Supplementary: Shape-controlling effects of hydrohalic and carboxylic acids in TiO_2 nanoparticle synthesis

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I. COMPARISON OF PBE AND OPTB88-VDW XC FUNCTIONALS

A comparison of the PBE[1] and optB88-vdW[2,3] XC functionals is presented in Table I. As expected the adsorption energies are more negative for the optB88-vdW functional, i.e. the binding to the surface is stronger, because it includes additional attraction by van-der-Waals interactions. Furthermore, the difference in adsorption energy between the PBE and optB88-vdW functional increases with increasing size of the halide ion involved ($F^- < Cl^- < Br^- < I^-$). The substitution energies, on the other hand, are similar for both functionals.

Table I. Calculated adsorption and substitution energies per molecule in eV for hydrohalic acids on anatase TiO_2 (001), (100), and (101) surfaces, for the PBE and optB88-vdW XC functionals.

Species	XC	$E_{\mathrm{ad}}(001)$	$E_{\mathrm{ad}}(100)$	$E_{\mathrm{ad}}(101)$	$E_{\mathrm{sub}}(001)$	$E_{\mathrm{sub}}(100)$	$E_{\mathrm{sub}}(101)$
HF	optB88-vdW	−1.43	−1.33	−1.41	−0.40	−0.24	−0.11
	PBE	−1.24	−1.10	−1.16	−0.45	−0.33	−0.22
HCl	optB88-vdW	−1.12	−1.11	−1.25	2.43	0.30	0.47
	PBE	−0.83	−0.78	−0.87	2.45	0.34	0.49
HBr	optB88-vdW	−1.19	−1.21	−1.36	1.83	0.60	0.77
	PBE	−0.86	−0.84	−0.95	1.90	0.65	0.80
HI	optB88-vdW	−1.12	−1.17	−1.34	1.06	1.11	1.19
	PBE	−0.72	−0.75	−0.88	1.15	1.09	1.17

