On the Role of the Nitrogen Source in Determining Structure and Morphology of N-doped Nanocrystalline TiO_2

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Supporting Information

Content index

Table S1. XRPD refinement statistical agreement parameters. See the main text for the meaning of the various nitrogen source labels.

Sample (N/Ti nominal ratio)	Source of N	wR_p	R_p	χ^2	$R(F^2)$
0.0	None	0.037	0.030	1.844	0.019
0.01	TNT	0.037	0.030	1.835	0.018
0.025	TNU	0.047	0.037	1.304	0.019
0.05	TNT	0.040	0.032	2.162	0.018
	TNN	0.041	0.032	2.146	0.022
0.1	TNT	0.031	0.025	1.791	0.015
	TNN	0.040	0.032	1.865	0.021
	TNU	0.038	0.029	1.535	0.011
0.2	TEA	0.034	0.027	2.099	0.018
	TNN	0.039	0.032	1.711	0.021
	TNU	0.038	0.029	1.465	0.010
0.4	TEA	0.032	0.025	1.880	0.013
	TNN	0.037	0.030	1.660	0.024
	TNU	0.036	0.027	1.476	0.009
0.5	TEA	0.035	0.028	1.867	0.017
	TNU	0.034	0.027	1.400	0.012

Figure S1. XPS scans of the characteristic spectral region of the N 1s peak at source energy of 500 eV for nominal N/Ti ratios of 0.0 (0.5) after 30' (20') sputtering by Ar^+ ions. Measured intensity (empty circles) is reported in arbitrary unit as a function of the binding energy (B.E.) in eV. Purple curve: background; yellow and violet curves: individual peak contributions; red curve: total sum signal. The least-squares fitting was performed through the XPSPeak41 program [R. W. M. Kwok, *XPS Peak Fitting Program for WIN95/98, XPSPEAK Version 4.1*, User manual, 1999].

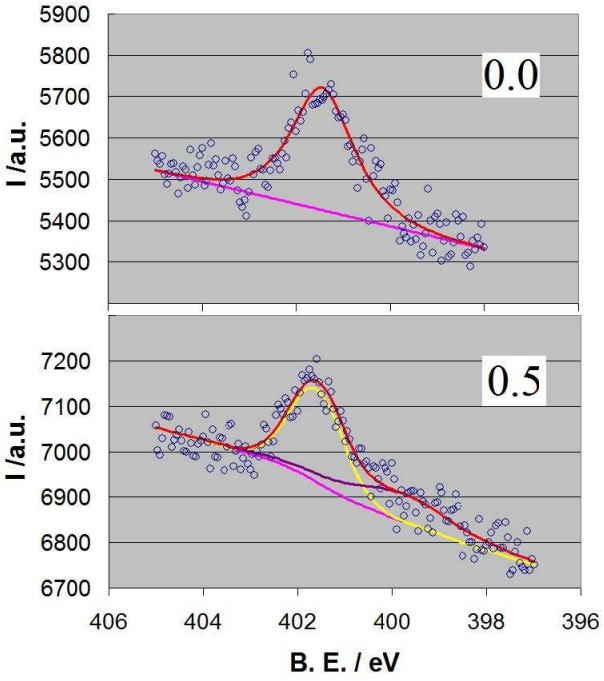


Table S2. Binding energies (B.E., eV) and area ratios (A[N_b(1s)]/A[Ti 2p]) of the N_b(1s) and total Ti(2p) characteristic lines in representative samples of the TNT series. For nitrogen, just the minority component at ≈399.8 eV was taken into account (see text). The integration was performed through the XPSPeak41 program [R. W. M. Kwok, *XPS Peak Fitting Program for WIN95/98, XPSPEAK Version 4.1*, User manual, 1999].

Nominal N/Ti	Surface N (1s) B.E.	N_b(1s) B.E.	Ti(2p) *J*=1/2B.E.	Ti(2p) *J*=3/2 B.E.	Ti shoulder [a] B.E.	A[N_b(1s)]/A[Ti 2p]
0.0	400.9	//[b]	465.2	460.1	459.7	0.000
0.1	401.6	399.8	466.0	460.3	459.9	0.021
0.5	401.4	399.9	465.9	460.1	459.7	0.024

[a] Broad shoulder at lower B.E. with respect to the Ti(IV) $2p_{3/2}$ peak (see text).
[b] No peaks are safely recognizable at lower B.E. with respect to the main surface N(1s) signal.

Figure S2. Same as Figure S1, for the Ti $2p_{3/2}$ spectral region (no sputtering).

