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Electronic Supplementary Material

Mesocrystalline anatase nanoparticles synthesized by a simple hydrothermal approach with enhanced light harvesting for gas-phase reaction

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MATERIALS AND METHODS

Techniques of characterization

X-ray diffraction (XRD) analysis (model D-8 Advance, Bruker) was performed using CuK$_\alpha$ radiation. X-ray diffraction (XRD) analysis (model D-8 Advance, Bruker) was performed using CuK$_\alpha$ radiation. Crystalline structure was refined with the Rietveld technique, by using FulProf software, on diffractograms acquired from 5 to 120° 2θ with a step size of 0.02° 2θ and an accumulated counting time of 2s. The refinement of anatase phase was started using the I4$_1$/amd space group and structure parameters derived by Li et al [1]. The pseudo-Voight function was used for modelling diffraction profiles. Peaks below 35° (2θ) were corrected for asymmetry effects. In the final refinement the following parameters were refined: a scale factor; 2θ zero; background parameters; unit cell parameters; peak profile parameters using a pseudo-Voight function; peak asymmetry; FWHW; Lorentzian ratio (η); asymmetry parameter; positional z parameter of O; overall isotropic temperature factor; and occupancy parameter.

The crystallite size of the as-prepared and annealed at 350 °C for 30 min (A and A350, respectively) materials was determined through the analysis of XRD data by Scherrer´s method, using LaB$_6$ to evaluate the instrumental XRD line broadening.

Raman spectra of samples were obtained by means of a Raman spectrometer (Model XploRA, Horiba) with 785 nm laser. The samples were measured in backscattering geometry at room temperature. A 100x microscope objective was used to focus the excitation laser on the sample and collect the scattered light to the spectrometer. More than 3 different areas were analyzed per sample, to obtain representative results. Exposure time was 10 s and number of acquisitions was 5. Data acquisition was carried out with the LabSpec 6 software packages from Horiba Scientific.

X-ray photoelectron spectra (XPS) were recorded using non-monochromated MgK radiation ($h\nu$= 1253.6 eV) and a hemi-spherical analyser operating at a constant pass energy of 29.35 eV (Physical Electronics PHI 5700 spectrometer) with the X-ray generator operating at 15 kV and 300

W. The pressure in the analysis chamber was about 10^{-7} Pa. Binding energies were corrected against that for C 1s peak of adventitious carbon fixed at 284.8 eV. The 1s peaks O and 2p of Ti were curve-fitted by the software MultiPak version 9.3 using a convolution of independent Gaussian and Lorentzian contributions (the so-called Voigt profile).

Probe NO (>99.9%, from Abello Linde S.A.) was carried out in an IR cell connected with a conventional outgassing/gas manipulation apparatus and spectra were recorded in a Nicolet Nexus 6700 spectrometer with MCT detector. For the study, 100 scans were registered in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and KBr beam splitters. The system was also composed of a vertical furnace that allowed the thermal treatment of the samples. The samples were pressed into 13 mm disks using a hydraulic press and placed in the sample holder of a quartz cell with KBr windows, permanently connected to a conventional vacuum line ($\approx 1\cdot 10^{-4}$ torr).

References

[1] Li, J.; Song, G.B.; Wang, M. L.; Zhang, B.S., Preparation and structure characters of nano-powder of $Ti_{1-x}Ce_xO_2$ system. *Chin. J. High Press. Phys.* **2006,** *20*, 211-216.

TABLES

Table S1. Particle size, surface area and photocatalytic efficiency for the removal of NO_X gases of different titania compounds.

Sample	Particle size (nm)	Surface Area ($m^2 \cdot g^{-1}$)	NO conversión (%)	NO_X conversion (%)	* Selectivity (%)
TiO_2 [a] N-TiO_2[a]	9 15	-- --	35 30	20 15	57 50
TiO_2 [b]	8	282.7	65	55	84
TiO_2/HT [c]	--	--	45	38	85
Fe-TiO_2 [d]	--	105.4	58	38	65
TiO_2/graphene [e]	10	142.7	53	45	85
Pt-TiO_2 [f]	9	112.7	25	--	66
WN-TiO_2 [g]	--	--	--	< 1.0	97
NF-TiO_2 film [h]		136	6.7	--	93

* Selectivity values were calculated from the cited articles by following the definition of MacPhee et al.[g] and using the equation (4).

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[f] Hu, Y.; Song, X.; Jiang S.; Wei, C., *Chem. Eng. J.*, **2015**, *274*, 102-112.

[g] Bloh, J. Z.; Folli, A.; Macphee, D. E., *RSC Adv.*, **2014**, *4*, 45726-45734.