II. ADDITIONAL ADSORPTION STRUCTURES

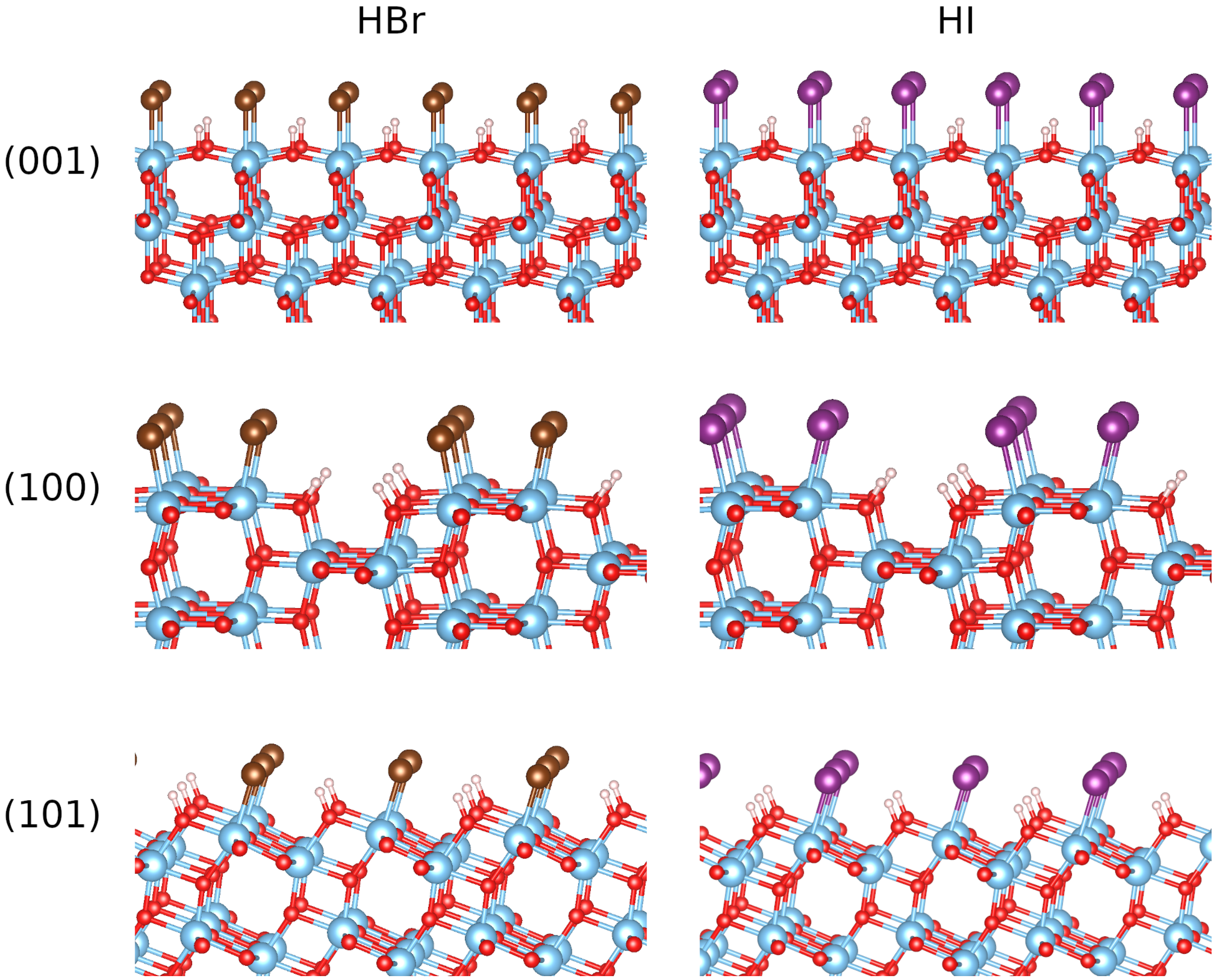


Figure 1. Surface structures after hydrohalic acid adsorption. Top to bottom: (001), (100), and (101) surfaces of anatase TiO_2. Left: structures containing Br. Right: structures containing I. Color code: Ti – blue, O – red, H – white, Br – brown, I – purple.

