Electronic Supplementary Material (ESI) for RSC Advances.
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XPS and NEXAFS study of fluorine modified TiO_2 nano-ovoids reveals dependence of Ti^{3+} surface population on the modifying agent.

Electronic Supplementary Information

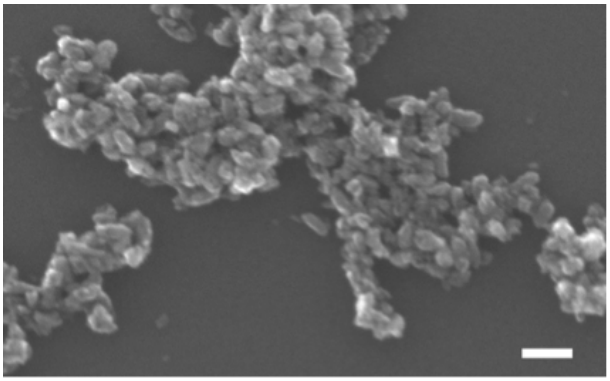

Fig. S1. SEM image of titania synthesised in the absence of SMA. Scale bar: 100nm.

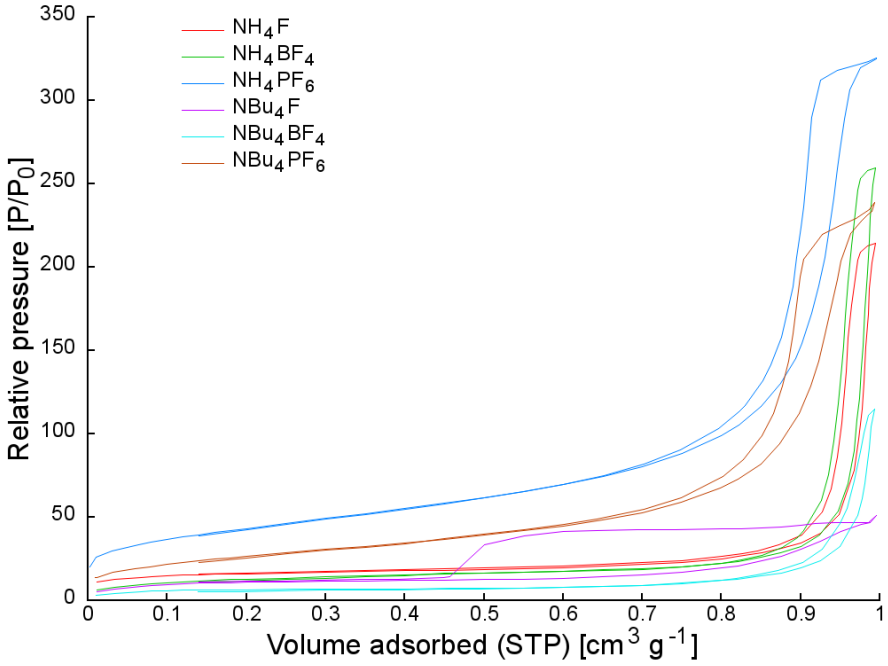

Fig. S2. Surface area BET isotherms for SMA-modified TiO_2 materials.

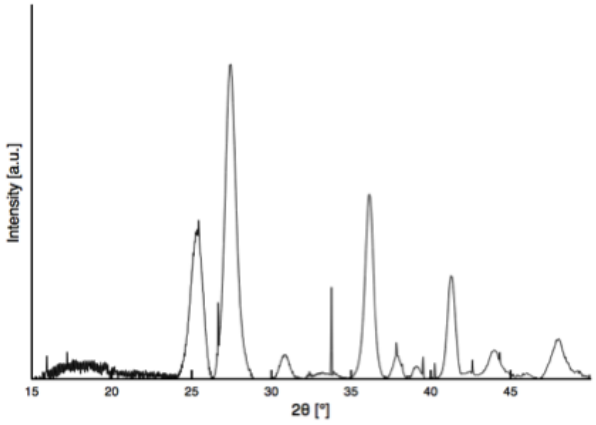

Fig. S3. PXRD diffraction pattern for TiO_2 synthesised *via* the peroxo method in the absence of surface modifying agent.