[h] Katsanaki, A.V.; Kontos, A.G.; Magos, T.; Peláez, M.; Likodimos, V.; Pavlatou, E.A.; Dionysiou, D.D.; Falaras, P., *Appl. Catal. B: Environ.*, **2013**, *140-141*, 619-625.

Table S2. Crystallographic data and details of the Rietveld refinement, and crystallite sizes, of samples A and A350.

Samples	a=b / Å	c / Å	B overall (Å^2)	O (z position)	R_{wp}	R_{exp}	Chi2	Crystallite size
A	3.7934 (1)	9.5071 (2)	1.2488(1)	0.1653(1)	8.77	5.41	2.62	26.0(2)
A350	3.7844 (1)	9.5001 (2)	1.1716(1)	0.1664(1)	8.82	5.78	2.33	25.9(3)

Table S3. N and C chemical analysis for TiO_2 samples obtained at different temperatures and time of calcination

Samples	Temperature / °C	Time / h	N content / %	C content / %	C/N ratio
A *	140	72	0.32	1.9	5.93
A350	350	30	0.14	0.51	3.64
A400	400	4	0.20	0.16	0.82
A600	600	4	0.23	0.16	0.70
A800	800	1	0.06	0.007	0.11
P25	---	----	0.07	---	---

* Sample A was obtained by hydrothermal method. The series of samples correspond to that obtained after a specific calcination procedure.

Table S4. Surface area and pore volume for TiO_2 samples.

Samples	**A**	**A350**	**P25**
BET Surface Area / $m^2 \cdot g^{-1}$	74.9	63.6	52.4
Pore Volume / $cm^3 \cdot g^{-1}$	0.23	0.22	0.18

FIGURES

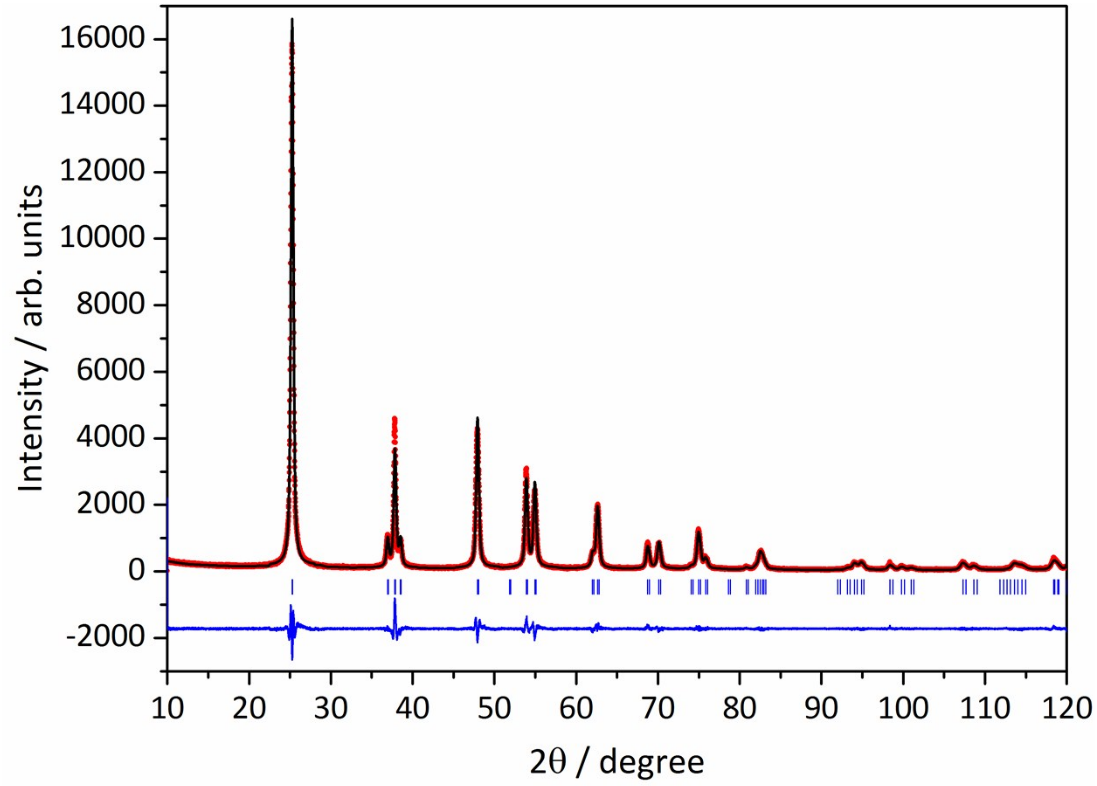

Figure S1. Rietveld plot of sample A showing the difference between the experimental and calculated diffracted intensities.

