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Transparent TiO_2 thin films with high photocatalytic activity for indoor air purification

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Supplementary Information Section

Content

1. Spray pyrolysis setup

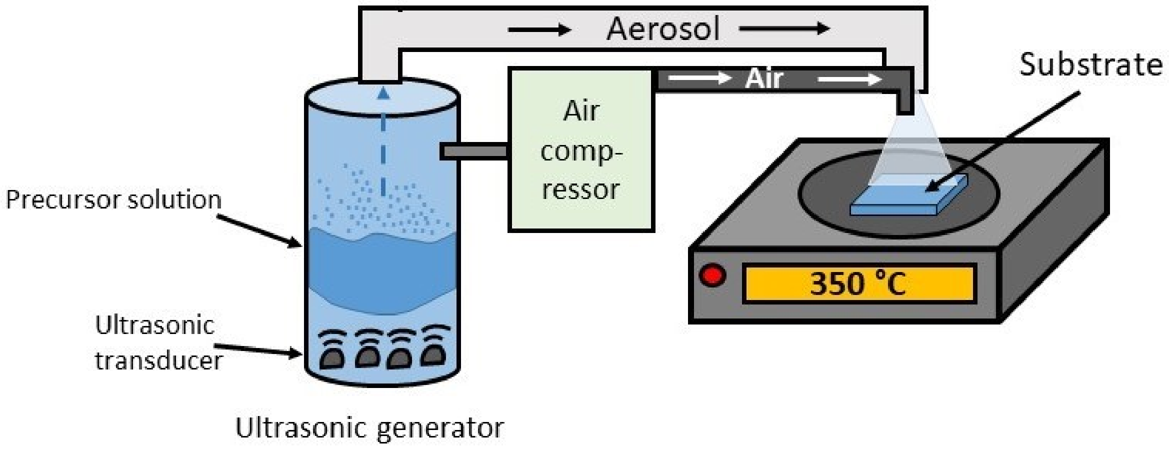

Fig. SI-1 The sheme of the ultrasonic spray pyrolysis setup.

