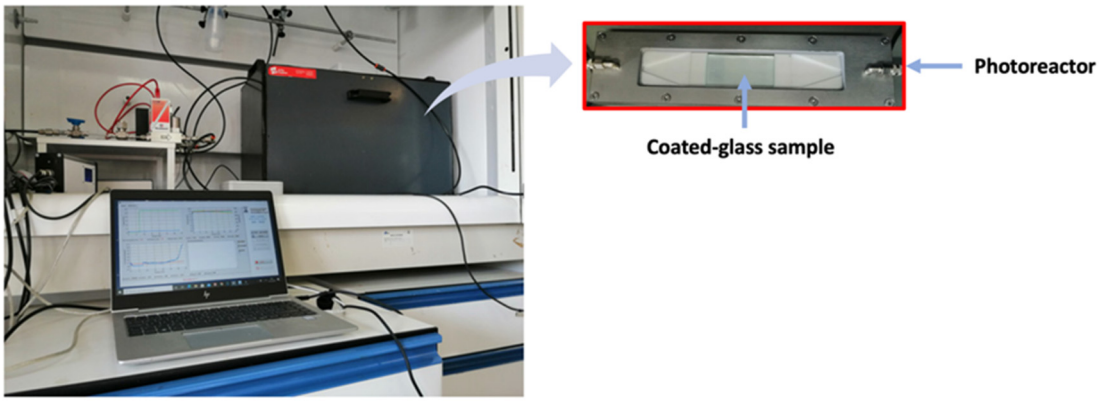


Figure S15. Photograph of the experimental setup including a detailed image of the photoreactor.

4. Raman, XRD and UV-Vis spectra for selected photocatalytic coatings.

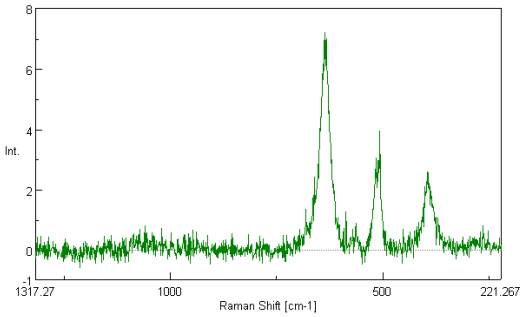


Figure S16. Raman spectra of a coated-glass fabricated from an MLD thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S2. Absorption bands: 639, 513, 399 cm^{-1}.

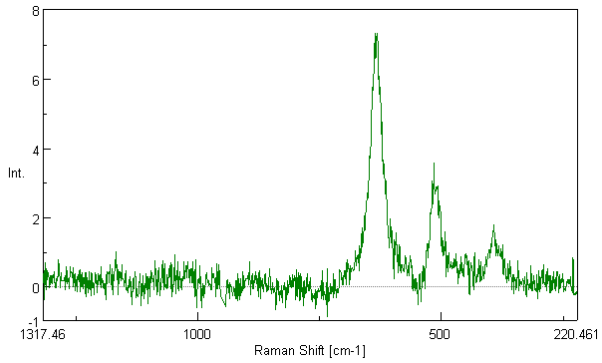


Figure S17. Raman spectra of a coated-glass fabricated from an ALD thin film ($TiCl_4$/H_2O) with deposition and annealing conditions according to Table S9. Absorption bands: 639, 513, 399 cm^{-1}.

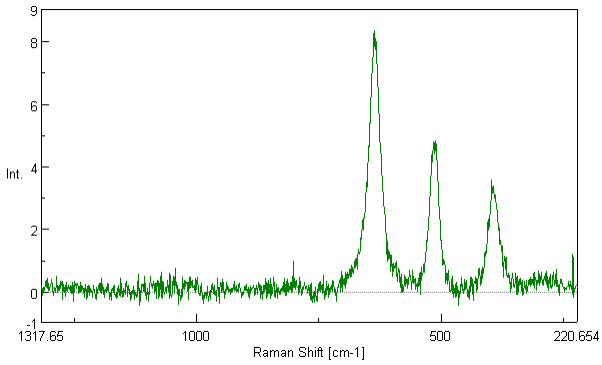


Figure S18. Raman spectra of a coated-glass fabricated from an ALD/MLD thin film ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S11. Absorption bands: 639, 513, 399 cm^{-1}.

