

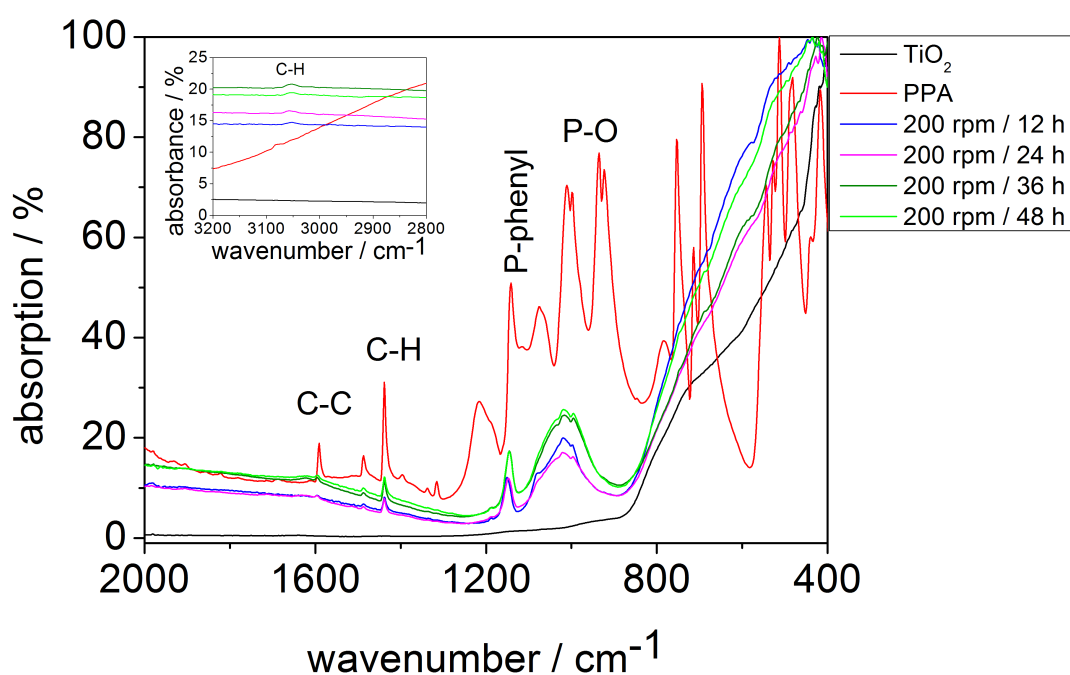
Supporting Information

Important Reaction Parameters in the Synthesis of Phenylphosphonic Acid Functionalized Titania Particles by Reactive Milling