2. Setup used for gas-phase photocatalytic experiments.

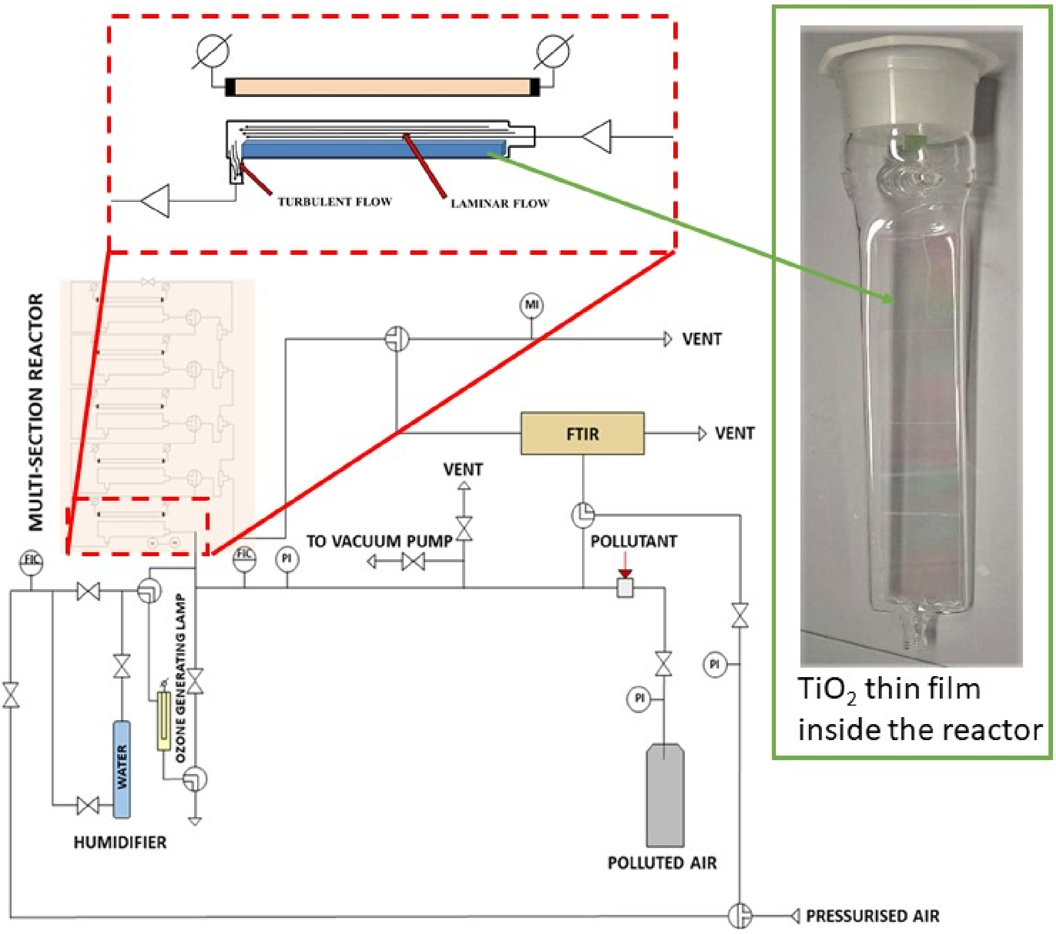

Fig. SI-2 The sheme of setup used for gas-phase photocatalytic experiments.

3. Surface morphology

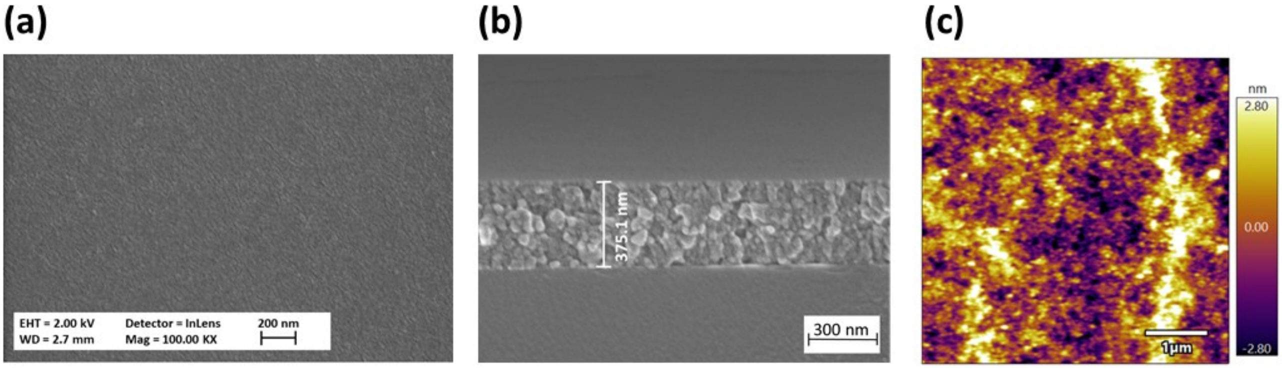

Fig. SI-3 Scanning electron microscopy (SEM) (a), cross-sectional SEM (b) and atomic force microscopy (AFM) (c) images of TiO_2 film.

4. Quantum efficiency calculations

$$QE = \frac{Number\ of\ degraded\ molecules}{Number\ of\ incident\ photons}$$

$$Number\ of\ degraded\ molecules\ per\ second = \frac{G * A * r_o}{V_M}$$

Where G – Gas flow rate: G=0.5 L/min=0.0083 L/s

A – Avogadro number: $A= 6.02 \cdot 10^{23}$

r_o– Initial reaction rate: $r_o = -\frac{dC}{dt}$ For example, at heptane initial concentration 5 ppm r_o= 0.34 ppm per 1 s = $0.34 \cdot 10^{-6}$ mol / mol air

V_M – Molar volume of ideal gas: V_M= 22.4 L/mol air

$$Number\ of\ degraded\ molecules\ per\ second = \frac{0.0083 \cdot 6.02 \cdot 10^{23} \cdot 0.34 \cdot 10^{-6}}{22.4} = 7.58 \cdot 10^{13}\ 1/s$$

Number of incident photons per second:

$$Number\ of\ incident\ photons = \frac{Energy\ of\ the\ lamp}{Energy\ of\ photons} = \frac{0.42}{5.442 \cdot 10^{-19}} = 7.72 \cdot 10^{17}\ 1/s$$