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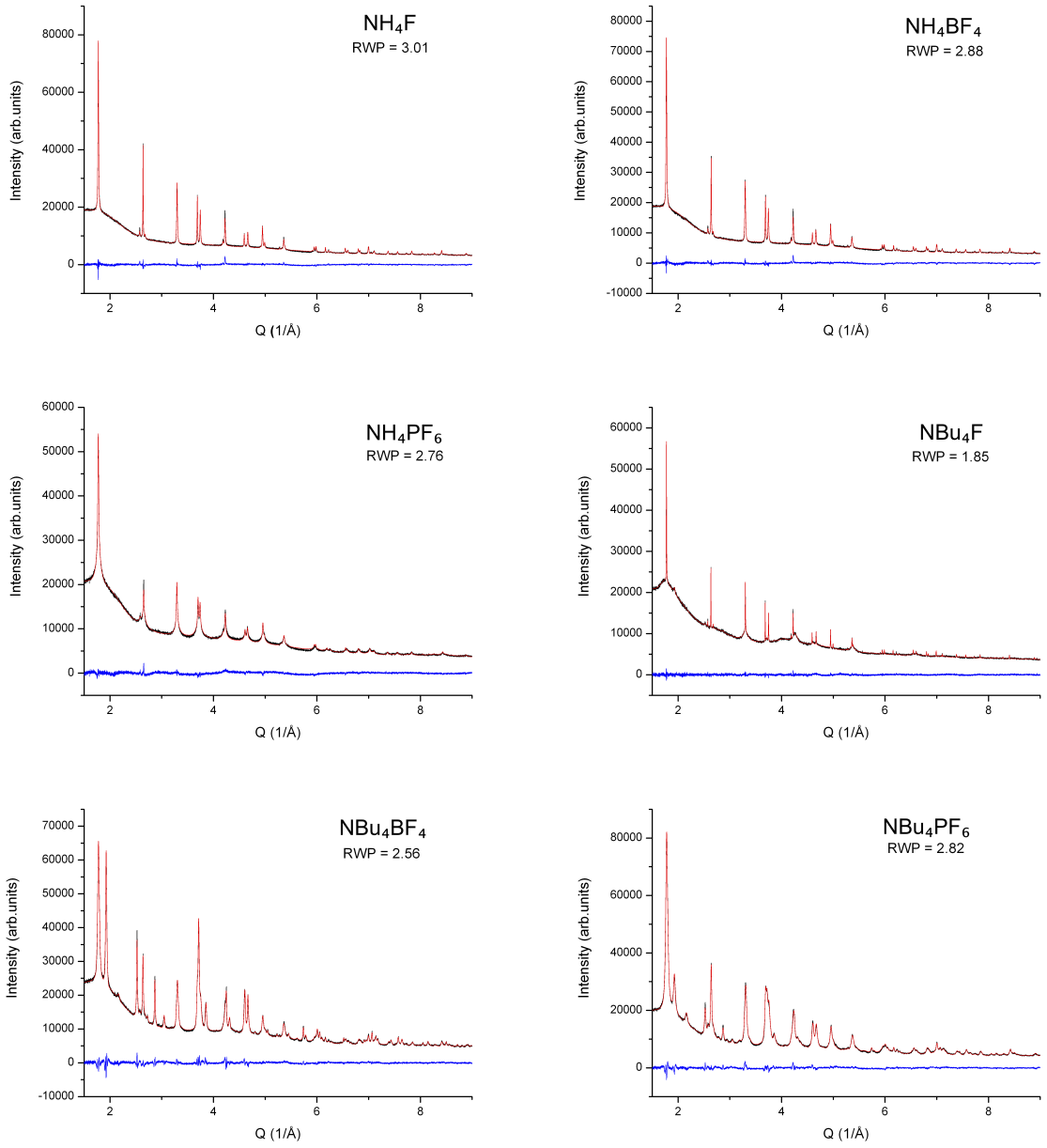

Fig. S4. XRD data fitting for SMA-modified TiO_2. Experimental data shown in black, fitting in red and residual in blue.

