Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information (ESI) for:

Covalent graphite modification by low-temperature photocatalytic oxidation using titanium dioxide thin film prepared by atomic layer deposition

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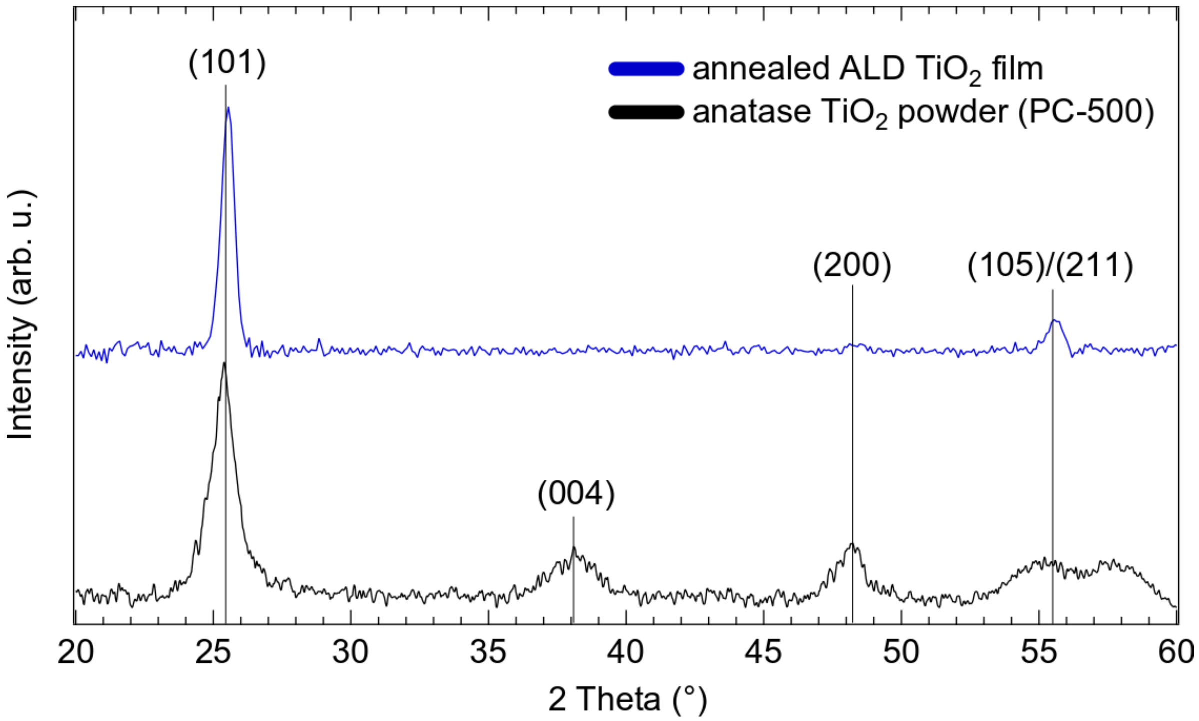


Fig. S1. XRD patterns of annealed TiO_2 thin film prepared by ALD (in blue) and reference anatase TiO_2 powder (≥ 99.0 wt%, CristalACTIV™ PC-500) (in black). A 15 nm TiO_2 film was deposited on a Si(100) substrate using the TDMAT/H_2O ALD process (200 cycles) described in the manuscript. Annealing of the ALD TiO_2 film was performed in air at 550 °C for 3 h (heating rate of 1 °C/min). The crystallographic composition of the annealed thin film is compared with reference anatase TiO_2 particles. All XRD data were normalized and background subtracted.