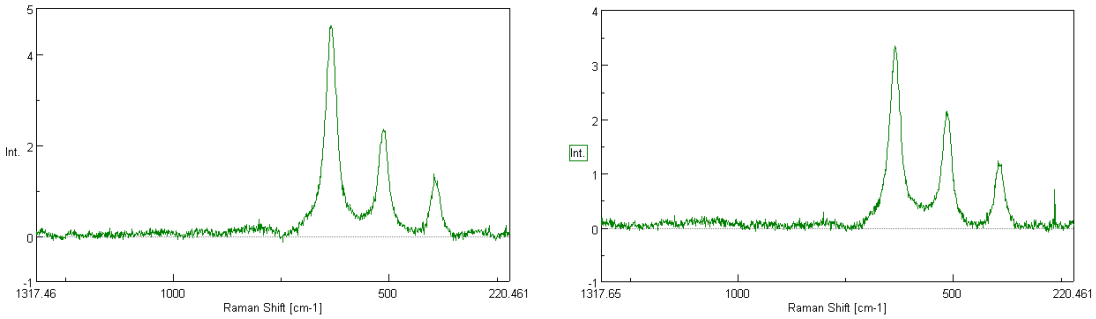


Figure S19. Raman spectra of a coated-glass fabricated from an ALD/MLD thin film ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to TS12: no iridescent zone (left) and iridescent zone (right). Absorption bands: 639, 513, 399 cm^{-1}.

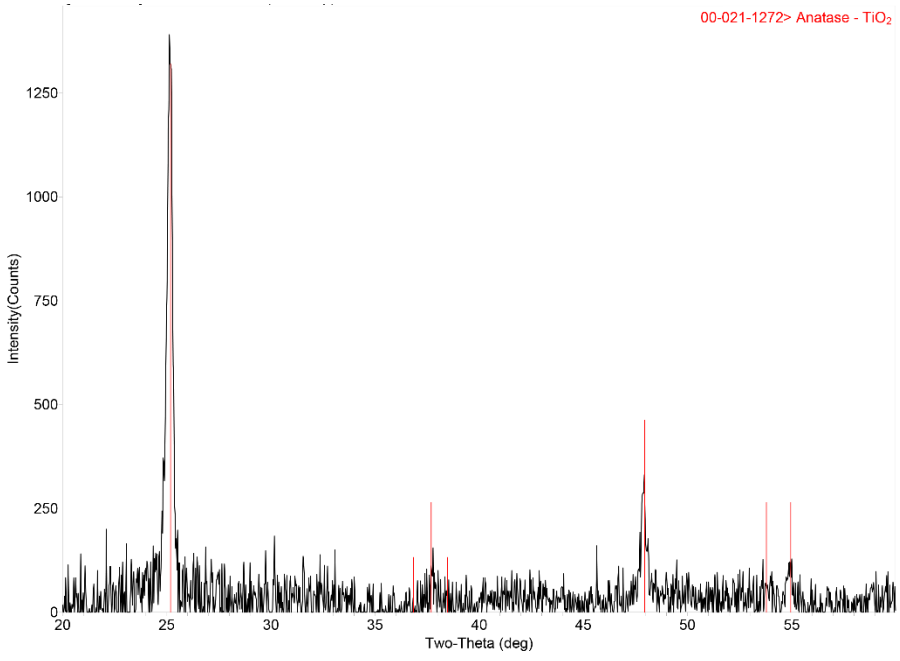
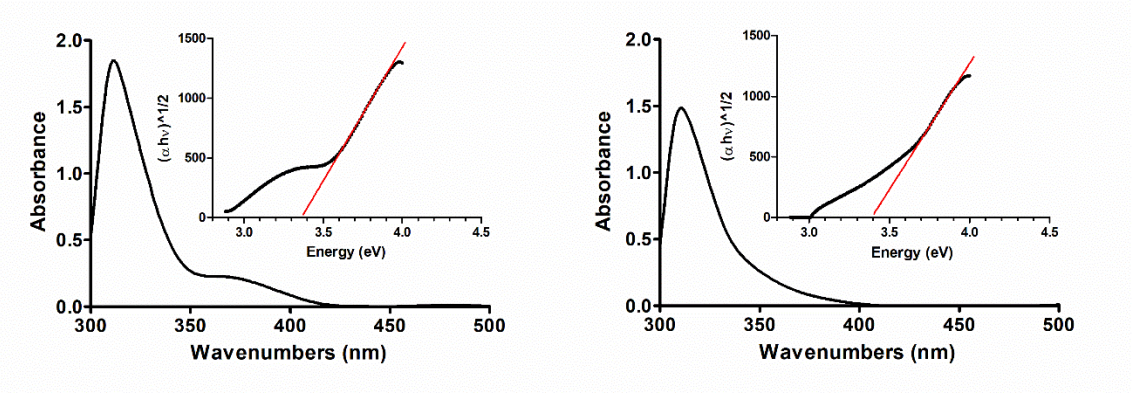