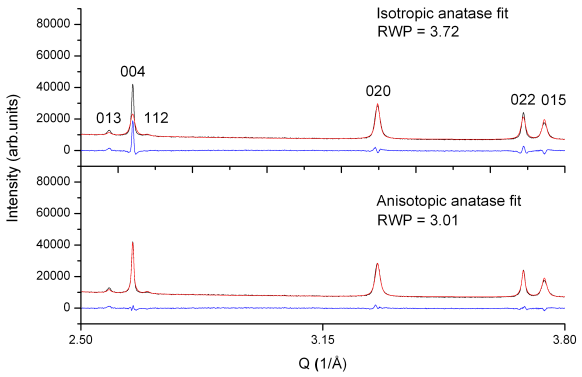

Fig. S5. Isotropic and anisotropic XRD fits for NH_4F-TiO_2. The residual (blue) is considerably noisier for the isotropic fit, which indicates that the crystals are anisotropic.

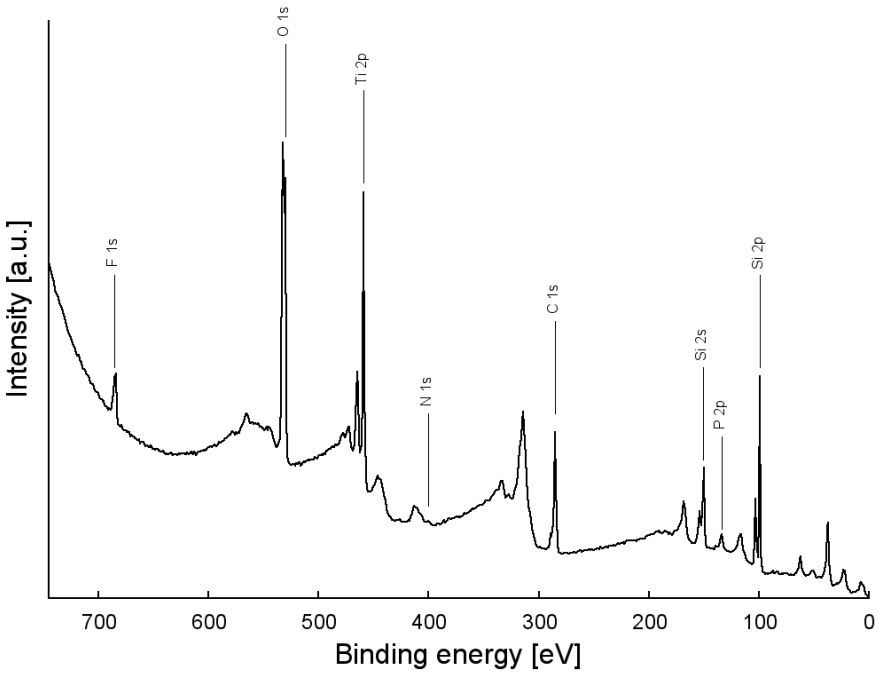

Fig. S6. Survey XP spectrum for a typical sample (here: $NH_4PF_6-TiO_2$). Photoelectron peaks are marked: unmarked peaks are auger peaks.