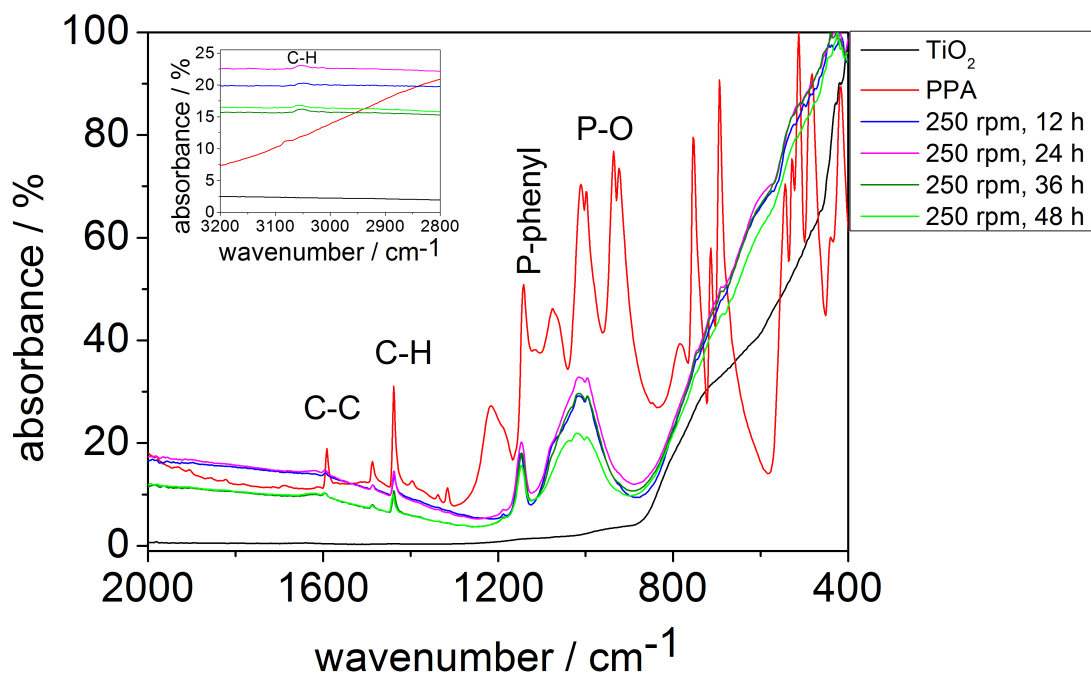
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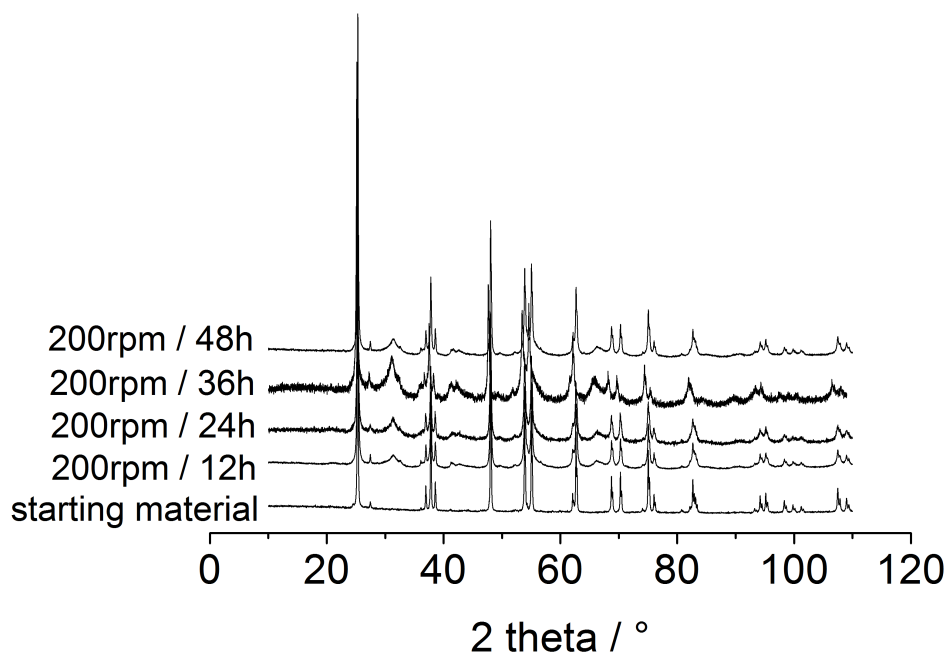
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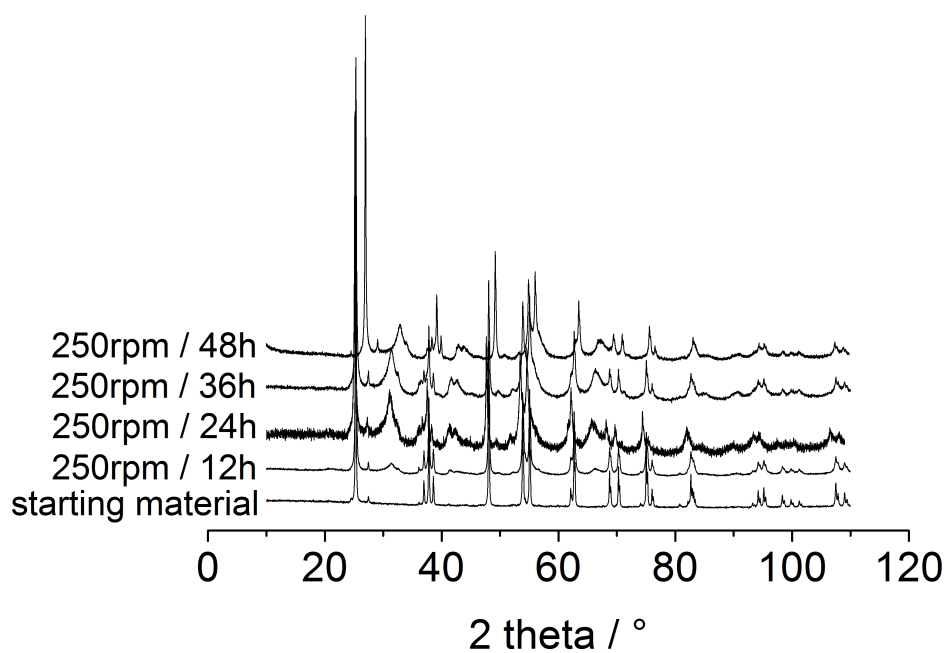
S 1: FTIR-spectra: starting material titania, coupling agent phenylphosphonic acid and samples after the milling process: 200 rpm / 12 h, 200 rpm / 24 h, 200 rpm / 36 h, 200 rpm / 48 h; surface modification has taken place after the milling process, which is indicated by the characteristic bands for aromatic C-C oscillation (1600 cm⁻¹), the C-H oscillation (1440 cm⁻¹), P-phenyl vibrations (1150 cm⁻¹), the wide band at 1000 cm⁻¹ (P-O region) and the aromatic C-H oscillation at 3050 cm⁻¹.



