Fluorine and Niobium doped TiO_2: chemical and spectroscopic properties of polycrystalline n-type doped anatase.

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S.I.

Several samples were prepared in this work in order to clarify the role of amount of fluorine concentration on the phase composition of the final materials. Nevertheless, within the entire set of samples and with the exception of Nb1 only materials based the anatase polymorph were chosen for the characterization (sample reported in Table1 of the paper). Table S1 resume the main features of all samples prepared in this work.

Sample abbreviation	Nb/Ti Nominal	Nb/Ti (XRF)	F/Ti Nominal	Calc. Temp. (°C)	Phase (w/w %)*				Cryst.*† (nm)	Eg (eV)
					A	R	B	TF		
TiO_2	0	-	-	500	100	0	0	0	30	3.20
F1	0	-	0.01	500	100	0	0	0	28	3.20
F2	0	-	0.90	500	100	0	0	0	30	3.20
F3	0	-	1.80	500	100	0	0	0	34	3.20
F4	0	-	3.50	500	100	0	0	0	36	3.20
F5	0	-	5.50	500	98	0	0	2	91	3.20
F6	0	-	7.00	500	28	0	0	72	140	3.14
Nb1	0.05	0.05	-	500	55	10	35	0	12	2.91
Nb2	0.05	n.d.	-	700	31	69	0	0	27	2.95
NbF05	0.05	n.d	0.05	700	35	65	0	0	22	n.d.
NbF15	0.05	n.d	0.15	700	54	46	0	0	25	n.d
NbF25	0.05	0.05	0.25	700	98	2	0	0	21	3.03
NbF35	0.05	0.05	0.35	700	100	0	0	0	24	3.08
NbF45	0.05	0.06	0.45	700	100	0	0	0	32	3.11
NbF25a	0.05	0.05	0.25	700	100	0	0	0	23	3.18

Table S1: Abbreviation adopted for the samples of the present work and corresponding compositional, structural and optical properties. A=Anatase. R=Rutile. B=Brookite. TF=$TiOF_2$. n.d. = not determinate. *Data obtained via Rietveld refinement using Maud program. † Data related to the anatase polymorph only.

F-TiO_2 systems.

Experimental evidence clearly indicates that a limit of fluorine solubility occurs. In this work different concentration of fluorine in solution (with a nominal F/Ti ratio ranging from 0.01 to 7.00) were employed in the F-TiO_2 preparation. In all cases the anatase polymorph was obtained but, starting from a F/Ti ratio of 5.00, the $TiOF_2$ phase is also formed (Fig.S.I.-1 A).

In Fig.S.I.-1B, DR-UV-Vis absorption spectra of the different F-TiO_2 samples are reported. Optical properties do not significantly change until a F/Ti ratio of 7.00, all samples show an optical absorption edge of about 3.20 eV (Fig.S.I.-2) which is the commonly reported value for the anatase polymorph. At higher level of doping the absorption edge is shifted to 3.14 eV (Fig.S.I.-2), however in this case the $TiOF_2$ component in this sample become predominant and a possible contribution of this crystallographic phase cannot be excluded.