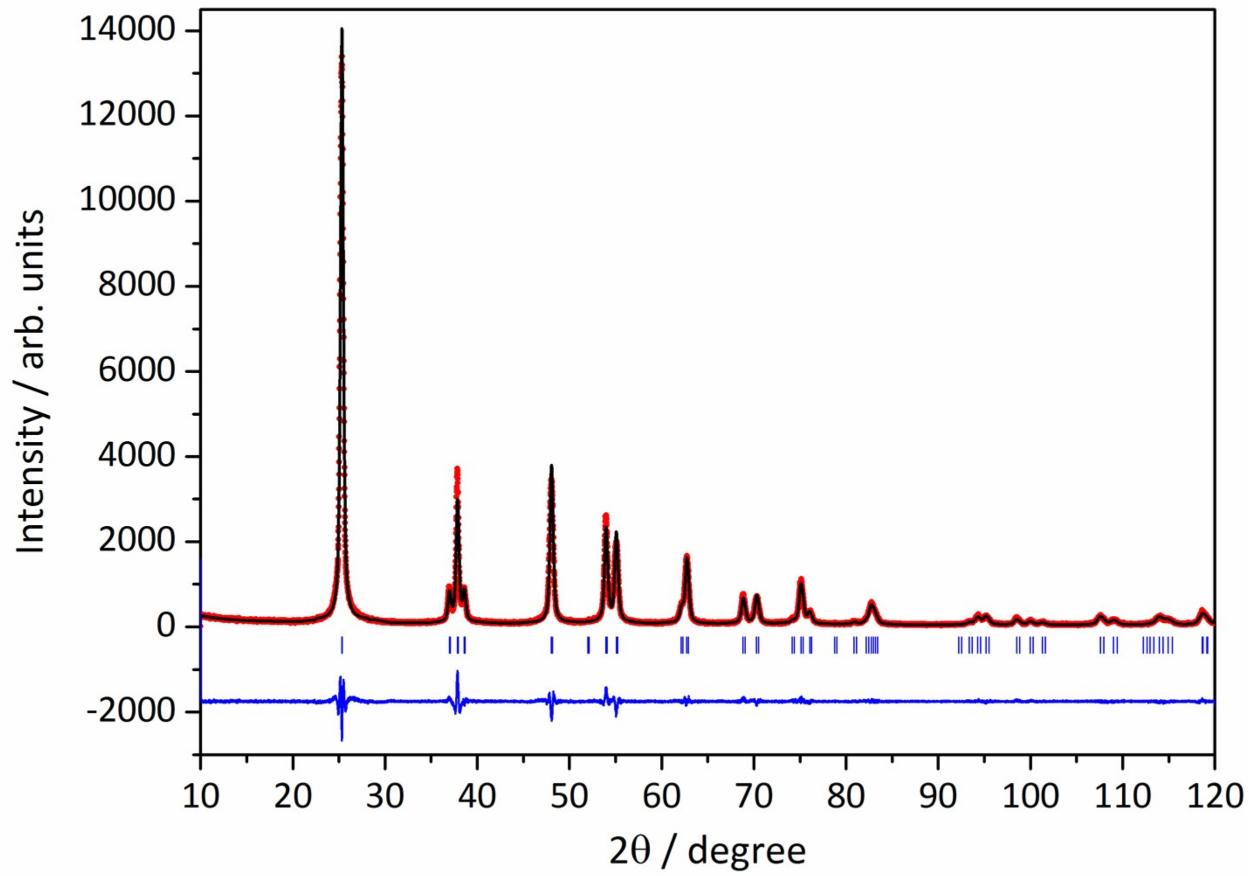

Figure S2. Rietveld plot of sample A350 showing the difference between the experimental and calculated diffracted intensities.