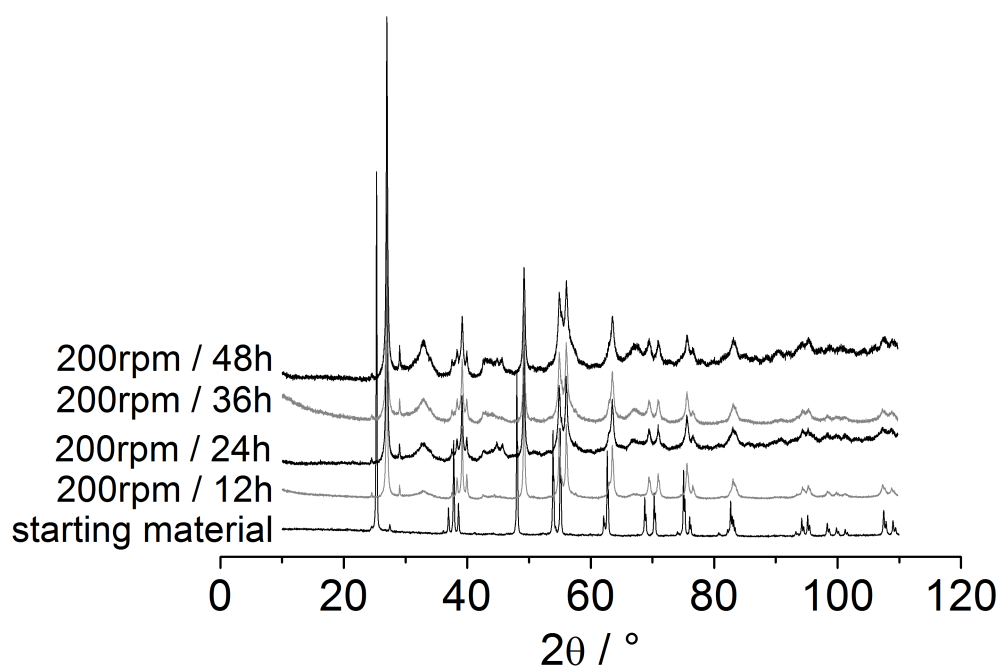
S 2: FTIR-spectra: starting material titania, coupling agent phenylphosphonic acid and samples after the milling process: 250 rpm / 12 h, 250 rpm / 24 h, 250 rpm / 36 h, 250 rpm / 48 h; surface modification has taken place after the milling process, which is indicated by the characteristic bands for aromatic C-C oscillation (1600 cm^{-1}), the C-H oscillation (1440 cm^{-1}), P-phenyl vibrations (1150 cm^{-1}), the wide band at 1000 cm^{-1} (P-O region) and the aromatic C-H oscillation at 3050 cm^{-1} .