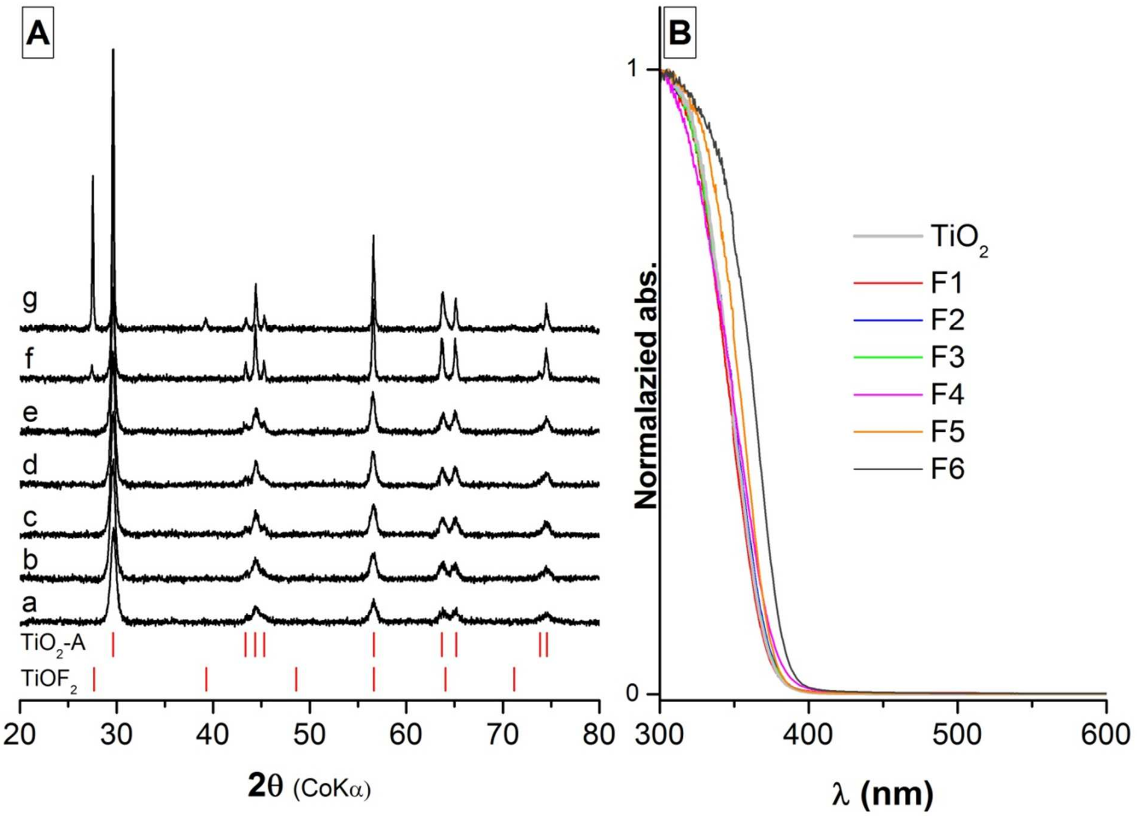

Fig SI-1. F- TiO_2 samples. Panel A: XRD patterns of a) TiO_2, b) F1, c) F2, d) F3, e) F4, f) F5, g) F6. TiO_2-A and $TiOF_2$ indicate the peaks position of Anatase and $TiOF_2$ phases. Panel B: DR-UV-Vis spectra.