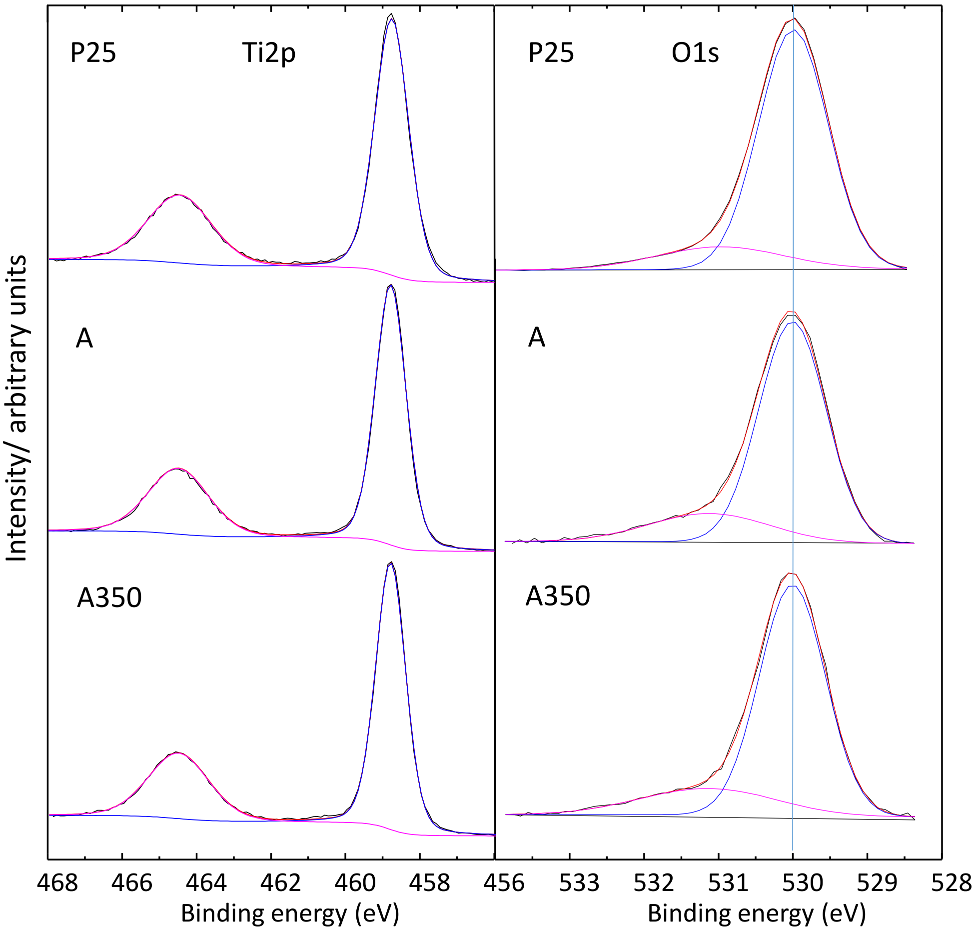

Figure S3. Ti 2p (left) and O 1s (right) XPS regions of the samples A, A350 and the reference P25.

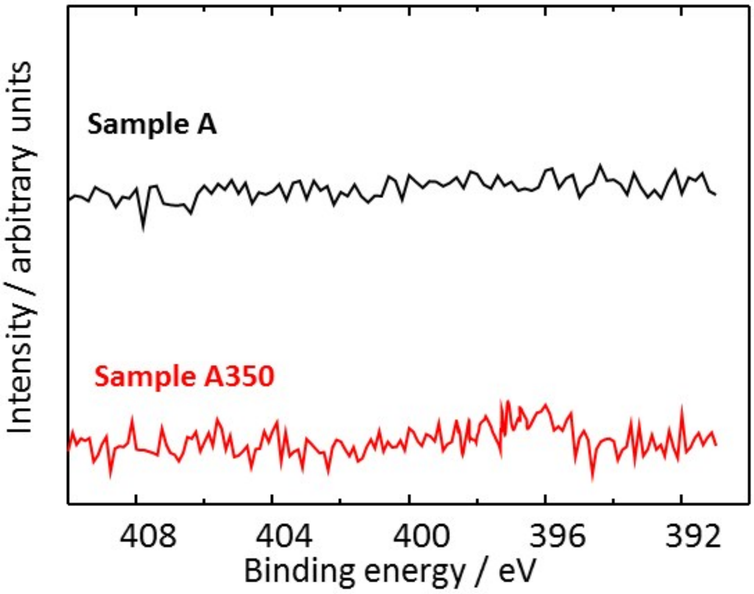

Figure S4. N 1s XPS region of the samples A and A350 .