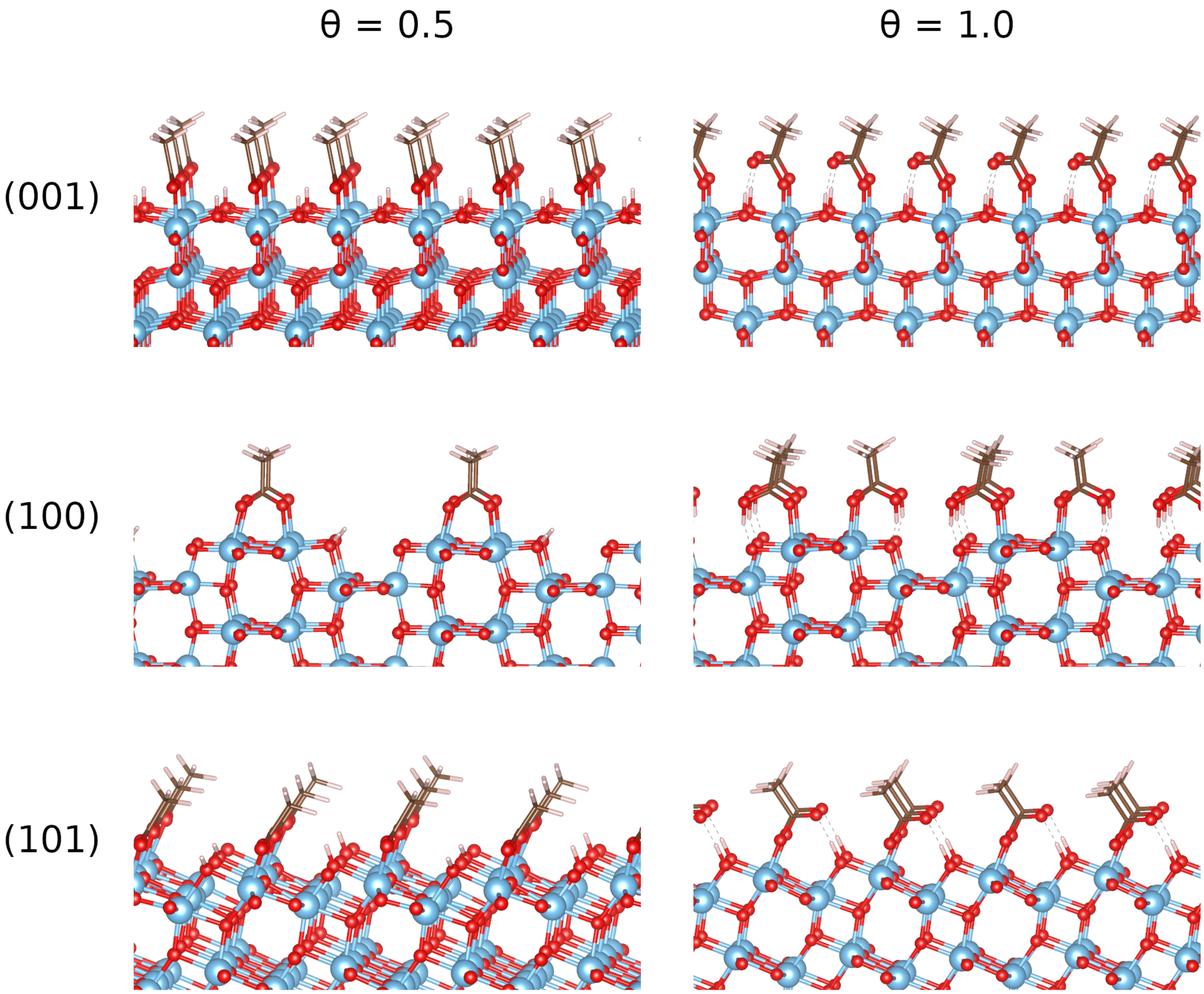


Figure 2. Surface structures after acetic acid adsorption. Top to bottom: (001), (100), and (101) surfaces of anatase TiO_2. Left: structures with a coverage θ of half a monolayer. Right: structures with full coverage θ. Color code: Ti – blue, O – red, C – brown, H – white.