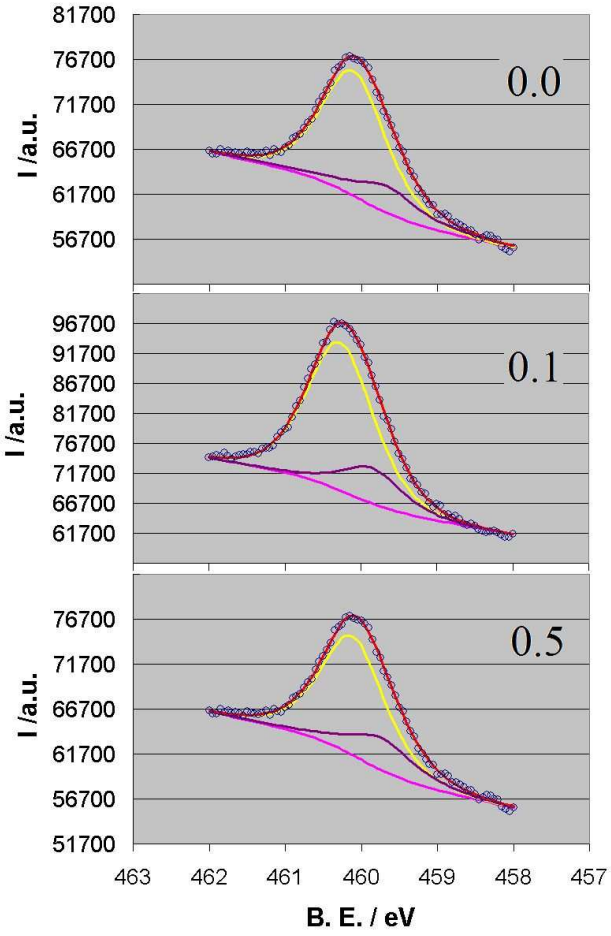


Figure S3. Same as Figure S1, for the $2p_{3/2}$ peak of Ti after sputtering with Ar^+ ions.