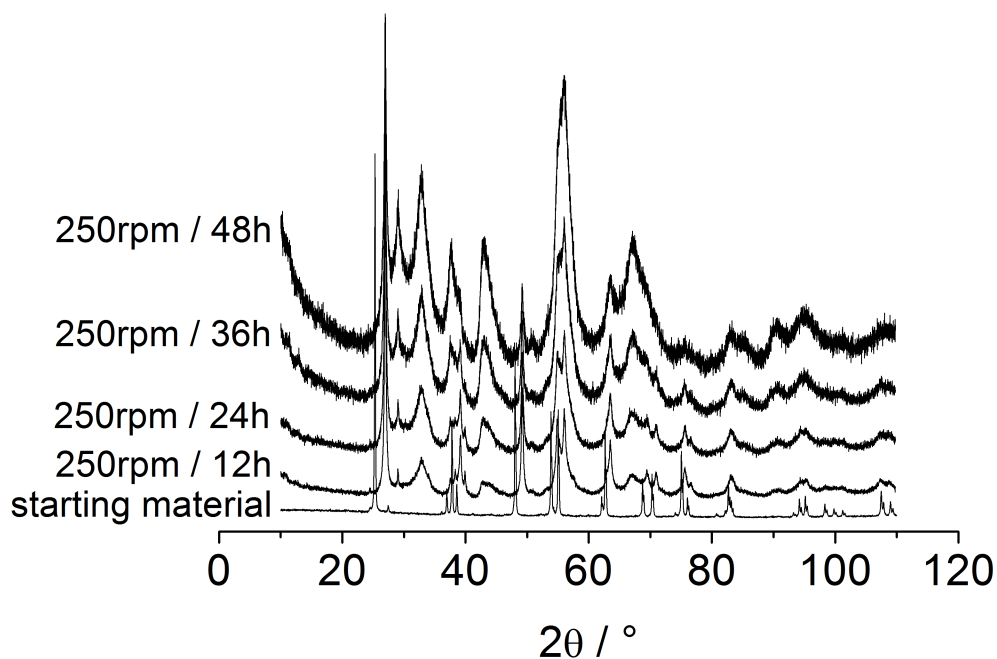
S 3: XRD patterns of the starting material anatase and the samples after milling with phenylphosphonic acid at 200 rpm with different durations. After the milling the presence of high pressure TiO_2 ($2\theta = 31^\circ, 42^\circ$ and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.



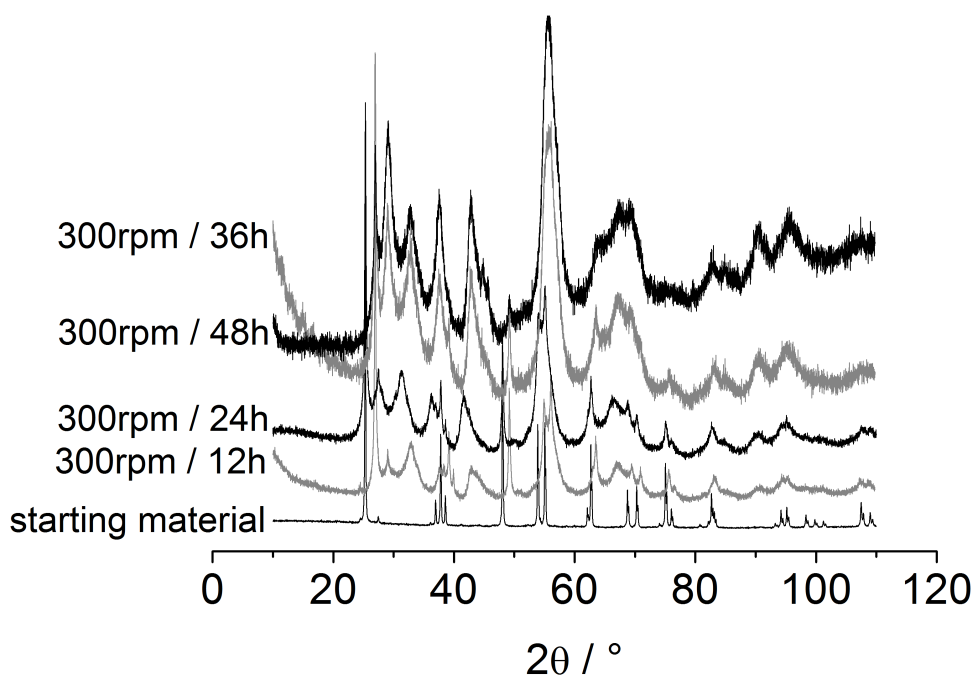
S 4: XRD patterns of the starting material anatase and the samples after milling with phenylphosphonic acid at 250 rpm with different durations. After the milling the presence of high pressure TiO₂ ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.