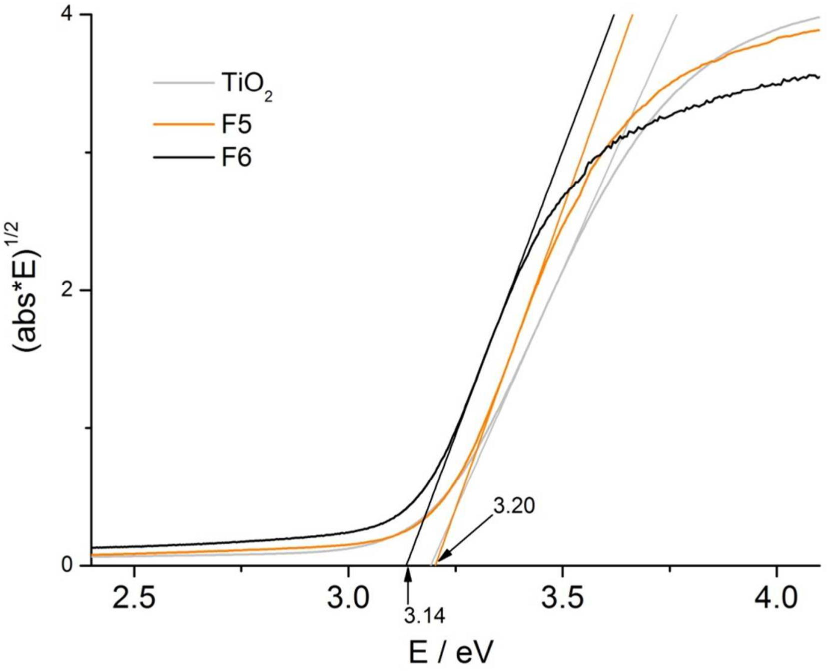

Fig SI-2. Optical absorption edge determinated via Tauc plot method for TiO$_2$, F5 and F6 samples.

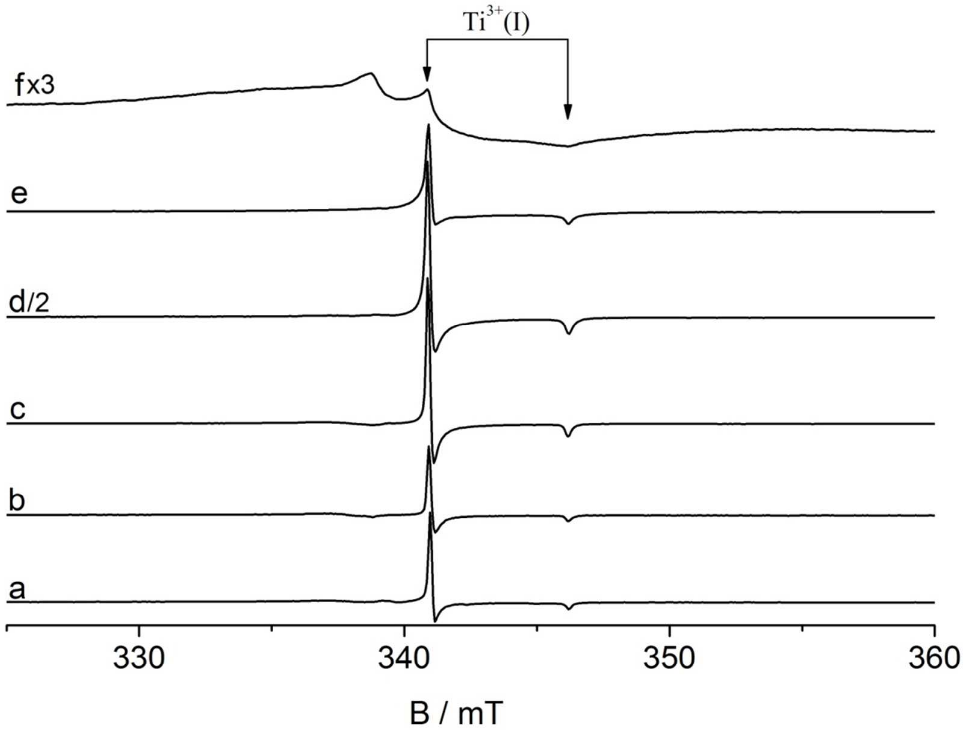

Fig SI-3. EPR spectra of F-TiO$_2$ samples. a) F1, b) F2, c) F3, d) F4, e) F5, f) F6.

As already reported in our previous work[1], TiO_2 doping with fluorine ions leads to the formation of Ti^{3+} centres. EPR spectra reported in Fig.S.I.-3 confirms the formation of these centres but at the same time EPR analysis shows that the amount of observed Ti^{3+} centres due to the fluorine insertion in the TiO_2 lattice is not proportional to the nominal amount of dopant adopted in the preparation. These two experimental evidences clearly indicate that a limit of fluorine solubility occurs.

Nb-TiO₂ systems.