III. ADDITIONAL SUBSTITUTION STRUCTURES

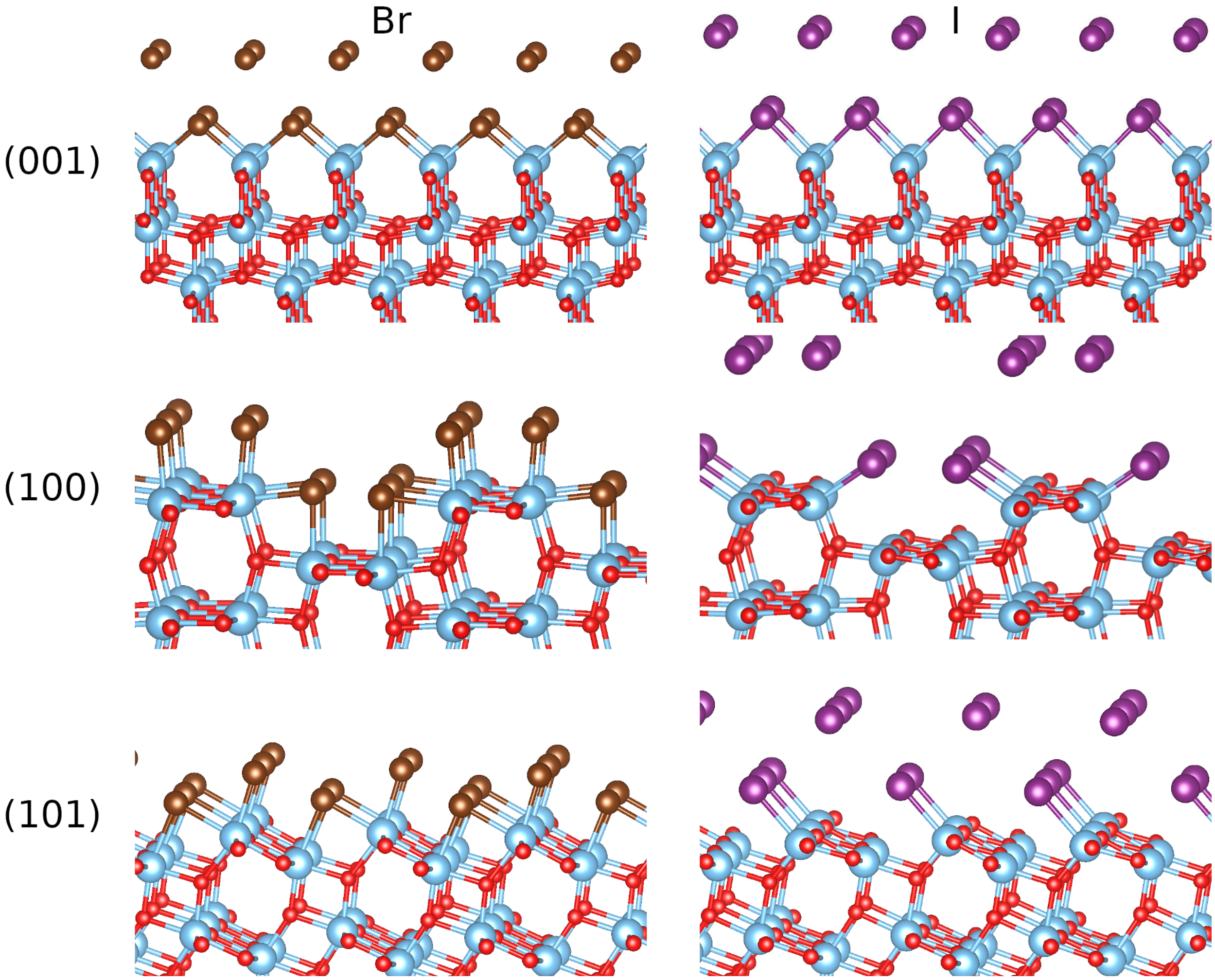
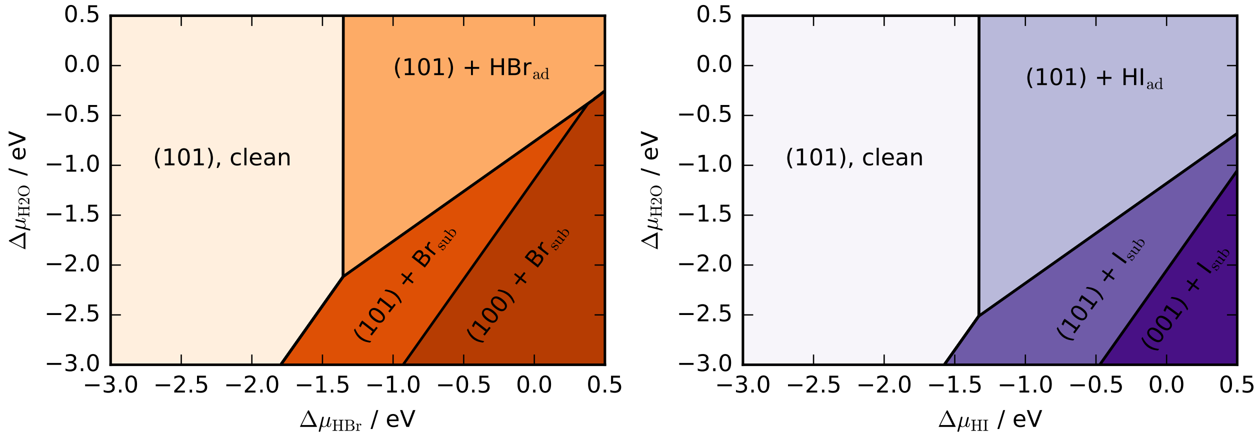