Table S1 H_2O vapor concentrations used in reactor gas mixture by heating a water saturator to different temperatures

Saturator temperature [°C]	**H_2O vapor concentration [vol%]**
21	1.8
35	4.2
40	5.5
45	7.3
50	9.6

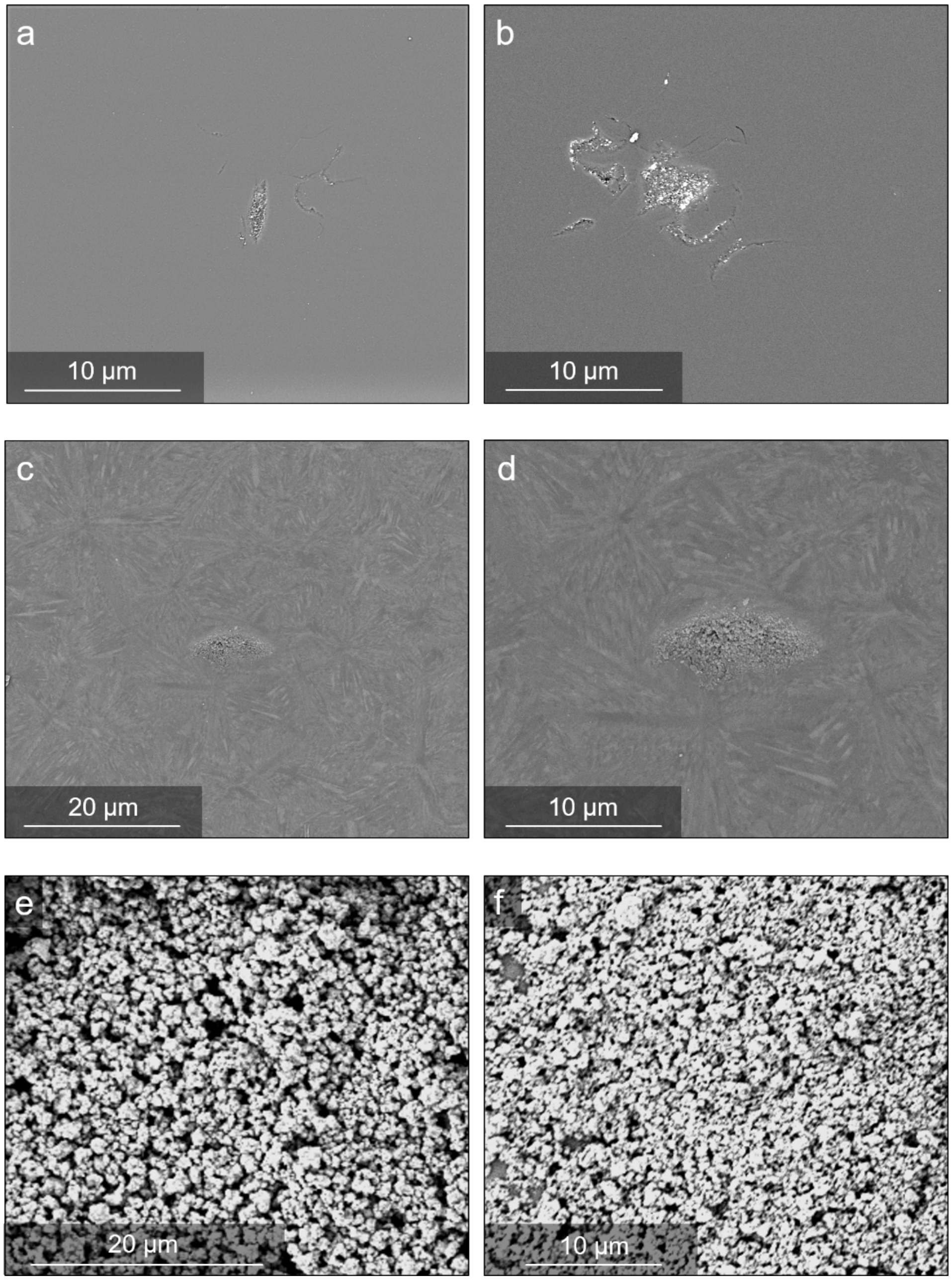


Fig. S2 HRSEM images of ALD TiO_2 films subjected to 50 deposition cycles (2.9 nm thickness) and 400 deposition cycles (22.5 nm thickness), coated on a quartz glass support plate, and powder TiO_2 layers. (a) 50-Cycled amorphous ALD TiO_2 film. (b) 50-Cycled anatase ALD TiO_2 film after calcination in air at 600 °C for 5 h (heating at 1 °C min^{-1}). (c and d) 400-Cycled anatase ALD TiO_2 film after identical calcination treatment. The micrographs show little presence of surface cracks and discontinuities in the conformal TiO_2 thin films. Increased surface roughness upon calcination and transformation to the crystalline phase is attributed to local sintering of small TiO_2 particles due to the high-temperature treatment. (e and f) Powder anatase TiO_2 layers deposited on support plate from TiO_2-isopropanol suspension.