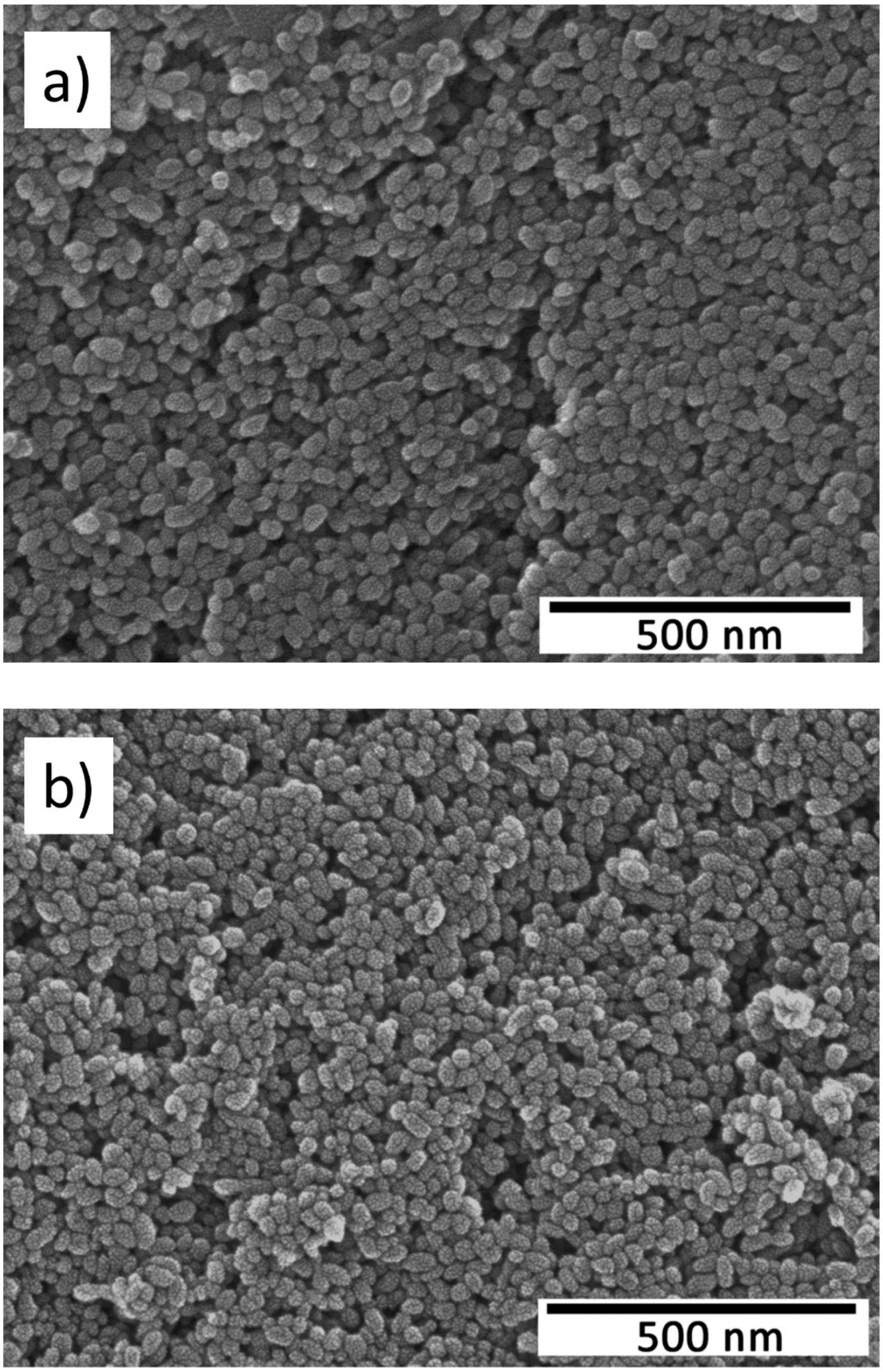

Figure S5. SEM micrographs of samples (a) A and (b) A350.