S 5: XRD patterns of the starting material anatase and the samples after milling without any additive at 200 rpm with different durations. After the milling the presence of high pressure TiO₂ ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.



S 6: XRD patterns of the starting material anatase and the samples after milling without any additive at 250 rpm with different durations. After the milling the presence of high pressure TiO_2 ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.



S 7: XRD patterns of the starting material anatase and the samples after milling without any additive at 300 rpm with different durations. After the milling the presence of high pressure TiO_2 ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.

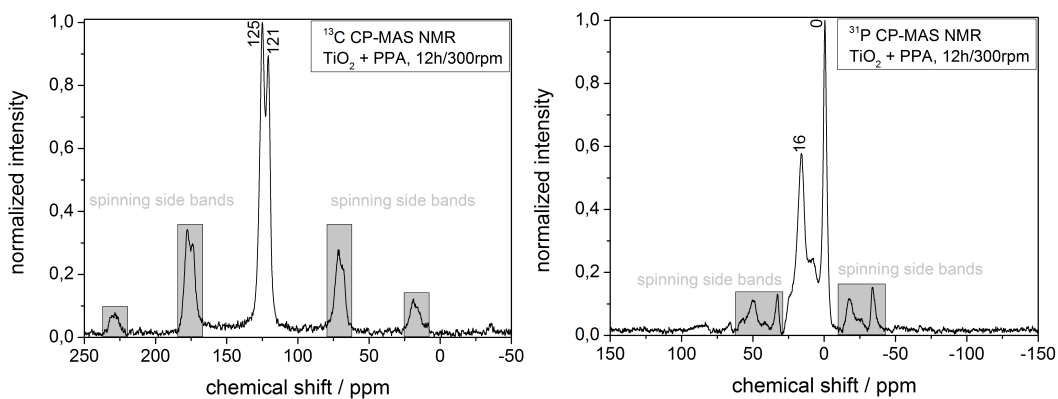
Table S 1: Composition of titania milled with phenylphosphonic acid as coupling agent at specific process parameters

Process parameters	anatase / wt%	rutile / wt%	high pressure / wt%
starting material	98.2 ± 0.1	1.8 ± 0.1	0
200 rpm / 12 h	69.1 ± 0.2	2.9 ± 0.1	28.0 ± 0.2