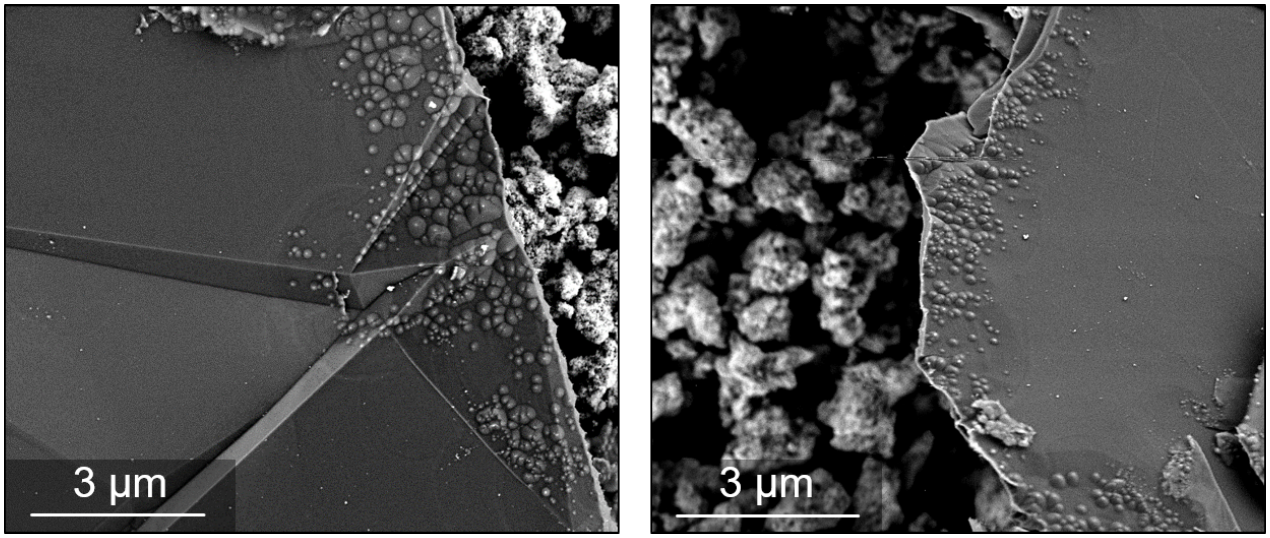


Fig. S3 HRSEM images of natural graphite photocatalytically oxidized in contact mode (front UV irradiation) under 30 vol% O_2 and 1.8 vol% H_2O vapor for 96 h at 140 °C. The graphite surface areas in closest contact with TiO_2 are more oxidized than the basal planes.