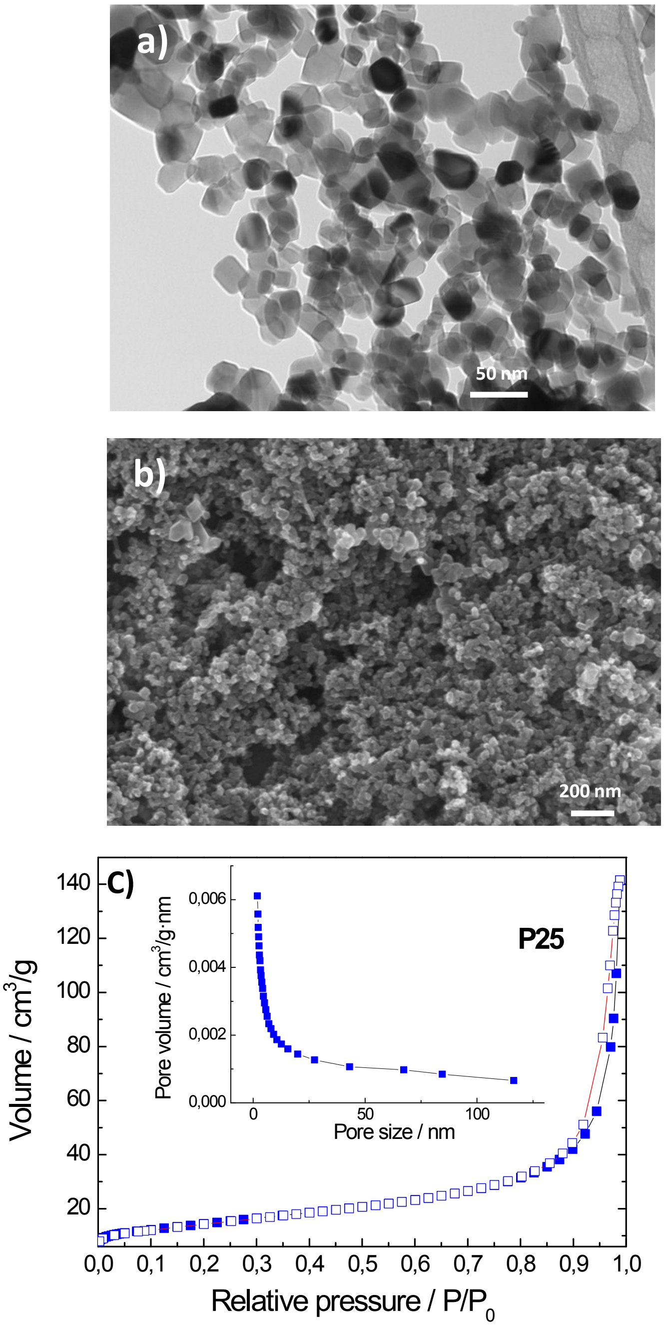

Figure S6: (a) TEM, (b) SEM micrographs and (c) N_2 adsorption-desorption isotherm of TiO_2 P25 sample.

The P25 nanoparticles, around 20-50 nm in size, are flat in surface and do not show any kind of voids, Fig S5 a. Moreover, a very narrow hysteresis loop at relative pressure higher than 0.9 is observed in the corresponding N_2 isotherm shown in Fig. S6c. It is to note the surface area of 52.4 m^2 g^{-1} measured for the reference P25 which is significantly lower to that of prepared titania samples, and being the pore size nanometric (< 5 nm): Table S4. As can be seen in Fig. 3b, the UV-Vis DR spectrum of the reference P25 displays a rather weak absorption over the range between 400 and 450 nm. As it is known this P25 contains around 25 % of rutile.

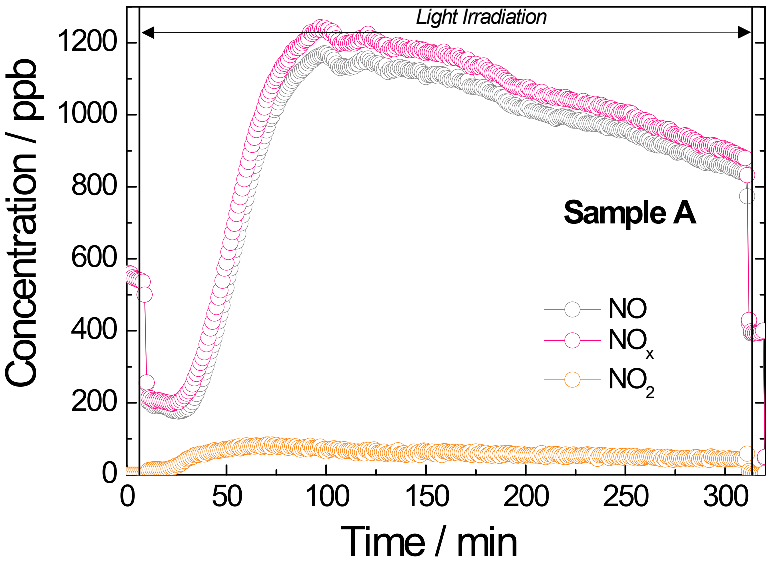

Fig. S7. Nitrogen oxides concentration profiles obtained during the photo-degradation of gaseous NO under UV-Vis irradiation on Sample A.