Figure S20. XRD pattern of a coated-glass fabricated from an inorganic-organic thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions

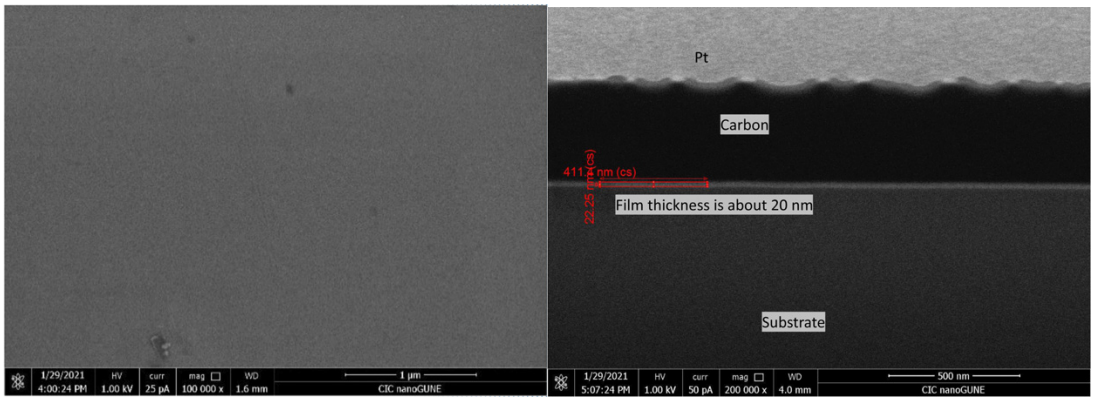
according to Table S12: 2θ 25.2º, 36.8 º, 37.7 º, 38.5 º, 48.0 º, 53.8 º and 55.0 º. The anatase pattern obtained from the JCPDS-International Centre for Diffraction Data-2000 database is shown in red.



(a) **(b)**

Figure S21. UV-Vis spectra of coated-glasses fabricated from an inorganic-organic thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to: a) Table S12, and b) Table S14. Insets show bandgap determination using a Tauc method.

5. SEM/TEM images for selected photocatalytic coatings.



FigureS22. Surface (left) and cross-sectional (right) SEM images of a coated-glass fabricated from an MLD titanicone thin film ($TiCl_4$/EG) with deposition and annealing conditions according to Table S1.

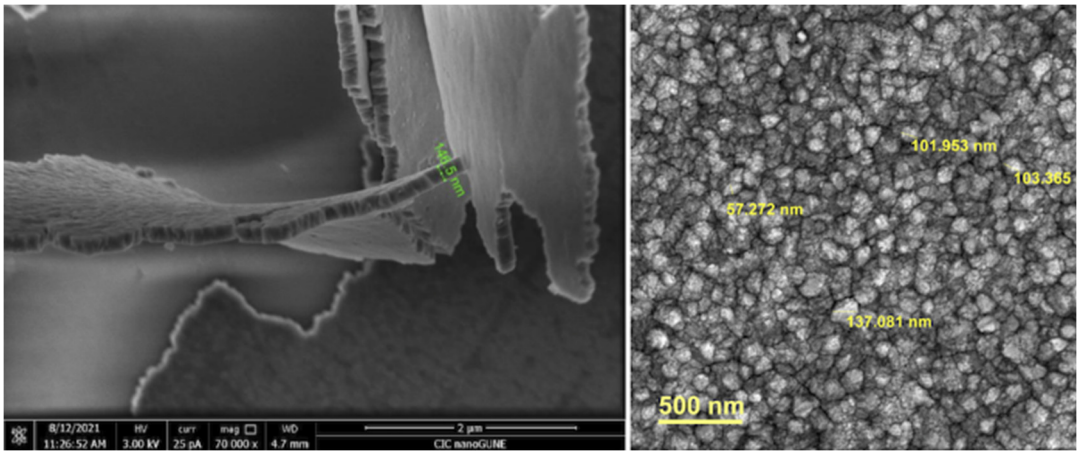


Figure S23. SEM image of the film detached from the substrate (scratch) showing a columnar structure (left) and HR SEM image of the surface (right) of a coated-glass fabricated from an inorganic-organic thin film using a combined ALD/MLD deposition strategy ($TiCl_4/H_2O/HQ$) with deposition and annealing conditions according to Table S12.