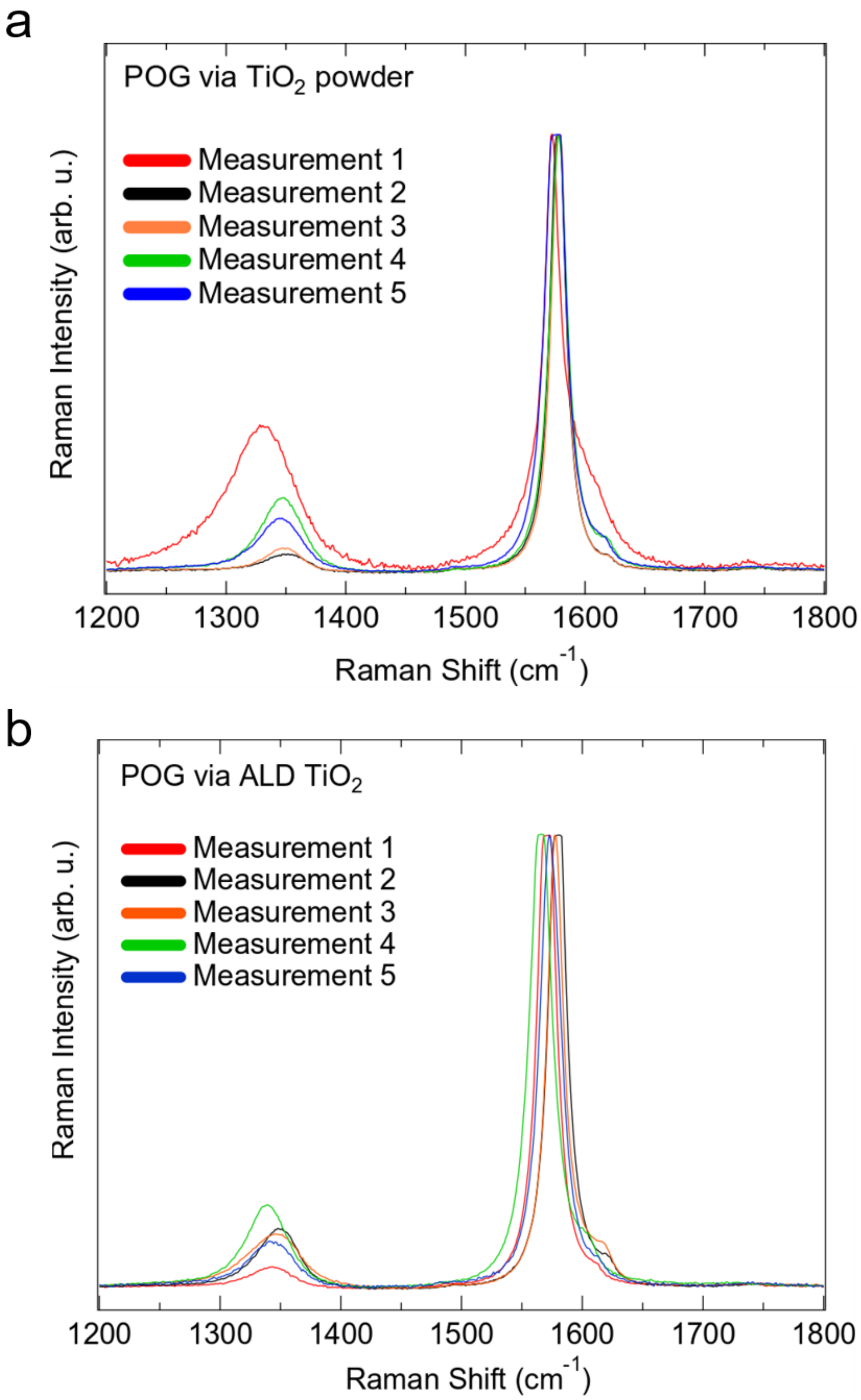
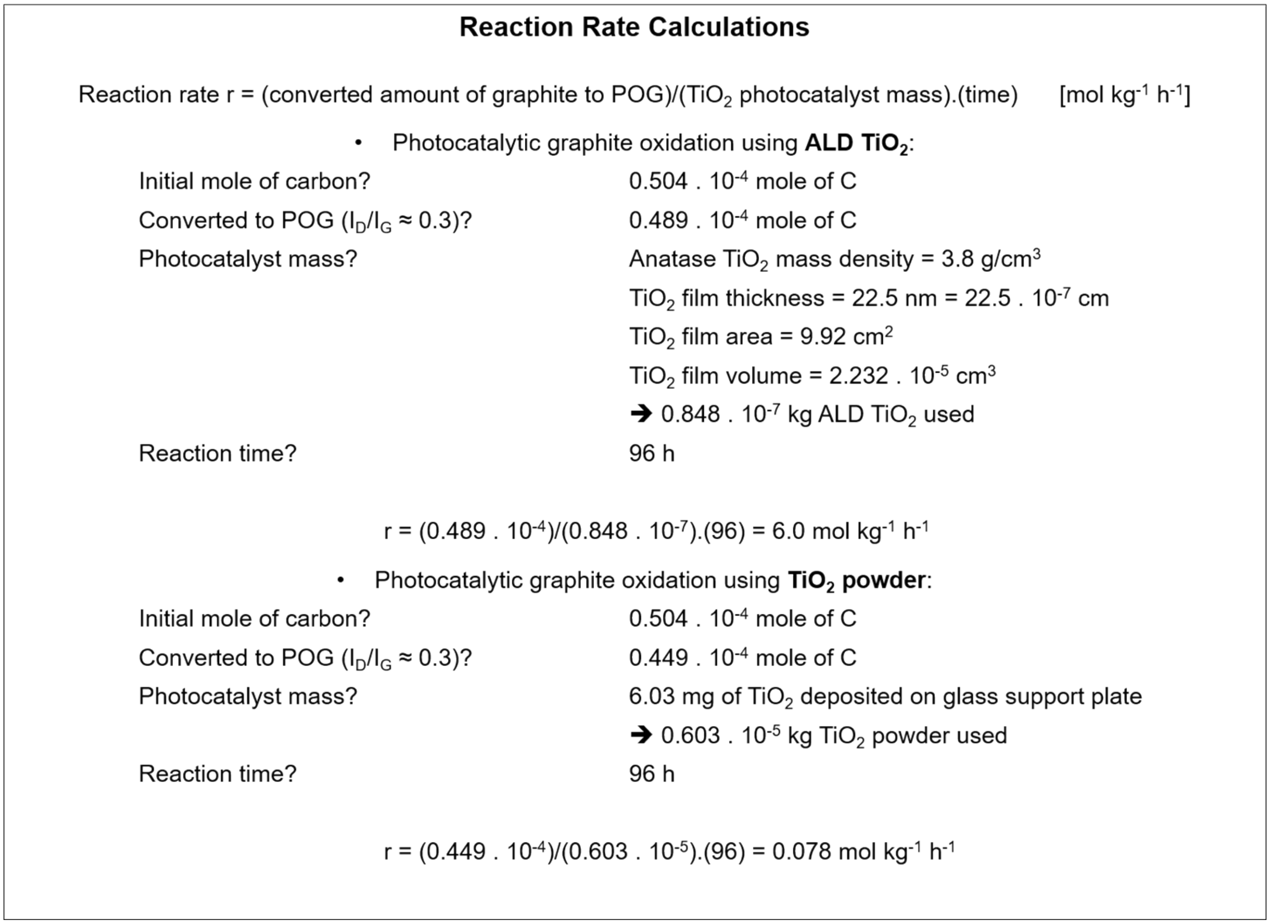