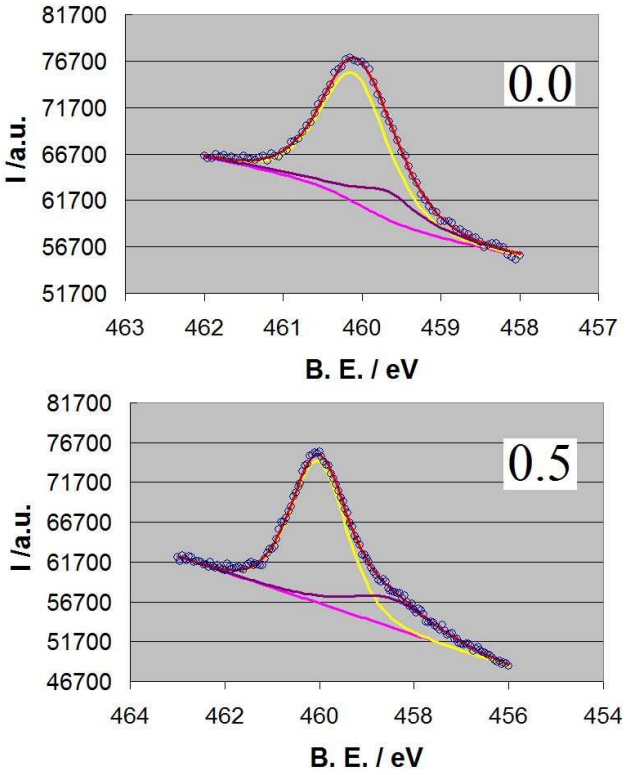
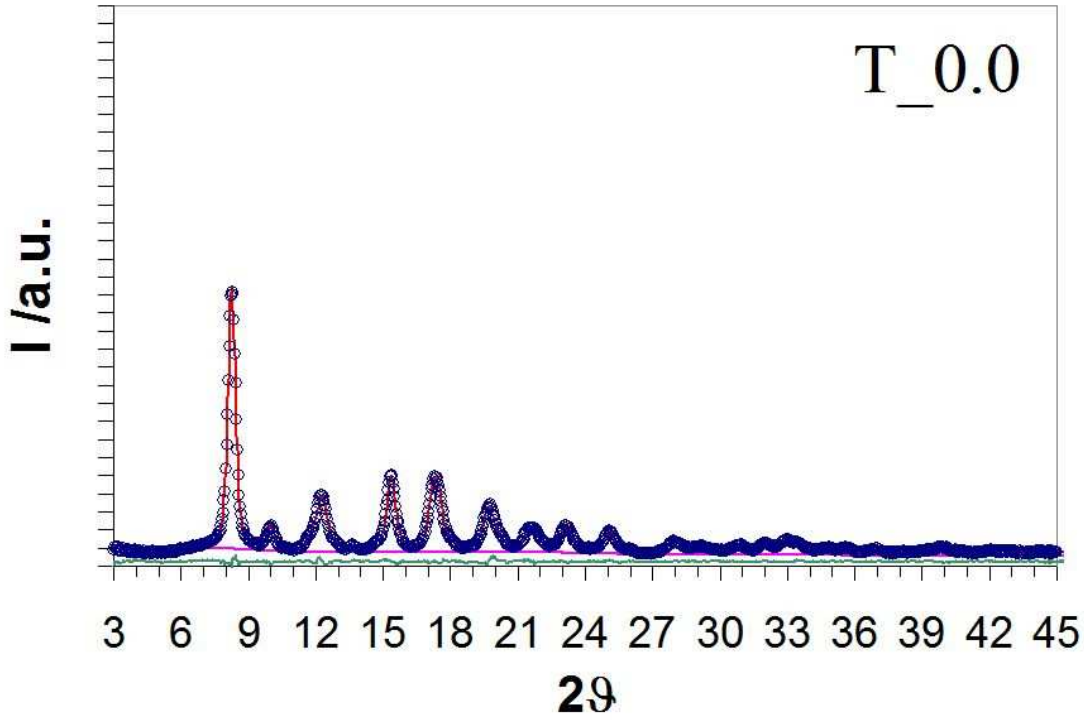
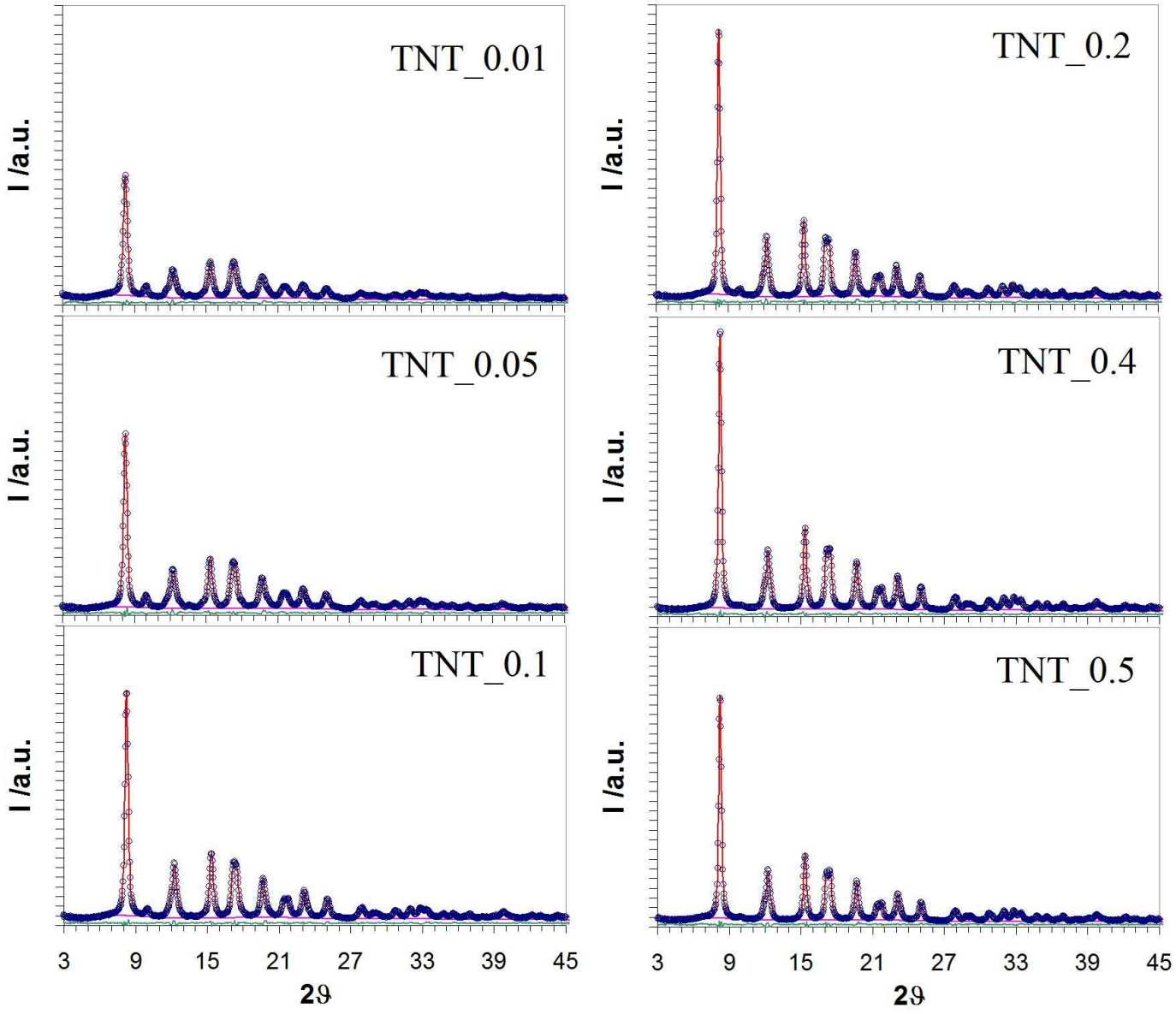