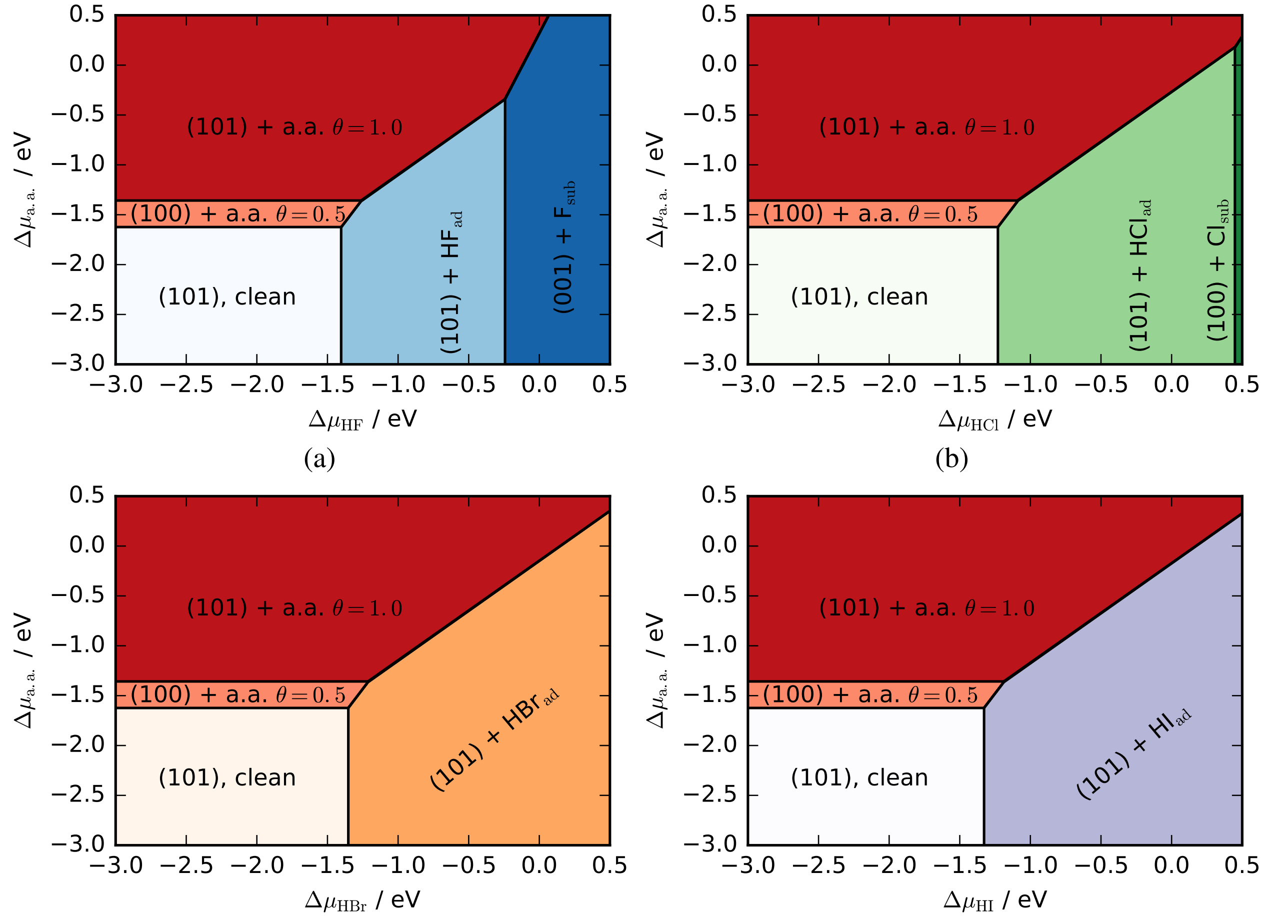
Figure 3. Surface structures after the hydroxyl ↔ halide substitution process. Top to bottom: (001), (100), and (101) surfaces of anatase TiO_2. Left: structures containing Br. Right: structures containing I. Color code: Ti – blue, O – red, Br – brown, I – purple.

IV. ADDITIONAL PHASE DIAGRAMS



(a) (b)

Figure 4. Surface phase diagrams of anatase TiO_2 surfaces in hydrohalic acid environment. Influence of bromic acid and water chemical potential (a), and iodic acid and water chemical potential (b) on the stability of the {001}, {100} and {101} facets.



(a) (b)

(c) (d)

Figure 5. Surface phase diagrams of anatase TiO_2 surfaces in carboxylic and hydrohalic acid environment. Influence of acetic acid (a.a.) and (a) fluoric acid, (b) chloric acid, (c) bromic acid, (d) iodic acid on the stability of the {001}, {100} and {101} facets. For the substitution structures the water chemical potential shift $\Delta\mu_{H_2O}$ was fixed to 0 eV.