Fig. S4 Raman spectra measured at 5 random locations on the POG product surface following remote oxidation in 70 vol% O_2 and 4.2 vol% H_2O vapor for 96 h at 70 °C. (a) Photo-oxidation using TiO_2 powder photocatalyst and (b) photo-oxidation using ALD TiO_2 thin film photocatalyst (22.5 nm thick).

Table S2 Averaged Raman spectroscopic parameters (5 measurements/sample) and product yields of natural graphite photo-oxidized in remote mode for 74 h at 70 °C using varying H_2O vapor concentrations, 70 vol% O_2 and TiO_2 powder photocatalyst

H_2O vapor concentration [vol%]	**D band FWHM [cm^{-1}]**	**G band FWHM [cm^{-1}]**	**I_D/I_G**	**Carbon recovery [%]**
1.8	42 ± 8	17 ± 2	0.09 ± 0.01	73
4.2	45 ± 9	17 ± 0.4	0.09 ± 0.003	93
5.5	44 ± 3	19 ± 2	0.10 ± 0.06	92
7.3	43 ± 8	21 ± 6	0.18 ± 0.07	89



Reaction Rate Calculations

Reaction rate r = (converted amount of graphite to POG)/(TiO_2 photocatalyst mass).(time) [mol kg^{-1} h^{-1}]

- Photocatalytic graphite oxidation using **ALD TiO_2**:

Initial mole of carbon?	$0.504 \cdot 10^{-4}$ mole of C
Converted to POG ($I_D/I_G \approx 0.3$)?	$0.489 \cdot 10^{-4}$ mole of C
Photocatalyst mass?	Anatase TiO_2 mass density = 3.8 g/cm^3
	TiO_2 film thickness = 22.5 nm = $22.5 \cdot 10^{-7}$ cm
	TiO_2 film area = 9.92 cm^2
	TiO_2 film volume = $2.232 \cdot 10^{-5}$ cm^3
	➔ $0.848 \cdot 10^{-7}$ kg ALD TiO_2 used
Reaction time?	96 h

$$r = (0.489 \cdot 10^{-4})/(0.848 \cdot 10^{-7}).(96) = 6.0 \text{ mol kg}^{-1} \text{ h}^{-1}$$

- Photocatalytic graphite oxidation using **TiO_2 powder**:

Initial mole of carbon?	$0.504 \cdot 10^{-4}$ mole of C
Converted to POG ($I_D/I_G \approx 0.3$)?	$0.449 \cdot 10^{-4}$ mole of C
Photocatalyst mass?	6.03 mg of TiO_2 deposited on glass support plate
	➔ $0.603 \cdot 10^{-5}$ kg TiO_2 powder used
Reaction time?	96 h

$$r = (0.449 \cdot 10^{-4})/(0.603 \cdot 10^{-5}).(96) = 0.078 \text{ mol kg}^{-1} \text{ h}^{-1}$$

Fig. S5 Reaction rate calculations of remote mode photocatalytic graphite oxidation to POG with moderate oxidation degree ($I_D/I_G \approx 0.3$) using different TiO_2 photocatalysts under 70 vol% O_2 and 4.2 vol% H_2O vapor for 96 h at 70 °C.