Figure S4. Diffractograms for the T reference sample (a) and TNT (b), TNN (c) (synchrotron data at λ = 0.50581 Å) and TNU (d) (in-home data using graphite-monochromated Cu Kα radiation) series of nitrogen-doped materials. See the main text for experimental details. The diffracted intensity is given in arbitrary units (a.u.) with a maximum value of 24600 (T and TNT), 13200 (TNN) or 9600 (TNU) and divisions as large as 800 a.u. (T and TNT) or 200 a.u. (TNN and TNU). Empty circles: experimental observation; red line: fitting function; purple line: background; green line: point-by-point difference $I_{obs} - I_{calc}$ between the measured and the computed intensities.



(a)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TNT_0.2
TNT_0.05
TNT_0.4
TNT_0.1
TNT_0.5
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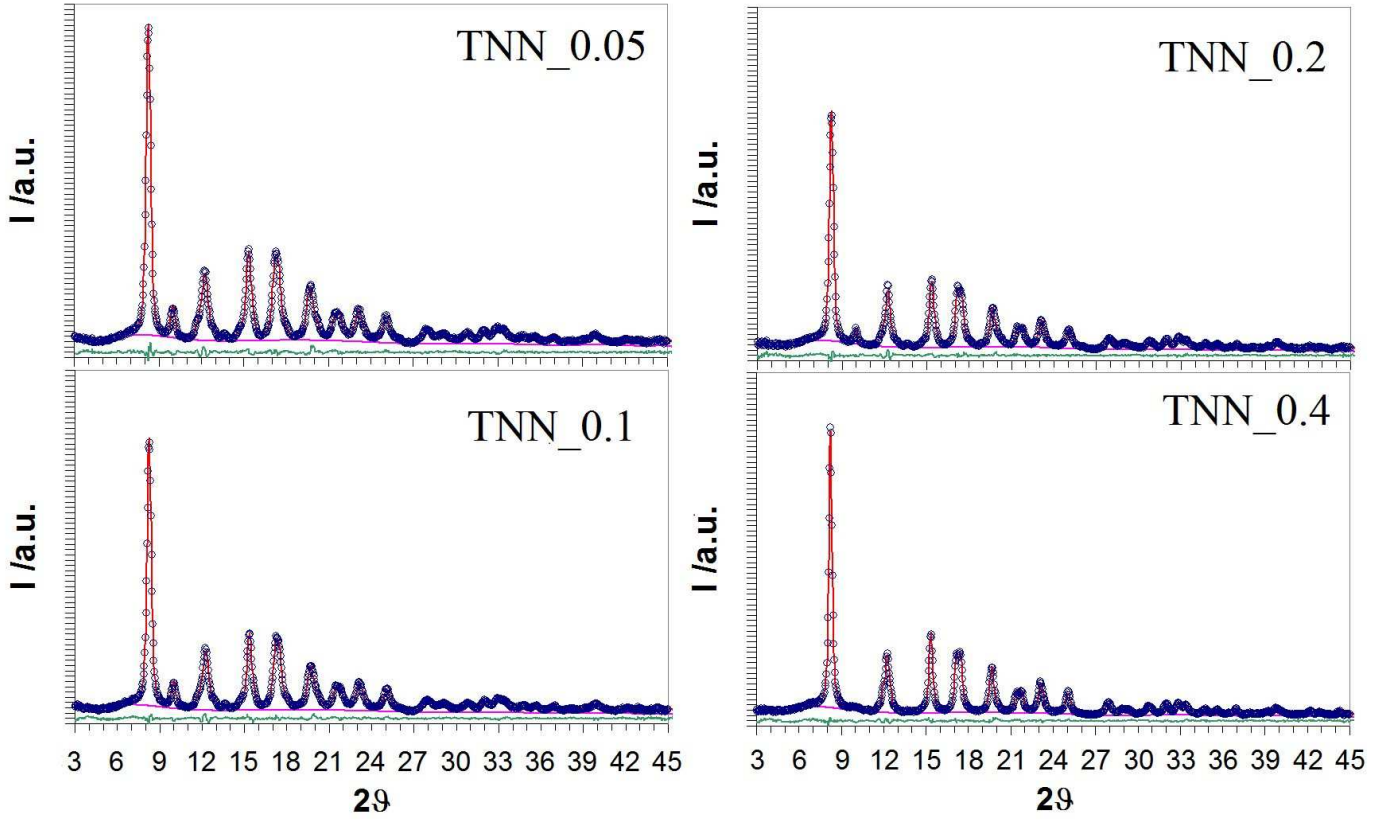
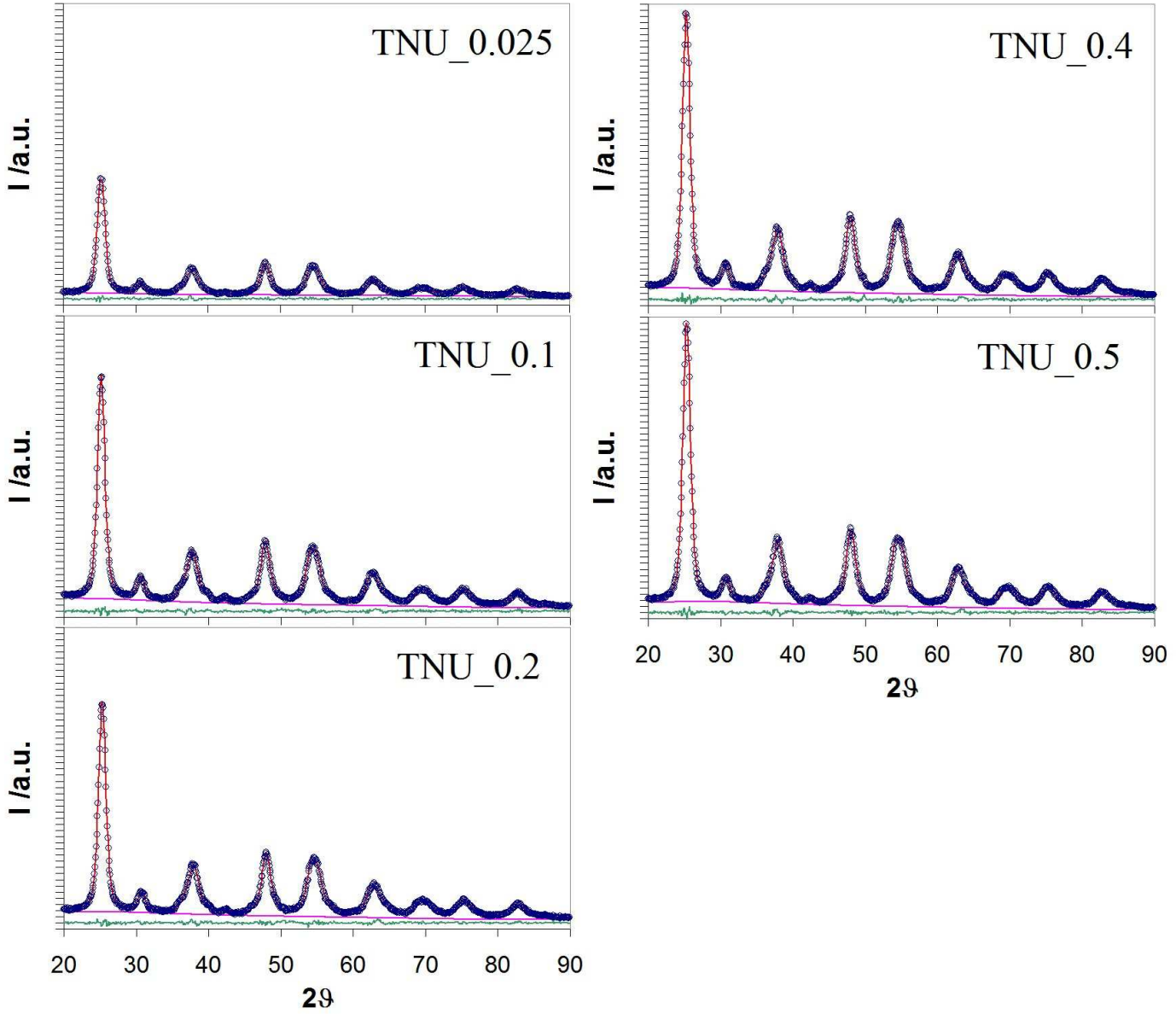
3
9
15
21
27
33
39
45
2θ