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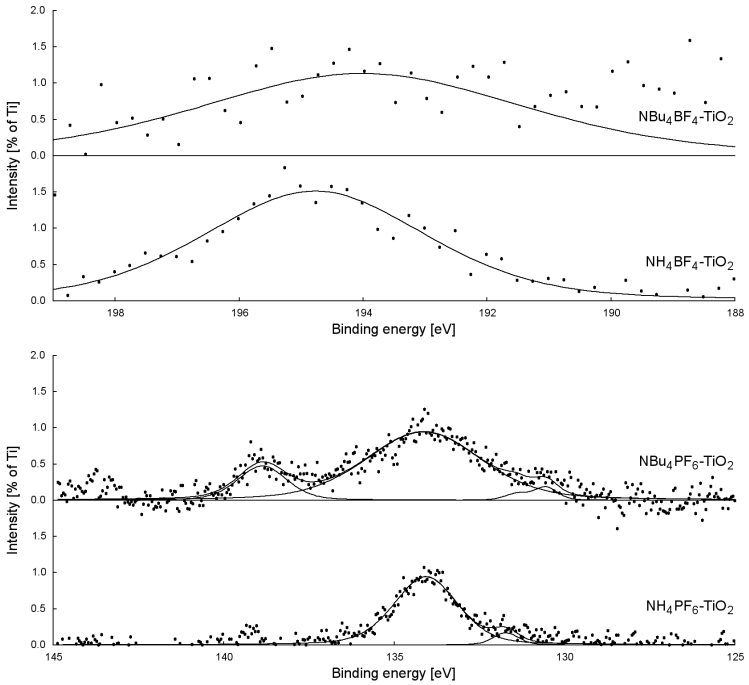

Fig. S7. B and P XP spectra for BF_4^-- and PF_6^--modified TiO_2 materials.

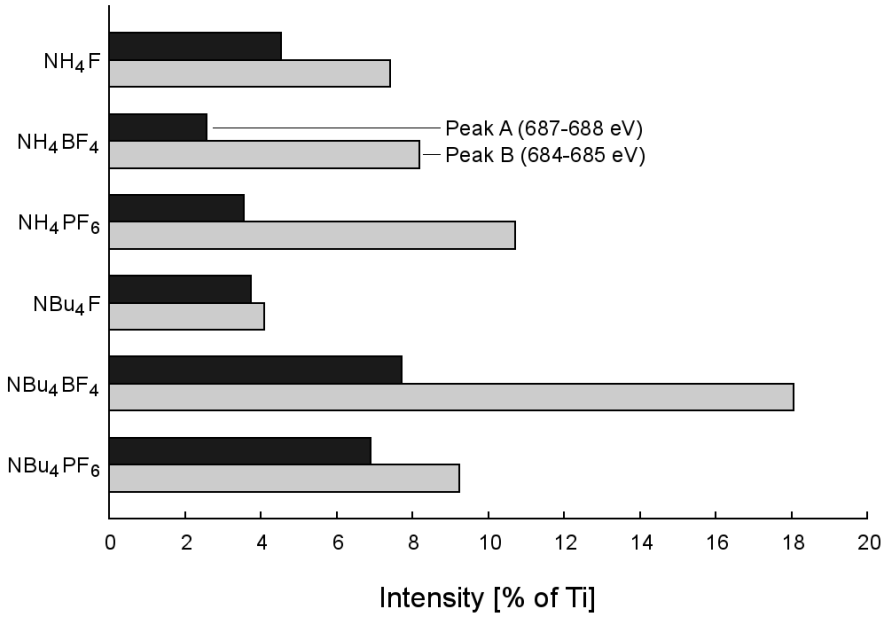

Fig. S8. Fluorine XPS peak intensities for fluorine-modified TiO_2. Intensity is normalised against titanium.