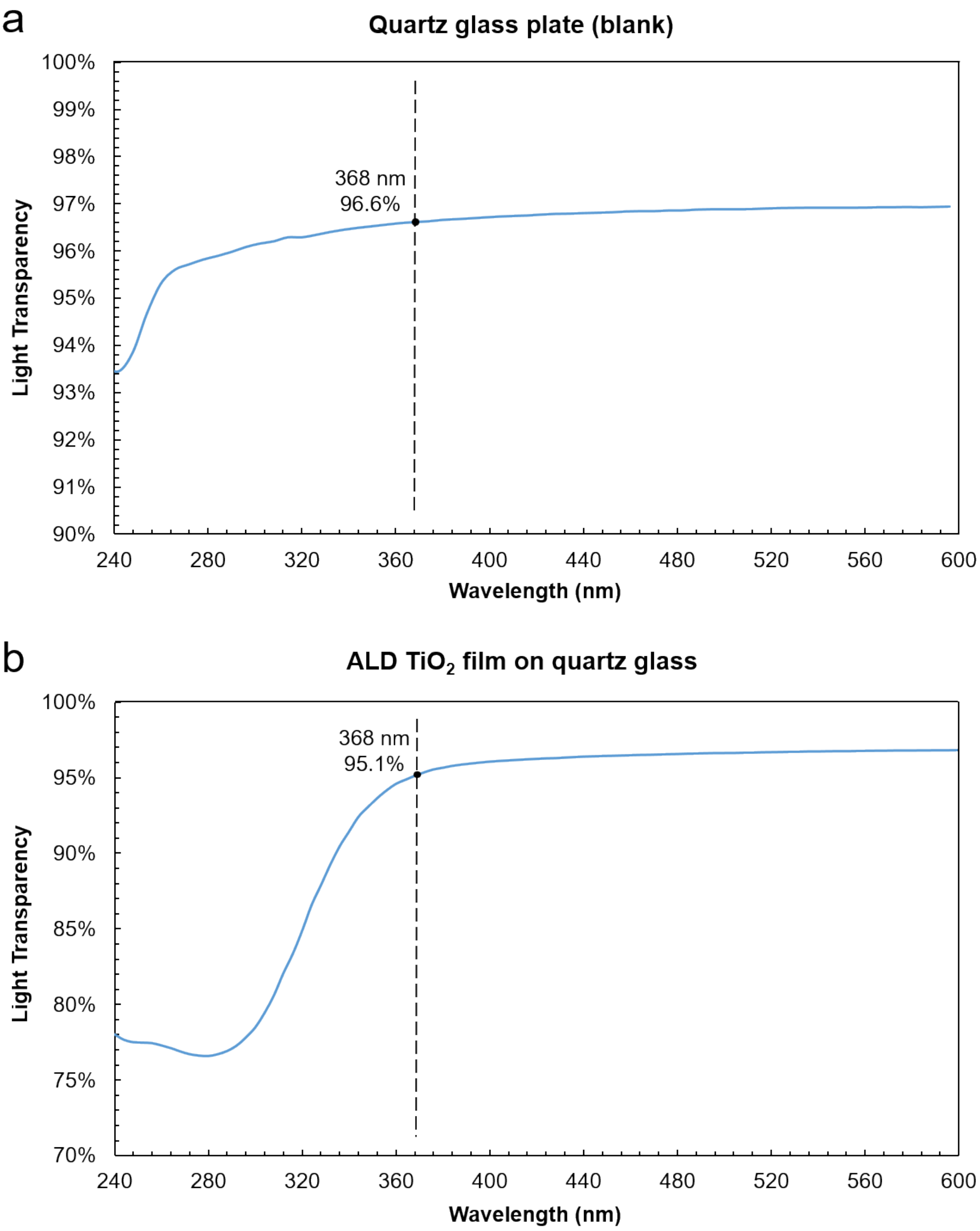
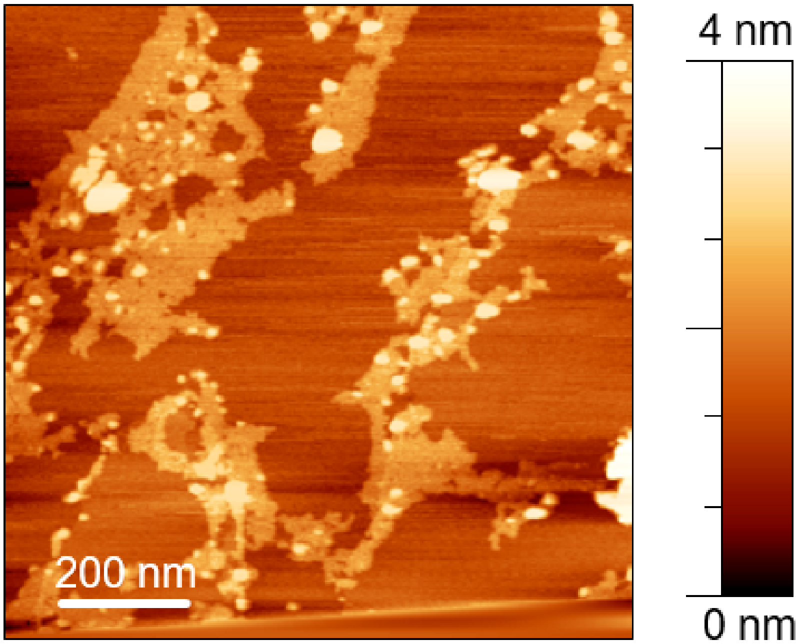


Fig. S6 Transparency measurements which show the transmission of light within a wavelength range 240-600 nm. (a) Quartz glass support plate and (b) 22.5 nm thick ALD TiO_2 film supported on quartz glass plate.



RMS roughness	0.5 nm
Minimum value	0 nm
Maximum value	4.1 nm
Roughness average	0.4 nm
Analyzed surface area	1.0 µm^2

Fig. S7 AFM topography image and roughness analysis results of HOPG photocatalytically oxidized in remote mode using 80 vol% O_2 and 1.8 vol% H_2O vapor for 120 h at 100 °C in presence of TiO_2 thin film.