(b)


TNN_0.05
TNN_0.2
TNN_0.1
TNN_0.4
I /a.u.
I /a.u.
I /a.u.
I /a.u.
3 6 9 12 15 18 21 24 27 30 33 36 39 42 45
2θ
3 6 9 12 15 18 21 24 27 30 33 36 39 42 45
2θ

(c)



(d)

Table S3. Room temperature XRPD cell parameters as a function of the nominal dopant concentration, from various nitrogen sources (triethylamine, TEA; ammonia, NH_3; urea). Entries labelled as TEA and NH_3 correspond to refinements against synchrotron data (see text), whereas the urea ones were obtained in-home. Least-squares estimated standard deviations are reported in parentheses.

	Anatase $I4_1/amd$				*Brookite* Pbca				
Sample (N/Ti nominal ratio)	*Source of N*	*a*	*c*	*V*		*a*	*b*	*c*	*V*
0.0	No dopant	3.7869(3)	9.4581(12)	135.64(3)	No dopant	9.176(4)	5.445(3)	5.176(2)	258.60(19)
0.01	TEA	3.7876(3)	9.4603(12)	135.71(3)	TEA	9.178(4)	5.435(3)	5.175(2)	258.14(21)
0.025	Urea	3.7849(4)	9.4606(21)	135.53(4)	Urea	9.170(7)	5.447(4)	5.175(4)	258.48(36)
0.05	TEA	3.7870(2)	9.4689(10)	135.79(2)	TEA	9.165(4)	5.443(3)	5.178(2)	258.32(20)
	NH_3	3.7865(3)	9.4597(12)	135.63(3)	NH_3	9.157(4)	5.446(3)	5.170(2)	257.82(18)
0.1	TEA	3.7867(2)	9.4819(6)	135.96(1)	TEA	9.210(7)	5.444(4)	5.202(3)	260.85(31)
	NH_3	3.7866(3)	9.4649(11)	135.71(3)	NH_3	9.165(4)	5.436(3)	5.173(2)	257.72(19)
	Urea	3.7854(3)	9.4629(14)	135.60(3)	Urea	9.171(5)	5.446(2)	5.172(2)	258.30(20)
0.2	TEA	3.7864(1)	9.4854(6)	135.99(1)	TEA	9.165(8)	5.439(6)	5.200(4)	259.25(40)
	NH_3	3.7866(3)	9.4794(10)	135.92(2)	NH_3	9.170(5)	5.448(4)	5.169(2)	258.21(24)
	Urea	3.7860(3)	9.4640(13)	135.65(3)	Urea	9.165(4)	5.446(3)	5.172(2)	258.13(20)
0.4	TEA	3.7864(1)	9.4884(6)	136.03(1)	TEA	9.159(20)	5.469(13)	5.229(11)	261.91(97)
	NH_3	3.7867(2)	9.4769(8)	135.89(2)	NH_3	9.161(19)	5.455(13)	5.205(10)	260.08(96)
	Urea	3.7845(3)	9.4641(12)	135.55(3)	Urea	9.171(4)	5.438(2)	5.172(2)	257.92(19)
0.5	TEA	3.7864(1)	9.4880(6)	136.03(1)	TEA	9.169(21)	5.440(14)	5.231(11)	261(1)
	Urea	3.7854(3)	9.4635(11)	135.61(2)	Urea	9.153(4)	5.440(3)	5.173(2)	257.58(19)

Figure S5. Lattice vector modules and cell volumes for the anatase ($I4_1/amd$) and brookite (Pbca) phases as a function of the doping extent and the nitrogen precursor. Error bars correspond to ±1 estimated standard deviation. The same colour code as in Figure 4 in the main text was employed.