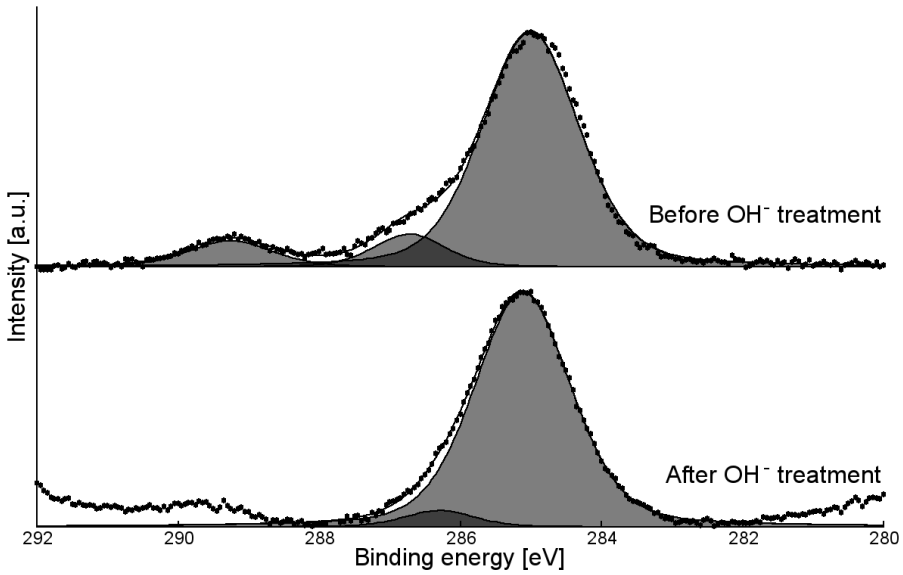

Fig. S9. C 1*s* XP spectra for NH_4PF_6 before and after KOH treatment.