In Fig.S.I-4 XRD patterns of niobium doped materials prepared in this work are reported. Niobium, at variance with fluorine is not removed allowing thermal treatments at high temperature in order to ensure a full diffusion of the dopant cation in the TiO_2 lattice and to obtain well crystallized materials. Two different Nb doped samples were preparedcalcining the material at 770K (Nb1) and at 970K (Nb2) respectively. In these two cases it was not possible to obtain a single phase material. At the lower temperature small fractions of rutile and Brookite are formed (sample Nb1, Fig. SI-4c) while at higher temperature the Anatase to Rutile phase conversion easily occurs. (sample Nb2, Fig. SI-4d)

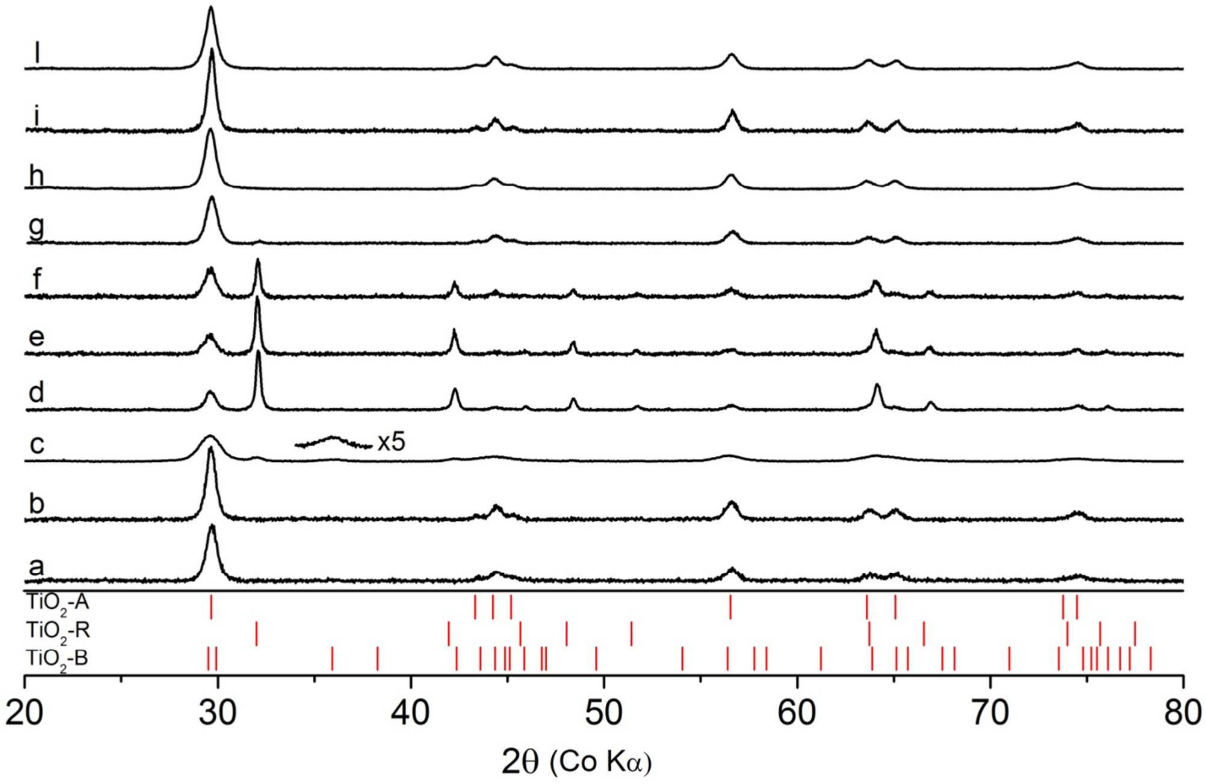

Fig SI-4. XRD patterns of TiO_2 based materials. a) Bare TiO_2, b) F2, c) Nb1, d) Nb2, e) NbF1, f) NbF2, g) NbF3, h) NbF4, i) NbF5, l) NbF6. The sticks corresponding to TiO_2-A, TiO_2-R, and TiO_2-B indicate the diffraction peaks of the anatase, rutile and brookite polymorph respectively.