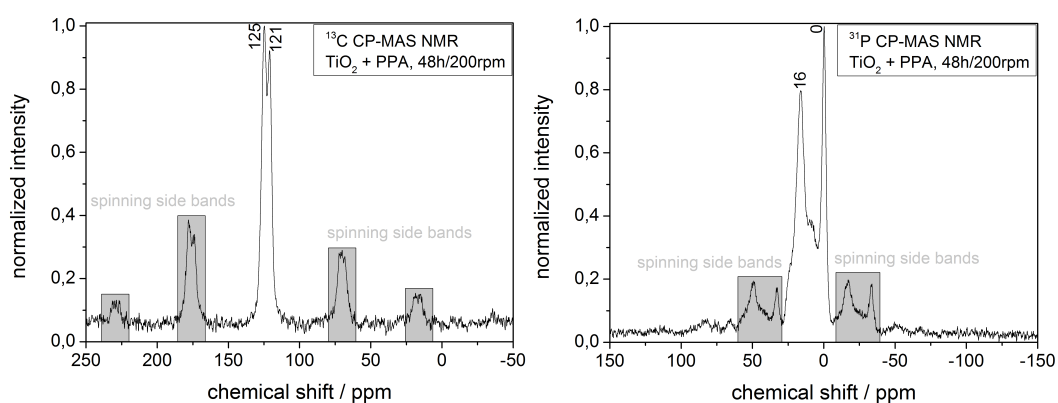
200 rpm / 24 h	64.4 ± 0.3	2.3 ± 0.2	33.3 ± 0.3
200 rpm / 36 h	42.5 ± 0.3	3.8 ± 0.2	53.7 ± 0.3
200 rpm / 48 h	62.4 ± 0.2	3.0 ± 0.1	34.6 ± 0.2
250 rpm / 12 h	71.9 ± 0.2	2.6 ± 0.1	25.5 ± 0.2
250 rpm / 24 h	36.7 ± 0.3	4.1 ± 0.2	59.2 ± 0.3
250 rpm / 36 h	36.9 ± 0.2	3.9 ± 0.1	59.2 ± 0.2
250 rpm / 48 h	41.2 ± 0.3	4.3 ± 0.2	54.2 ± 0.4
300 rpm / 12 h	41.3 ± 0.2	4.3 ± 0.2	54.4 ± 0.2
300 rpm / 24 h	18.3 ± 0.2	4.1 ± 0.1	77.6 ± 0.2
300 rpm / 36 h	13.4 ± 0.2	6.0 ± 0.2	80.6 ± 0.3
300 rpm / 48 h	18.3 ± 0.2	4.1 ± 0.1	77.6 ± 0.2

Table S 2: Composition of titania milled without any coupling agent at specific process parameters

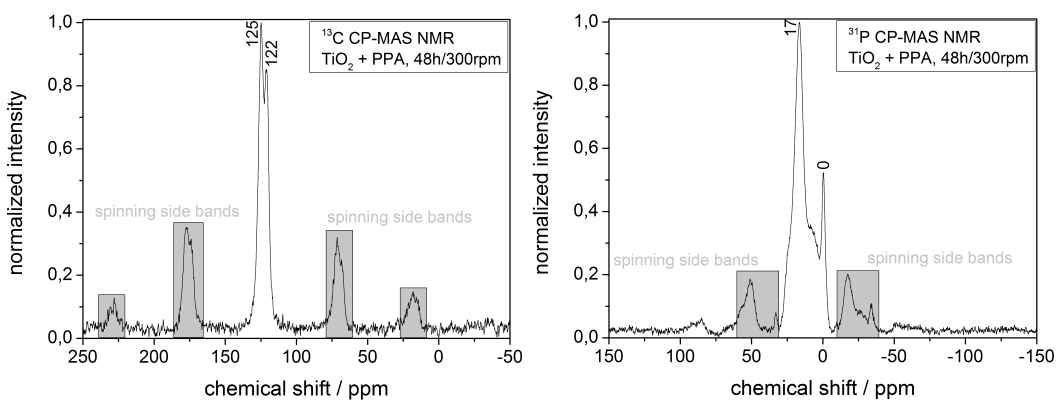
Process parameters	anatase / wt%	rutile / wt%	high pressure / wt%
starting material	98.2 ± 0.1	1.8 ± 0.1	0
200 rpm / 12 h	78.1 ± 0.3	2.4 ± 0.1	19.5 ± 0.3
200 rpm / 24 h	51.9 ± 0.6	2.0 ± 0.1	46.1 ± 0.6
200 rpm / 36 h	50.1 ± 0.4	3.1 ± 0.1	46.8 ± 0.4
200 rpm / 48 h	37.1 ± 0.4	3.8 ± 0.2	59.1 ± 0.4
250 rpm / 12 h	40.7 ± 0.4	3.3 ± 0.2	56.0 ± 0.4
250 rpm / 24 h	23.0 ± 0.3	11.0 ± 0.3	66.0 ± 0.4
250 rpm / 36 h	12.4 ± 0.2	18.0 ± 0.5	69.6 ± 0.5
250 rpm / 48 h	6.1 ± 0.1	26.6 ± 0.5	67.3 ± 0.5
300 rpm / 12 h	23.6 ± 0.2	14.5 ± 0.4	61.9 ± 0.4
300 rpm / 24 h	14.6 ± 0.3	19.0 ± 0.6	66.4 ± 0.6
300 rpm / 36 h	6.4 ± 0.1	36.1 ± 0.5	57.5 ± 0.5
300 rpm / 48 h	2.4 ± 0.1	38.0 ± 0.6	59.6 ± 0.6