Energy of the lamp = Irradiated surface area · Irradiance · Time = $120 \cdot 3.5 \cdot 10^{-3} \cdot 1 = 0.42$ J/s

Where irradiated surface area for one section of the reactor is 120 cm^2

Irradiance of the UV-A lamp is 3.5 mW/cm^2 = · $3.5 \cdot 10^{-3}$ W/cm^2

Photon energy: $E= \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34}\ J \cdot s \cdot 299792458\ m/s}{3.65 \cdot 10^{-7}\ m} = 5.442 \cdot 10^{-19}$ J,

Where h – is the Planck constant: $h=6.626 \cdot 10^{-34}$ J·s

c – is the speed of the light in vacuum: c=299792458 m/s

λ – is the photon's wavelength for UV-A lamps: $\lambda=3.65 \cdot 10^{-7}$ m

Quantum efficiency for 5 ppm heptane degradation at air flow rate 0.5 L/min and RH 6%

$$QE = \frac{7.58 \cdot 10^{13}}{7.72 \cdot 10^{17}} = 9.82 \cdot 10^{-5} \text{ molecules / photons}$$

5. Langmuir-Hinshelwood reaction kinetics

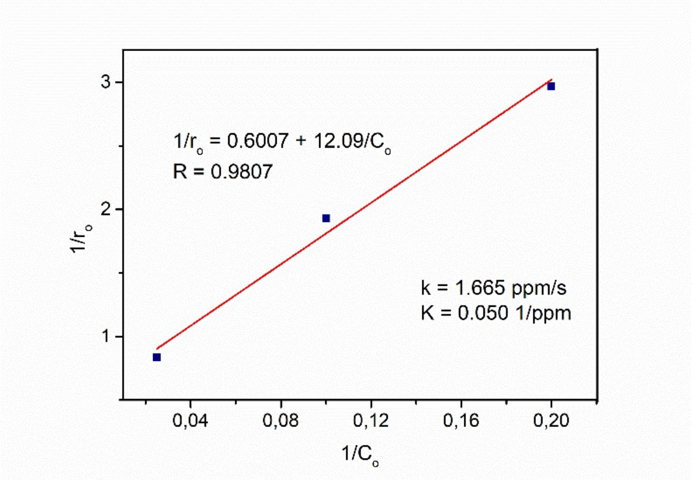

Fig. SI-4 Langmuir-Hinshelwood kinetic plot for the determination of heptane degradation reaction rate and adsorption constants.

6. Reynolds number calculations

To determine the flow pattern Reynolds number calculations were performed.

When Re < 2300 flow is laminar.

When 2300 < Re < 4000 transient.

When Re > 4000 turbulent.

Reynolds number was found:

$$Re = \frac{\rho \, v \, L}{\mu} \qquad \text{S1}$$

Where ρ – density of air, kg/m^3 for air at T = 40°C $\rho = 1.127$ kg/m^3

v – flow speed of air, m/s

L – characteristic linear dimension of the reactor, m

μ - dynamic viscosity of air, Pa·s for air at T =4 0°C $\mu = 19.07 \cdot 10^{-6}$ Pa·s

$$L = \frac{4\,A_{cross}}{P}$$

Where A_{cross} – cross-section area

P – wetting perimeter

For used in the study reactor $A_{cross} = 4.32\ cm^2$ and $P = 10.16\ cm$

$$L = \frac{4\ \cdot\ 4.32}{10.16} = 1.7\ cm = 0.017\ m$$

<u>At air flow rate 0.5 L/min</u>:

$$v = \frac{air\ flow\ rate}{Across} = \frac{500\,\frac{cm^3}{min}}{4.32\ cm} = 115.74\,\frac{cm}{min} = 0.0193\,\frac{m}{s}$$