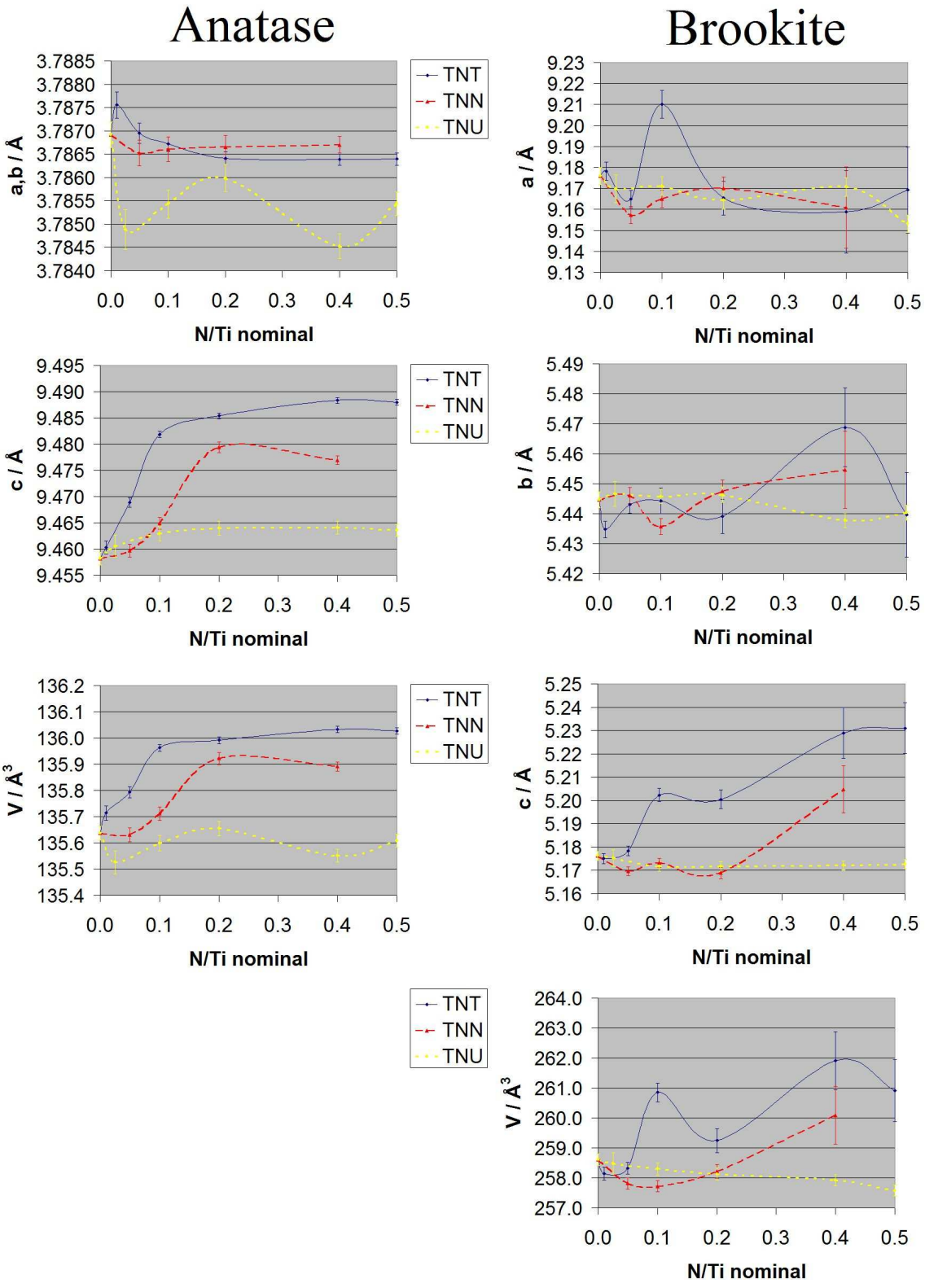


Figure S6. Adsorption isotherms (adsorbed specific volume, mL g^{-1}, vs. relative pressure, p/p_0, with respect to the saturation pressure, p_0) of N_2 obtained in subcritical conditions in the case of the bare sample and the TNT_0.1, with their relative hysteresis loops.