V. SEM MICROGRAPH

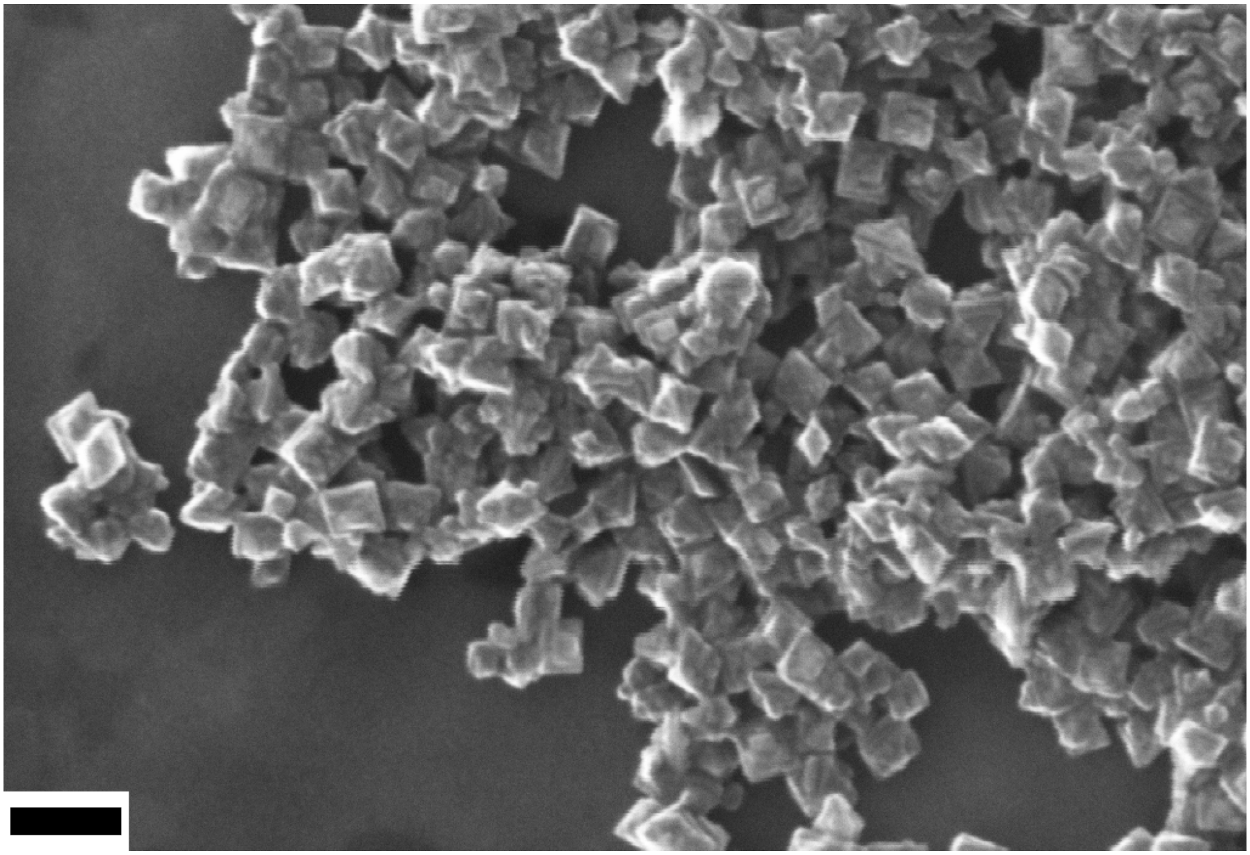


Figure 6. SEM micrograph for nanoparticles synthesized using titanium(IV)bromide (scale bar: 100 nm).