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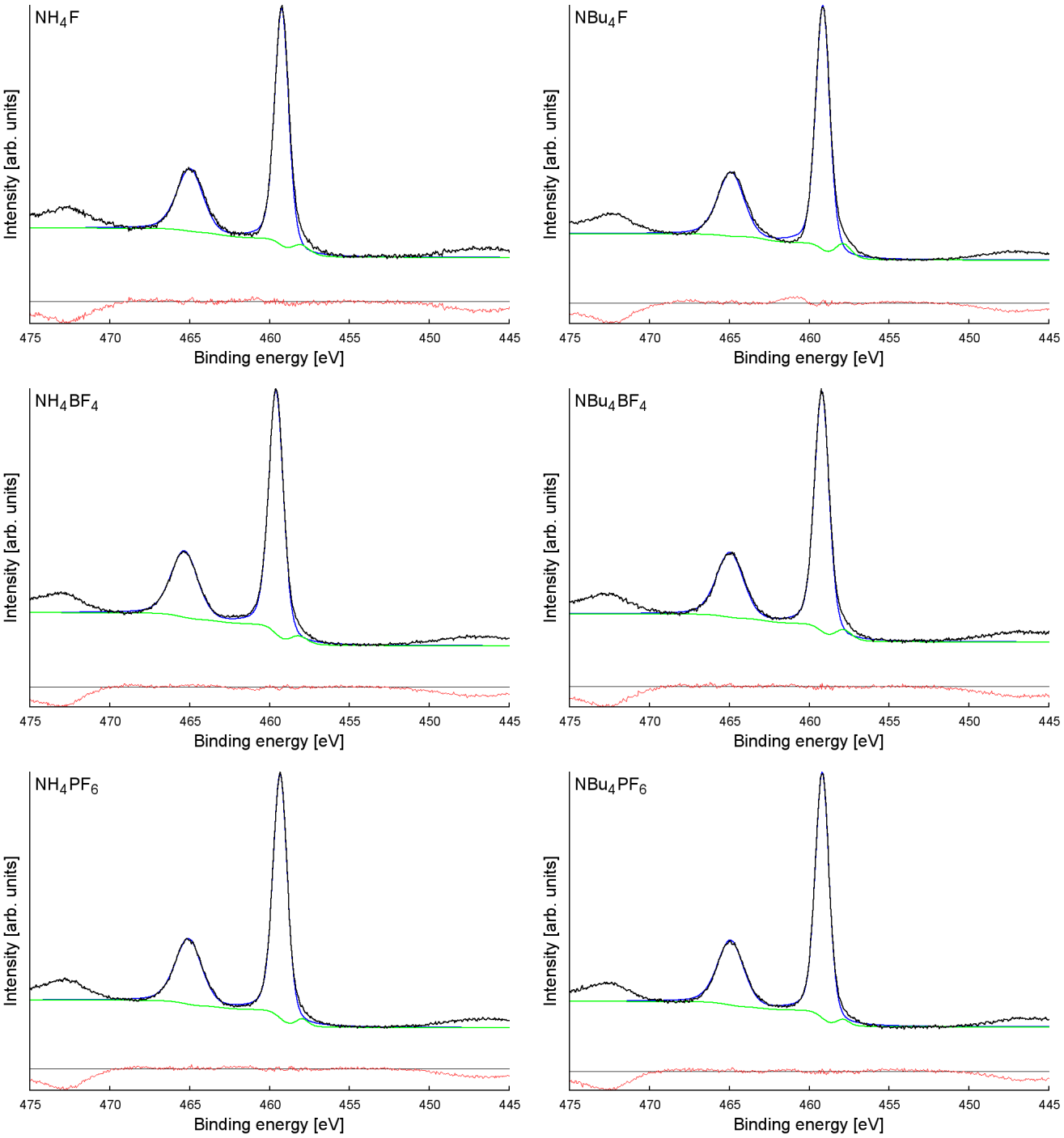