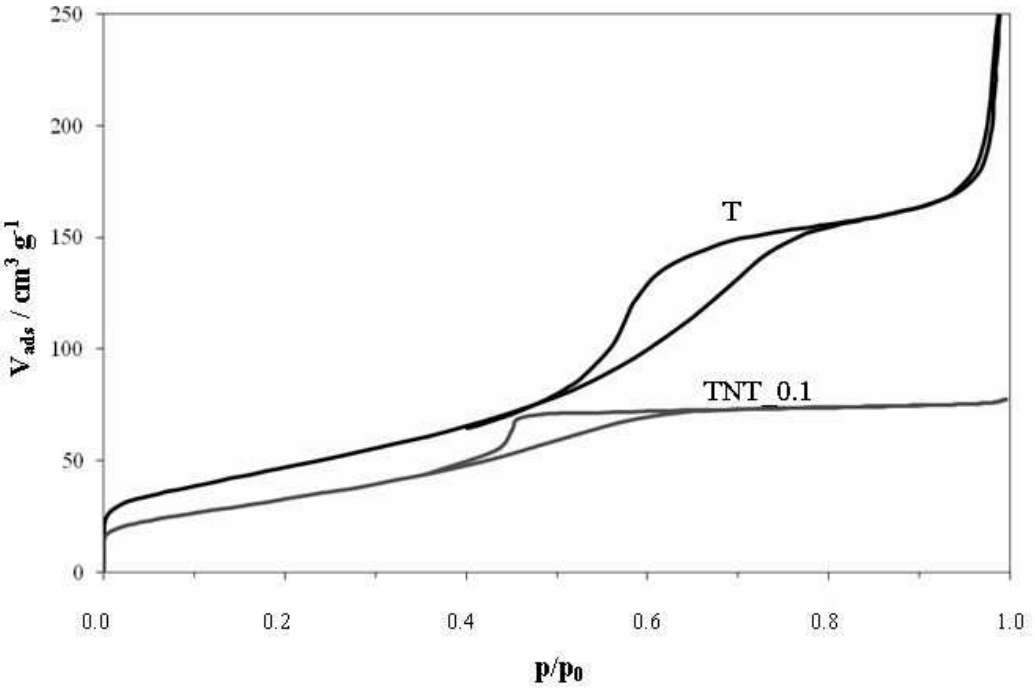


Table S4. Crystallographic cell edge lengths and volumes of anatase TiO_2 as predicted from periodic plane-wave (PAW) and linear combination of Gaussian-type functions (LCTGF) DFT calculations for the same 'defect'/Ti = 1/16 concentration, where 'defect' may either be an oxygen vacancy (O_{vac}) or a N atom that, in turn, may occupy a substitutional (N_s) or interstitial (N_i) site.

	Undoped		O_{vac}		N_s		N_i	
	PAW [i]	LCGTF [ii]	PAW [i]	LCGTF [ii]	PAW [i]	LCGTF [ii]	PAW [i]	LCGTF [ii, iii]
a /Å	3.8838	3.7800	3.8707	3.7585	3.8790	3.7648	3.8867	3.7760
	3.8039	3.8038	3.8123	3.7833	3.8039	3.7882	3.8122	3.8035
b /Å	3.8838	3.7800	3.8834	3.7446	3.8945	3.7838	3.8852	3.7631
	3.8039	3.8038	3.8060	3.7776	3.8231	3.8066	3.8023	3.7893
c /Å	9.5642	9.5971	9.5795	9.6615	9.5277	9.6611	9.5794	9.7325
	9.5515	9.7303	9.5175	9.7947	9.5055	9.7913	9.5571	9.8396
V /Å^3	144.3	137.1	144.0	136.0	143.9	137.6	144.7	138.3
	138.2	140.8	138.1	140.0	138.2	141.2	138.6	141.8

[i] First row: PBE Hamiltonian, U = 5 eV; second row: PBE Hamiltonian, U = 0 eV. A 2x2x2 primitive cell was considered for all the PAW calculations.

[ii] First row: PBE0 Hamiltonian. Second row: B3LYP Hamiltonian. A 2x2x1 crystallographic cell matching the mass content of the primitive 2x2x2 one was employed, with full symmetry compatible with the doping geometry having been exploited.

[iii] A frozen small-core Stuttgard-Dresden pseudopotential has been applied to Ti atoms to speed up convergence in these calculations.

LGTCF basis sets

```
TCM CRYSTAL basis set library: http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html

Title:   titanium "86-411d4-1"  TVAE**
Author:  N.M. Harrison
When:    1995
Comment:
Use:     TiO2
Refs:    Unpublished - used to study EFG in TiO2

22 7
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       73.2133  0.4033
       30.3718  0.1445
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      132.525  -0.0683  0.0603
       43.6801 -0.1245  0.2124
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        7.2248  0.6261  0.4097
        2.4117  0.282   0.2181
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        4.4653 -0.7946  0.1919
        1.8904  1.0107  1.3778
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        0.8126  1.0     1.0
0 1 1 0.0 1.0
        0.3297  1.0     1.0
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       16.2685  0.0675
        4.3719  0.2934
        1.464   0.5658
        0.5485  0.545
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TCM CRYSTAL basis set library: http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html

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Author:  unknown
When:    unknown
Comment: optimised in Li3N  - good for N3- cases.
Use:     Li3N
         ScN   outer sp(0.136)
         GaN outer sp (0.140) Jaffe et al J Phys Chem Solids 55, 1357 (1994)

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  190.1     0.05287
   52.69    0.1710
   18.10    0.3612
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CRYSTAL basis set library: http://www.crystal.unito.it/Basis_Sets/Ptable.html

O_8-411d1_cora_2005

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