$$Re = \frac{1.127\ \cdot\ 0.0193\ \cdot 0.017}{19.07\ \cdot\ 10^{-6}} = 19.39$$

<u>At air flow rate 1 L/min:</u>

$$v = 0.0386\,\frac{m}{s}$$

$$Re = \frac{1.127\ \cdot\ 0.0386\ \cdot 0.017}{19.07\ \cdot\ 10^{-6}} = 38.78$$

<u>At air flow rate 1.5 L/min:</u>

$$v = 0.0578\,\frac{m}{s}$$

$$Re = \frac{1.127\ \cdot\ 0.0578 \cdot 0.017}{19.07\ \cdot\ 10^{-6}} = 58.14$$

<u>At air flow rate 2 L/min:</u>

$$v = 0.0772\,\frac{m}{s}$$

$$Re = \frac{1.127\ \cdot\ 0.0772 \cdot 0.017}{19.07\ \cdot\ 10^{-6}} = 77.52$$

<u>At air flow rate 2.5 L/min:</u>

$$v = 0.0965\,\frac{m}{s}$$

$$Re = \frac{1.127\ \cdot\ 0.0965 \cdot 0.017}{19.07\ \cdot\ 10^{-6}} = 96.90$$

7. The comparative table of photocatalytic oxidation of heptane and toluene on TiO_2 thin films

Table SI-1. The comparative table of photocatalytic oxidation of heptane and toluene on TiO_2 thin films prepared in current study and on other thin films available from the scientific literature.

Photocatalyst	***Thickness***	***Pollutant***	***Initial Concentration***	***Reactor***	***Catalyst surface area***	***Light source***	***Oxidation conditions***	***Conversion/ degradation rate***	***Reaction time***	***Ref***
Spray pyrolysis-synthesized TiO_2 thin film	370 nm	Heptane	10 ppm	Continuous flow reactor	360 cm^2	UV-A, 3.5 mW/cm^2	Air flow rate 0.5 L/min, RH 6%	100%	46.8 s	This study
Spray pyrolysis-synthesized TiO_2 thin film	370 nm	Heptane	10 ppm	Continuous flow reactor	600 cm^2	UV-A, 3.5 mW/cm^2	Air flow rate 0.5 L/min, RH 40%	91%	78 s	This study
Spray pyrolysis-synthesized TiO_2 thin film	370 nm	Heptane	10 ppm	Continuous flow reactor	600 cm^2	VIS, 3.3 mW/cm^2	Air flow rate 0.5 L/min, RH 6%	44%	78 s	This study
Spray pyrolysis-synthesized TiO_2 thin film	200 nm	Heptane	10 ppm	Continuous flow reactor	600 cm^2	UV-A, 3.5 mW/cm^2	Air flow rate 0.5 L/min, RH 6%	48%	78 s	[S2]
Spray pyrolysis-synthesized TiO_2 thin film	200 nm	Heptane	10 ppm	Continuous flow reactor	600 cm^2	UV-A, 3.5 mW/cm^2	Air flow rate 0.5 L/min, RH 40%	20%	78 s	[S2]
Spray pyrolysis-	370 nm	Toluene	10 ppm	Continuous	600 cm^2	UV-A, 3.5	Air flow rate	55%	78 s	This

synthesized TiO_2 thin film				flow reactor		mW/cm^2	0.5 L/min, RH 6%			study
Spray pyrolysis-synthesized TiO_2 thin film	370 nm	Toluene	10 ppm	Continuous flow reactor	600 cm^2	UV-A, 3.5 mW/cm^2	Air flow rate 0.5 L/min, RH 40%	51%	78 s	This study
Spray pyrolysis-synthesized TiO_2 thin film	370 nm	Toluene	10 ppm	Continuous flow reactor	600 cm^2	VIS, 3.3 mW/cm^2	Air flow rate 0.5 L/min, RH 6%	6%	78 s	This study
Sol-gel dip-coated TiO_2 thin film	470 nm	Toluene	192 ppm	Batch 0.55 L recirculating reactor	20 cm^2	UV-A, 4W	Recirculation flow rate 0.075 L/min, Dry air	60%	2 h	[S3]
Sol-gel dip-coated $Ti_{0.90}Zr_{0.10}O_2$ thin film	540 nm	Toluene	192 ppm	Batch 0.55 L recirculating reactor	20 cm^2	UV-A, 4W	Recirculation flow rate 0.075 L/min, Dry air	70%	2 h	[S3]
Sol-gel dip-coated 10% ZrO_2/TiO_2 thin film	410 nm	Toluene	192 ppm	Batch 0.55 L recirculating reactor	20 cm^2	UV-A, 4W	Recirculation flow rate 0.075 L/min, Dry air	50%	2 h	[S3]
Sol-gel dip-coated TiO_2 thin film	Not reported	Toluene	50-180 ppm	Batch 1.1 L reactor	68 cm^2	UV-LED, 10 mW/cm^2	Dry air	1.83×10^{-4} mol m^{-3} min^{-1}	1 h	[S4]
Sol-gel dip-coated 0.7% Fe-TiO_2 thin film	Not measured	Toluene	50-180 ppm	Batch 1.1 L reactor	68 cm^2	UV-LED, 10 mW/cm^2	Dry air	2.57×10^{-4} mol m^{-3} min^{-1}	1 h	[S4]
Sol-gel dip-coated	0.9 µm	Toluene	1 ppm	Continuous	50 cm^2	UV-A, 1	Air flow rate	46%	0.2 s	[S5]