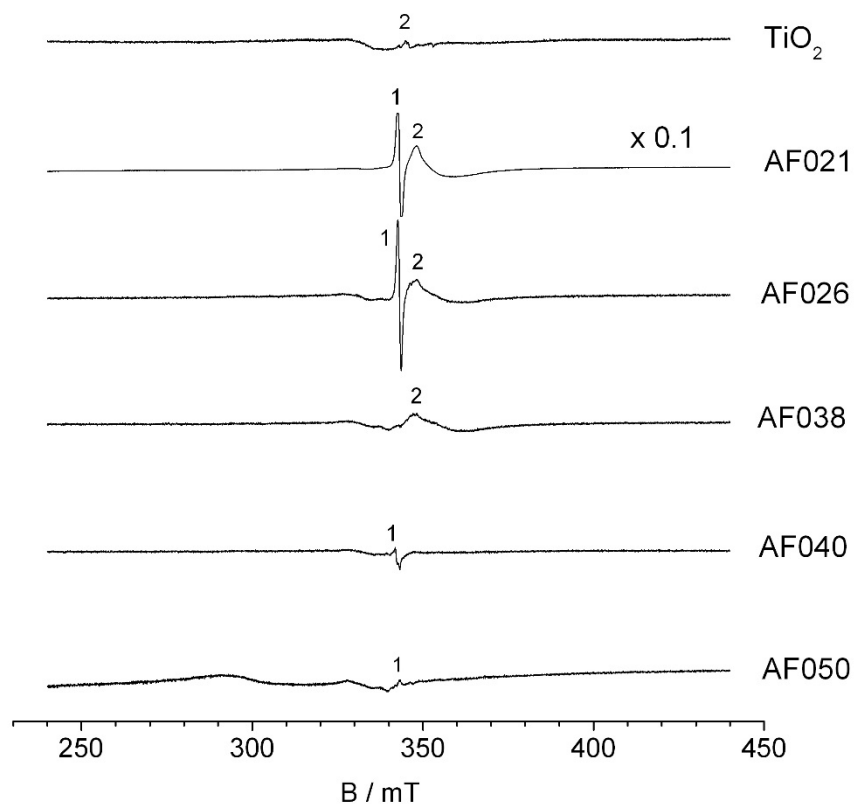
S 8: Titania milled with phenylphosphonic acid for 12 h at 300 rpm, ¹³C solid state NMR (left) and ³¹P solid state NMR (right)



S 9: Titania milled with phenylphosphonic acid for 48 h at 200 rpm, ¹³C solid state NMR (left) and ³¹P solid state NMR (right)



S 10: Titania milled with phenylphosphonic acid for 48 h at 300 rpm, ¹³C solid state NMR (left) and ³¹P solid state NMR (right)



S 11: ESR spectra of the starting material TiO₂ and samples after the milling process. Titania milled with phenylphosphonic acid in a WC/Co-hard metal grinding bowl (AF021) and in a zirconia grinding bowl (AF026), titania milled with dodecylphosphonic acid in a zirconia grinding bowl (AF038), titanina milled without any additive in a WC/Co-hard metal grinding bowl (AF050) and in a zirconia grinding bowl (AF040).