VI. FAST FURIER TRANSFOM OF HIGH-RESOLUTION TEM MICROGRAPHS

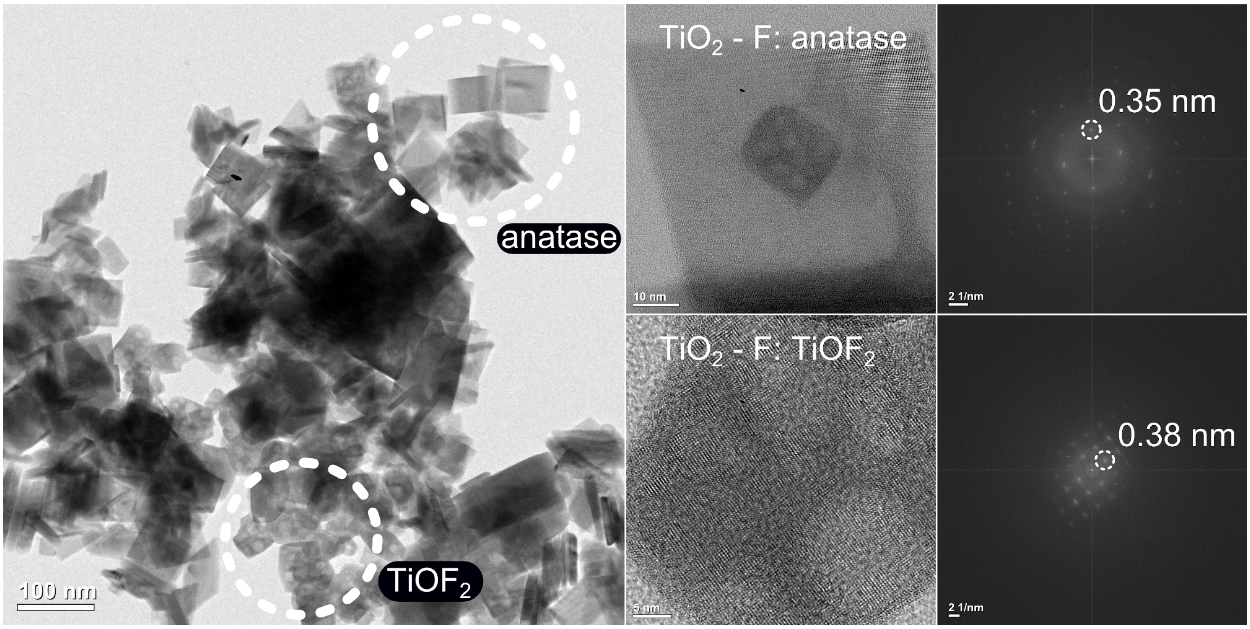


Figure 7. TEM micrographs of single nanoparticles TiO_2-F (left) and the corresponding FFTs (right). The dominant reflexes for anatase {101} (0.35 nm) and $TiOF_2$ {100} (0.38 nm) are marked in the FFT.

VII. ADDITIONAL EXPERIMENT AT REDUCED TEMPERATURE

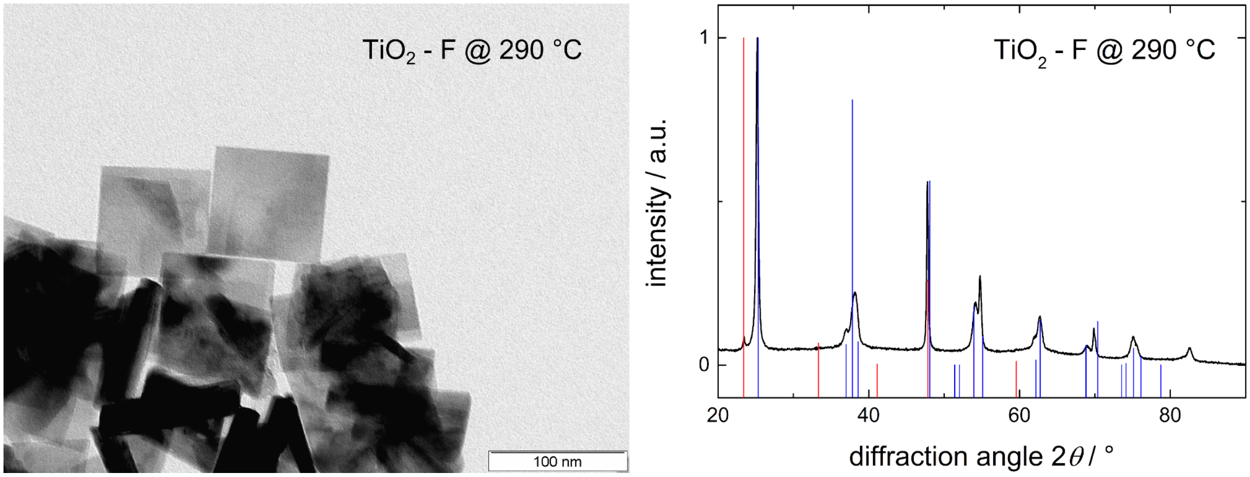


Figure 8. TEM micrographs (left) and XRD data (right) for nanoparticles synthesized using titanium(IV)fluoride at a reduced reaction temperature of 290 °C.

REFERENCES

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