TiO$_2$ thin film				flow reactor		mW/cm^2	0.5 L/min, RH 50%			
Sol-gel dip coated TiO$_2$ thin film	350 nm	Toluene	155 ppb	Benchtop continuous flow reactor	1.2 cm^2	UV-C, 3.0 mW/cm^2	Air flow rate 0.5 L/min, dry air	78%	1 s	[S6]
Sol-gel dip coated TiO$_2$	1.3 µm	Toluene	0.5 ppm	Continuous flow tubular reactor	184 cm^2	UV-A, 10W	Air flow rate 0.2 L/min, dry air	95%	25 s	[S7]
Sol-gel dip coated porphyrin-sensitized TiO$_2$ thin films	1.3 µm	Toluene	0.5 ppm	Continuous flow tubular reactor	184 cm^2	VIS, 10W	Air flow rate 0.2 L/min, dry air	15%	25 s	[S7]
E-beam evaporated TiO$_2$ thin films	20 nm	Toluene	5 ppm	Batch 0.314 L reactor	18.75 cm^2	UV-A, 0.304 W/cm^2	Water vapour atmosphere	40%	30 min	[S8]

8. Conversion of compounds in 9 ppm of mixture under different operating parameters

Table SI-2. Conversion of compounds in 9 ppm of mixture heptane, acetone and acetaldehyde (3 ppm each compound) under different operating parameters at different photocatalytic surface areas. ***AD*** – acetaldehyde, ***AC*** – acetone and ***HEP*** - heptane

Operating parameters			*Conversion (%)*														
Air flow rate (L/min)	*Relative humidity (%)*	*Irradiation*	*Surface of catalyst 120 cm^2*			*Surface of catalyst 240 cm^2*			*Surface of catalyst 360 cm^2*			*Surface of catalyst 480 cm^2*			*Surface of catalyst 600 cm^2*		
			AD	*AC*	*HEP*	*AD*	*AC*	*HEP*	*AD*	*AC*	*HEP*	*AD*	*AC*	*HEP*	*AD*	*AC*	*HEP*
0.5	6	UV-A	100	93	77	100	99	92	100	100	100	100	100	100	100	100	100
1	6	UV-A	63	63	56	86	84	81	92	91	90	100	100	100	100	100	100
0.5	40	UV-A	46	31	30	65	55	48	83	76	67	100	87	77	100	100	82
0.5	6	VIS	39	33	15	51	53	26	71	71	40	87	85	59	100	100	78

Table SI-3. Conversion of compounds in 9 ppm of mixture toluene, acetone and acetaldehyde (3 ppm each compound) under different operating parameters at different photocatalytic surface areas. ***AD –*** acetaldehyde, ***AC*** – acetone and ***TOL*** – toluene

Operating parameters			*Conversion (%)*														
Air flow rate (L/min)	*Relative humidity (%)*	*Irradiation*	*Surface of catalyst 120 cm^2*			*Surface of catalyst 240 cm^2*			*Surface of catalyst 360 cm^2*			*Surface of catalyst 480 cm^2*			*Surface of catalyst 600 cm^2*		
			AD	*AC*	*TOL*	*AD*	*AC*	*TOL*	*AD*	*AC*	*TOL*	*AD*	*AC*	*TOL*	*AD*	*AC*	*TOL*
0.5	6	UV-A	78	70	71	100	100	97	100	100	100	100	100	100	100	100	100
1	6	UV-A	40	40	48	61	60	67	82	81	85	91	86	100	100	93	100
0.5	40	UV-A	40	32	37	65	51	65	78	68	70	88	81	78	100	100	90
0.5	6	VIS	20	24	16	21	25	28	33	34	28	36	38	29	52	53	31

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