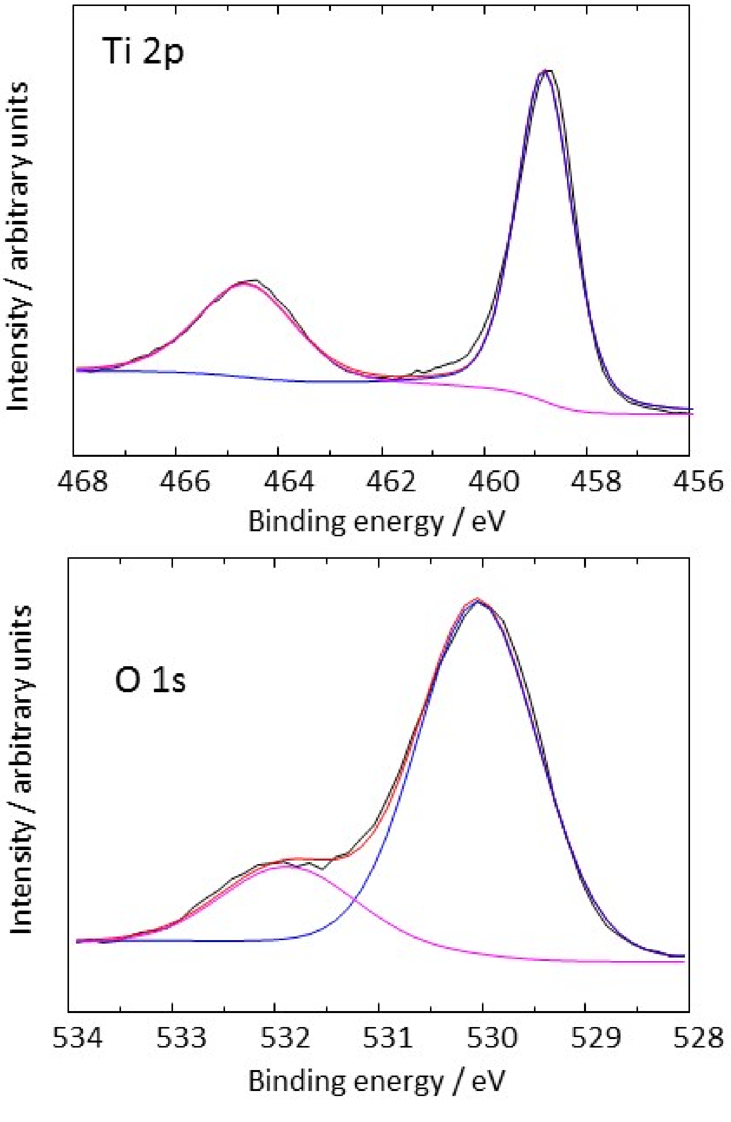

Figure S8. Ti 2p and O 1s XPS regions of the sample A350 subjected to washing process after the photocatalytic reaction.

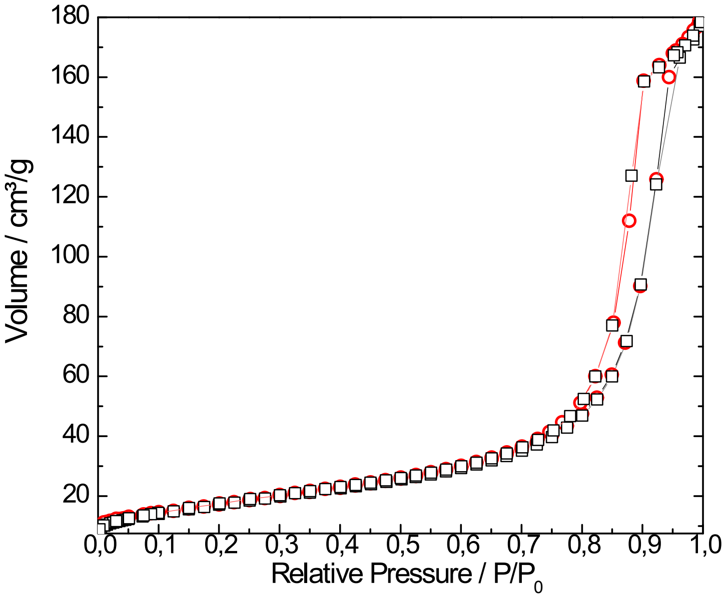

Figure S9. N_2 adsorption-desorption isotherm for sample A350 before (□) and after washing (o) process.

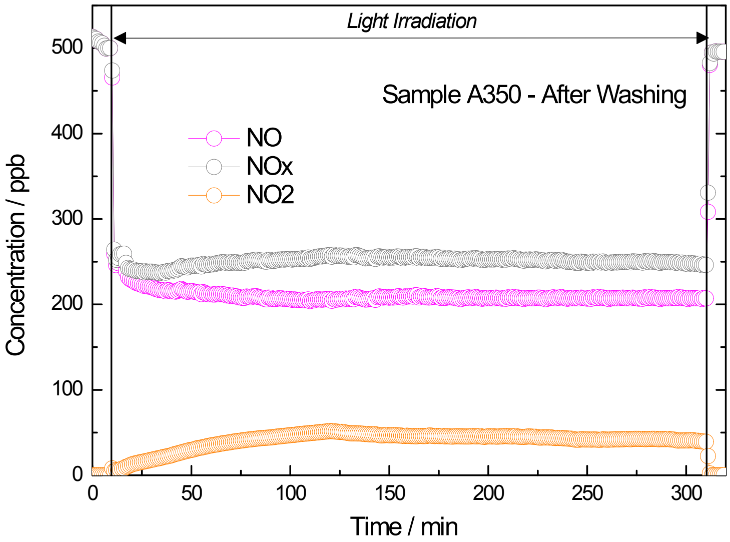

Fig. S10. Nitrogen oxides concentration profiles obtained during the photo-degradation of gaseous NO under UV-Vis irradiation on washed Sample A350 in a second photocatalytic cycle.