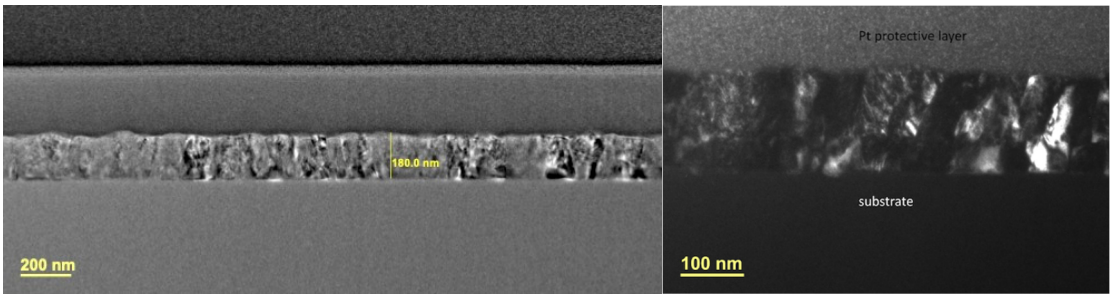


Figure S24. Low magnification TEM image (left) showing a film thickness of about 180 nm of the above sample and dark-field TEM image showing the crystalline grains in the film (right).

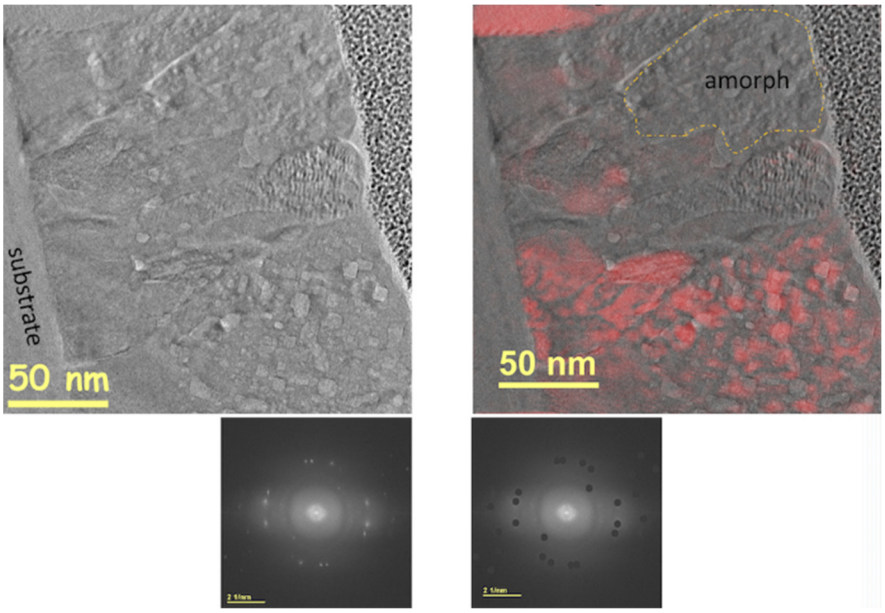


Figure S25. HRTEMimagen showing nanocrystals of different size and amorphous (or less ordered) phase (left) of the above sample and virtual dark field image showing the crystalline part (reflections marked on FFT).

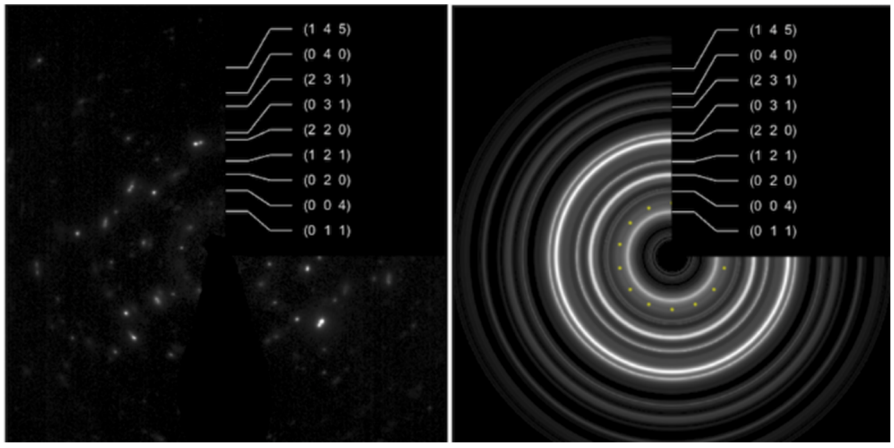


Figure S26. Electron diffraction pattern of a selected nanocrystal of the above sample showing the presence of TiO_2 (anatase).