Fig. S10. XPS Ti fitting curves for fluoride-modified TiO_2. Experimental data is shown in black, Ti^{4+} and Ti^{3+} fitting curves in blue and green respectively, and deviation between modelled and experimental data in red.

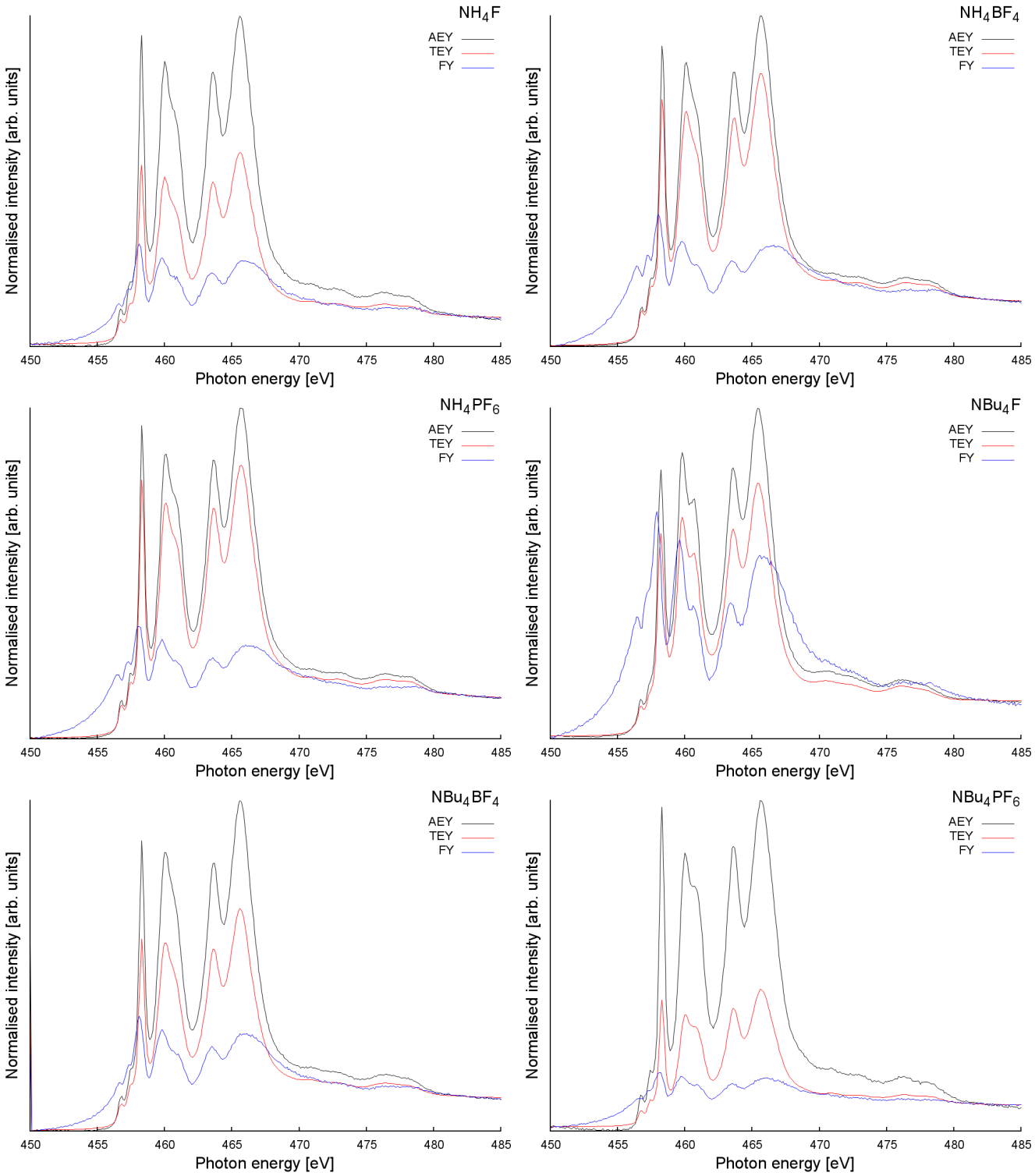

Fig. S11. NEXAFS AEY, TEY and FY spectra for fluoride-modified TiO_2 materials.

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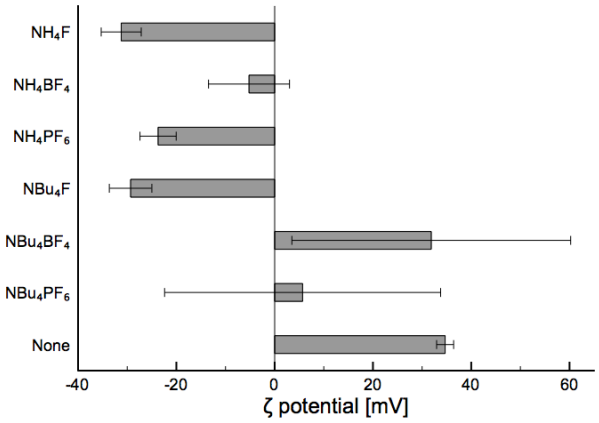

Fig. S12. Zeta potentials for fluoride-modified TiO_2 as compared against unmodified TiO_2. Error bars indicate 95% CI.

Table S1. XPS fitting data for NH_4^+-SMA-modified TiO_2 materials.