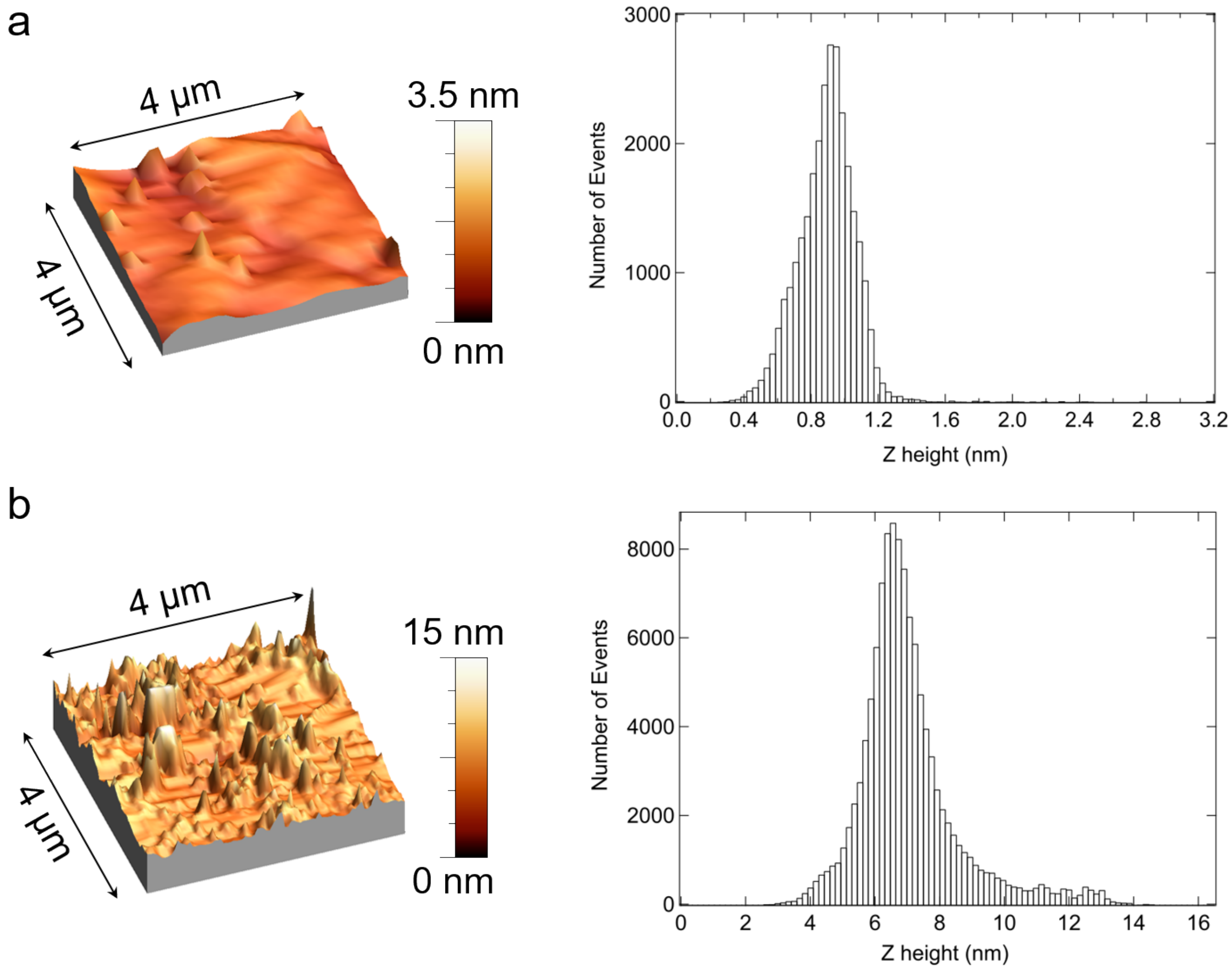


Fig. S8 AFM 3D profiles and height distribution profiles of 16 µm^2 HOPG surface areas. (a) Blank sample exposed to the gas mixture and UV illumination for 120 h at 70 °C in absence of ALD TiO_2 photocatalyst and (b) POG sample prepared in remote mode in 80 vol% O_2 and 5.5 vol% H_2O vapor for 120 h at 70 °C in presence of 22.5 nm ALD TiO_2 film.