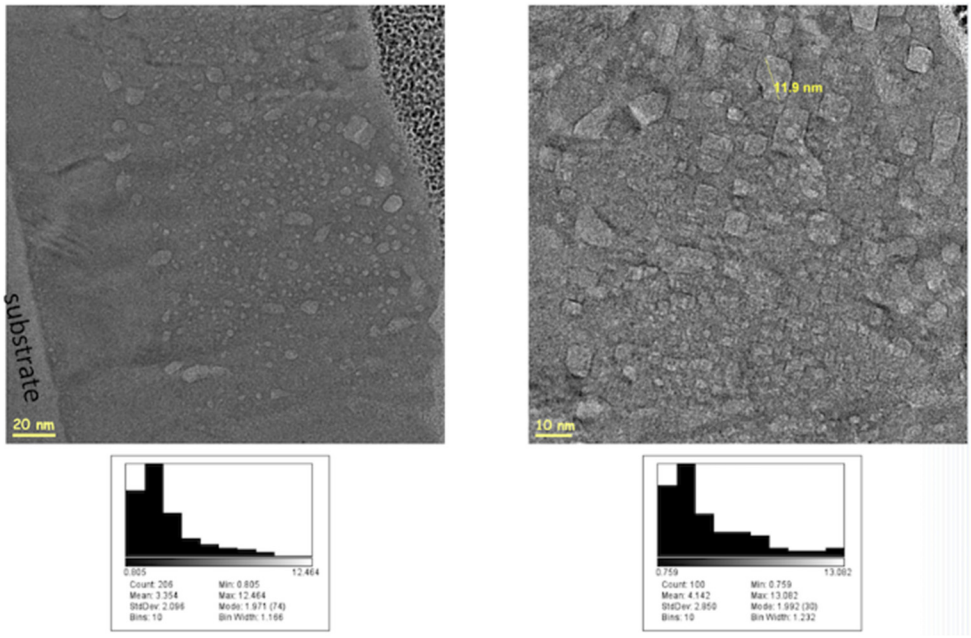


Figure S27. HRTEMimagen of the above sample showing the measured pore size: average 3-4 nm, min: 0.8 nm, max: 13 nm.

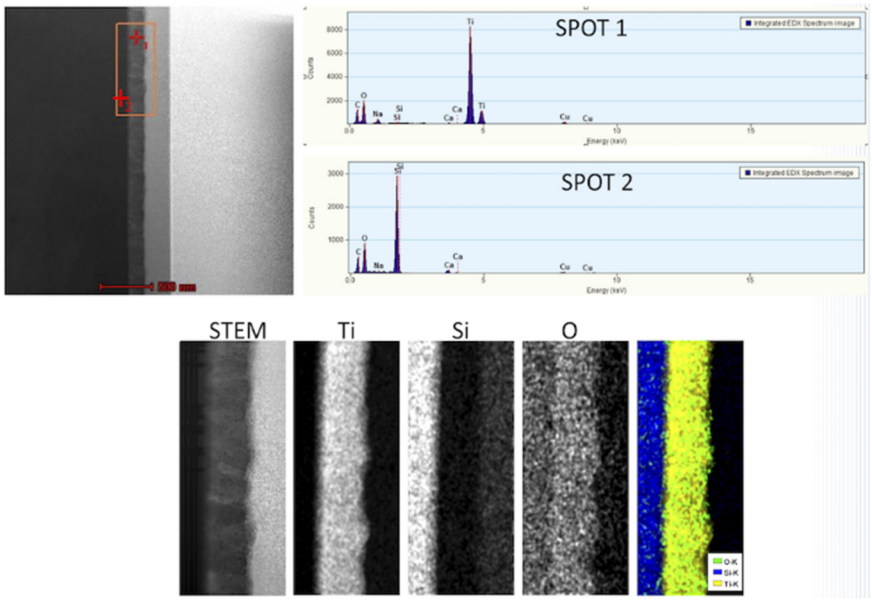


Figure S28. Composition analysis by STEM-EDX of the above sample at selected points on the substrate and coating, including EDX mapping.