NH_4F-TiO_2					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	459.21	74511	1.05	4.11
Ti	2	458.01	4882	1.34	0.27
C	1	285	24280	1.42	9.64
C	2	286.22	8375	2.15	3.33
C	3	289.28	1901	1.4	0.76
F	1	684.77	5879	1.55	0.58
F	2	686.81	3596	1.99	0.36
N	1	400.4	2895	2.99	0.68
N	2	400.25	459	0.94	0.11
Si	1	99.11	20400	0.48	7.5
Si	2	103.08	13865	1.43	5.1
Si	3	99.93	828	0.89	0.3
O	1	530.59	106229	1.23	15.98
O	2	532.64	340752	1.65	51.27
$NH_4BF_4-TiO_2$					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	459.34	179764	1.1	13.69
Ti	2	457.92	7453	1.25	0.57
C	1	285	18819	1.49	10.32
C	2	286.21	9703	2.31	5.32
C	3	289.24	3819	1.7	2.09
F	1	684.86	15328	1.51	2.1
F	2	686.73	4799	1.8	0.66
N	1	400.34	1552	1.26	0.51
N	2	399.32	236	0.86	0.08
Si	1	98.88	200	0.48	0.1
Si	2	102.85	550	1.43	0.28
Si	3	102.39	78	1.11	0.04
O	1	530.62	202620	1.14	42.09
O	2	531.97	106684	2.36	22.16
$NH_4PF_6-TiO_2$					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	459.18	149500	1.06	8.82
Ti	2	457.79	4268	0.9	0.25
C	1	285	28555	1.62	12.13
C	2	286.72	2944	1.19	1.25
C	3	289.26	2790	1.41	1.19
F	1	684.65	16461	1.56	1.75
F	2	686.76	5459	1.89	0.58
N	1	400.23	1622	1.25	0.41
N	2	399.73	1005	3.64	0.25
Si	1	99	13523	0.46	5.32
Si	2	102.98	7654	1.35	3.01
Si	3	99.64	1156	1.03	0.45
O	1	530.32	117686	1.02	18.94
O	2	532.48	201666	1.69	32.45
O	3	530.9	77182	1.31	12.42
P	1	133.7	2481	1.88	0.68
P	2	131.03	368	1.01	0.1

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Table S2. XPS fitting data for NBu_4^+-SMA-modified TiO_2 materials.

NBu_4F-TiO_2					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	458.97	178707	1.04	10.6
Ti	2	457.69	12923	1.21	0.77
C	1	285	47974	1.54	20.48
C	2	286.13	23811	1.87	10.17
F	1	684.67	7865	1.49	0.84
F	2	687.03	7159	1.79	0.76
N	1	402.02	5026	1.3	1.28
N	2	400.44	5717	2.64	1.45
Si	1	98.84	490	0.28	0.19
Si	2	102.99	2516	1.56	0.99
Si	3	99.03	3348	0.47	1.32
O	1	530.19	38842	0.89	6.28
O	2	532.4	67113	1.61	10.85
O	3	530.64	210239	1.2	34
$NBu_4BF_4-TiO_2$					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	459.18	125831	1.09	5.78
Ti	2	457.83	6797	1.25	0.31
C	1	285	40311	1.43	13.34
C	2	286.21	17784	2.09	5.89
C	3	289.22	2632	1.25	0.87
F	1	684.74	23942	1.61	1.98
F	2	686.86	10237	2.04	0.85
N	1	402.16	1302	1.22	0.26
N	2	400.14	2152	2.03	0.42
Si	1	99.11	22905	0.39	7.02
Si	2	103.15	20274	1.43	6.21
Si	3	99.27	11096	0.5	3.4
O	1	530.44	106793	1.05	13.39
O	2	532.74	267302	1.57	33.51
O	3	531.13	54036	1.34	6.77
$NBu_4PF_6-TiO_2$					
Element	#	E_B [eV]	Intensity	FWHM [eV]	Abundance [%]
Ti	1	459.03	137399	1.02	7.03
Ti	2	457.72	3592	0.94	0.18
C	1	285	41540	1.5	15.3
C	2	286.46	9029	1.79	3.33
C	3	289.17	4901	1.23	1.81
F	1	684.55	13037	1.66	1.2
F	2	686.79	9728	1.82	0.9
N	1	400.03	1663	1.73	0.36
Si	1	99	21071	0.38	7.19
Si	2	102.98	16245	1.43	5.54
Si	3	99.14	8956	0.49	3.06
O	1	530.24	123176	1.05	17.19
O	2	532.56	201380	1.56	28.1
O	3	530.94	53814	1.37	7.51
P	1	133.8	4265	3.83	1.01
P	2	138.55	981	1.61	0.23
P	3	130.49	246	0.8	0.06