Nb-F-TiO$_2$ systems.

Incremental amount of fluorine was added during the synthesis of Nb doped materials in order to avoid the rutile generation. Data reported in Figure SI-4 indicate that a critical amount of fluorine is needed during the synthesis to completely suppress the Rutile formation. With a F/Ti ratio lower than 0.25 the presence of rutile is always observed whereas for a F/Ti ratio of 0.25 (pattern g in Fig. SI-4) only a negligible trace of the polymorph (2%) is observed. For an F/Ti ratio of 0.35 or higher (pattern from h to l in Fig. SI-4) rutile formation is completely suppressed.

XPS

XPS analysis indicates that all samples show a Ti/O ratio higher than the expected stoichiometric value (see table 2 in the text). This is due to the presence of surface hydroxyl groups and chemisorbed water which alter the surface composition of the samples. The presence of such groups is confirmed by an absorption shoulder in the O 1s XPS spectra at high binding energy with respect to that of lattice oxygen. An example of such spectral feature in shown in Figure SI-5 where the O 1s XPS spectrum of sample NbF6 is reported.

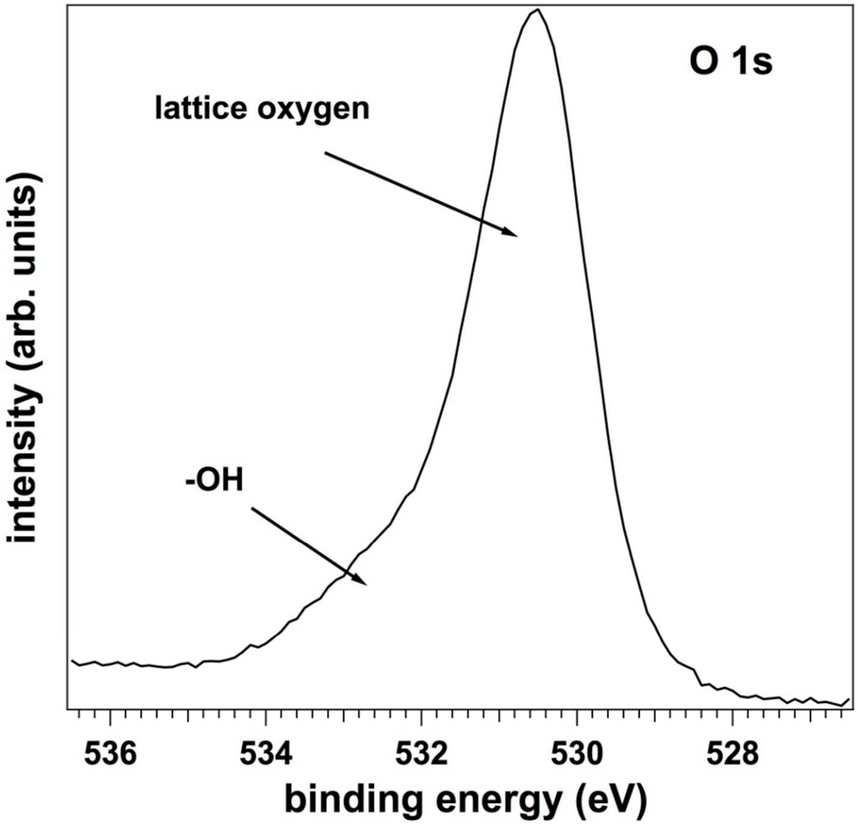

Fig SI-5. O 1s XPS spectrum of sample NbF25a sample.

References.

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[1] A. Czoska; S. Livraghi; M. Chiesa; E. Giamello; S. Agnoli; G. Granozzi; E. Finazzi; C. Di Valentin; G. Pacchioni, *J. Phys. Chem. C* **2008**, *112*, (24), 8951-8956.