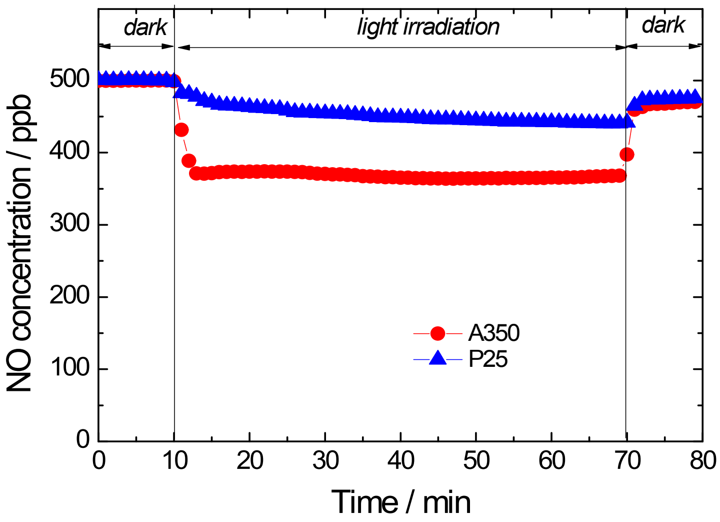

Figure S11. NO concentration profile recorded for A350 and P25 samples under Vis light irradiation (λ > 510 nm).

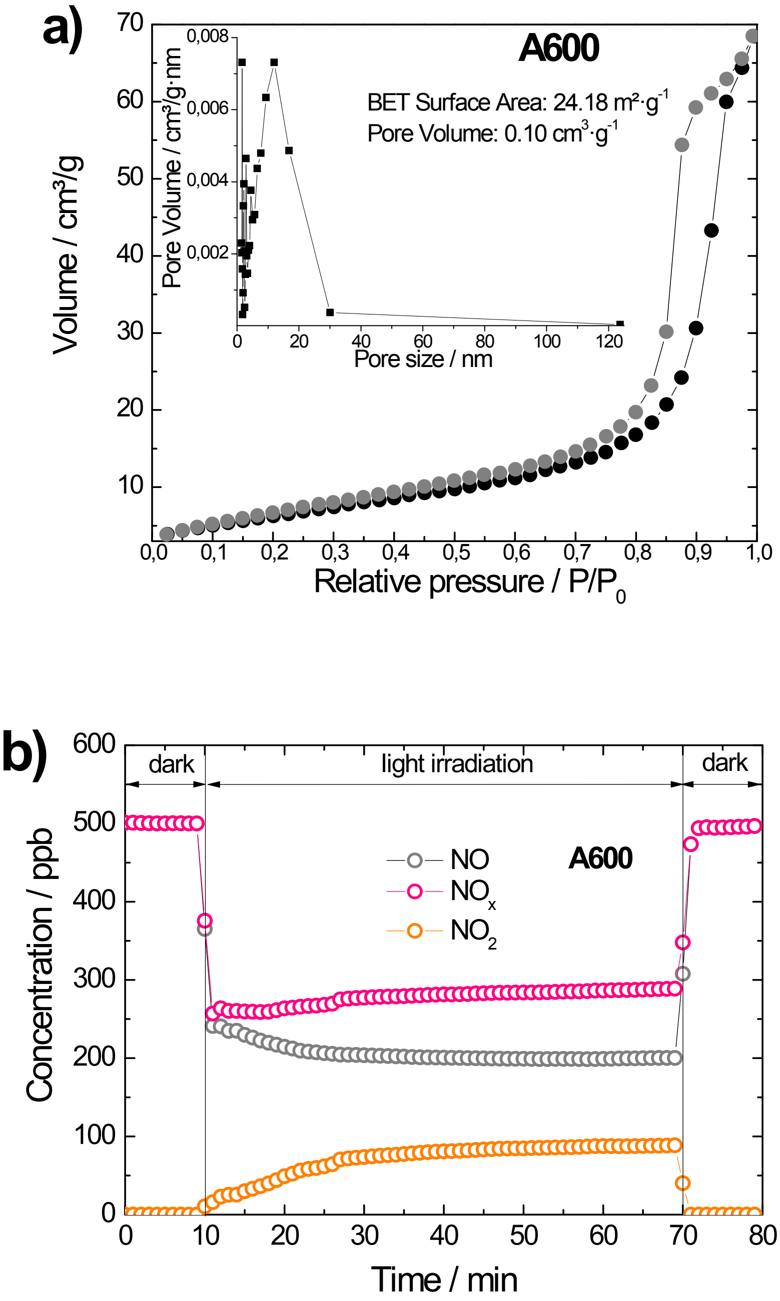

Figure S12. (a) N_2 adsorption-desorption isotherm for sample A600. (b) Nitrogen oxides concentration profiles obtained during the photo-degradation of gaseous NO under UV-Vis irradiation on Sample A600.