

Supplementary Information

The washing solution of the sample which was exposed to the strongest conditions was analyzed to clarify whether changes occurred at the dodecylphosphonic acid due to the milling process. It turned out that the NMR spectra depend on the concentration of the dodecylphosphonic acid. For this reason a serial dilution was prepared and analyzed by NMR spectroscopy. The concentration decreases from sample DPA_1 to DPA_3. At the end the washing solution was analyzed (Figures S1–S6). ^1H -, ^{13}C - and ^{31}P -NMR spectra show the phenyl phosphonic acid being the only species present in the washing solution, no side or decomposition products were detected. The few additional peaks are due to residues of the washing agent ethanol. Therefore it can be assumed that the coupling agent is not degraded during the milling process.

Figure S1. DPA_1: ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 1.76\text{--}0.83$ (25 H), 10.21 (2 H) ppm (**left**) and DPA_2: ^1H -NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 1.79\text{--}0.87$ (25 H), 9.19 (2 H) ppm (**right**).

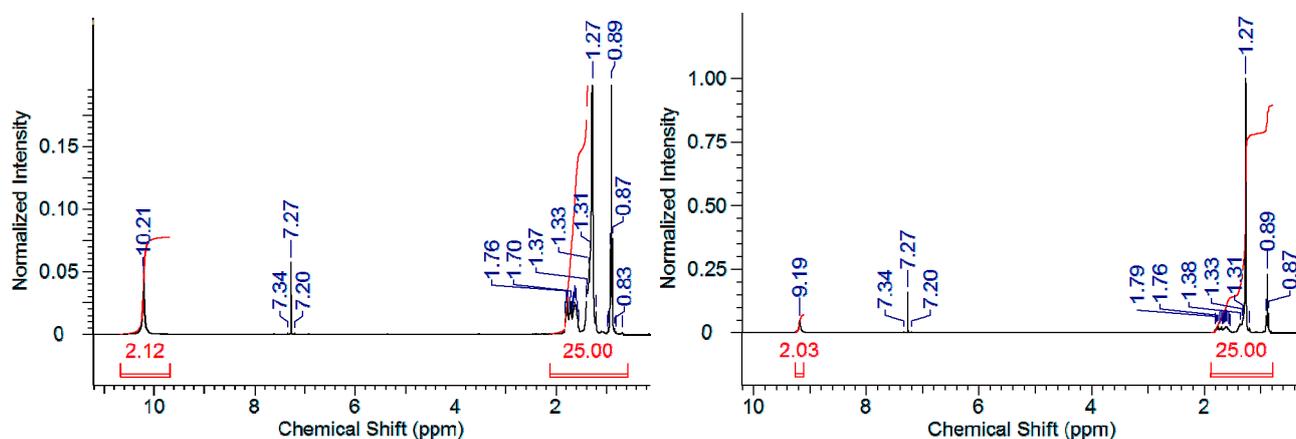


Figure S2. DPA_3: ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 1.63\text{--}0.87$ (25 H), 6.95 (2 H) ppm (**left**) and washing solution: ^1H -NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 1.78\text{--}0.87$ (25 H), 9.68 (2 H) ppm (**right**).

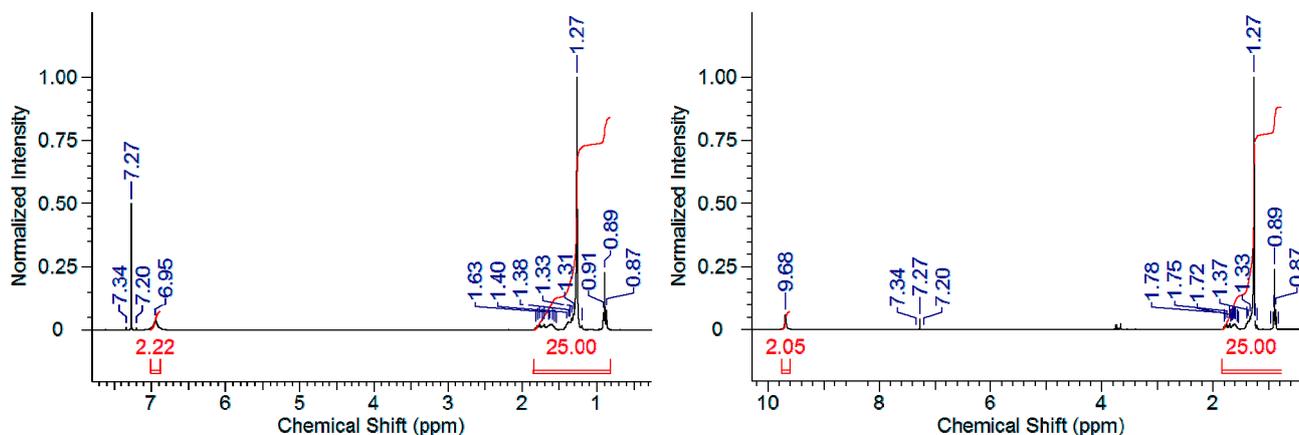


Figure S3. DPA_1: ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 25.24$ (d, $^1J = 145.25$ Hz, 1 C), 30.44 (d, $^2J = 17.06$ Hz, 1 C), 14.10 (1 C), 21.96 (1 C), 22.02 (1 C), 22.69 (1 C), 29.06 (1 C), 29.35 (1 C), 29.39 (1 C), 29.60 (1 C), 29.63 (1 C), 31.92 (1 C) (**left**) and DPA_2: ^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 25.23$ (d, $^1J = 145.25$ Hz, 1 C), 30.44 (d, $^2J = 17.06$ Hz, 1 C), 14.10 (1 C), 21.95 (1 C), 22.02 (1 C), 22.69 (1 C), 29.06 (1 C), 29.35 (1 C), 29.39 (1 C), 29.60 (1 C), 29.63 (1 C), 31.92 (1 C) (**right**).

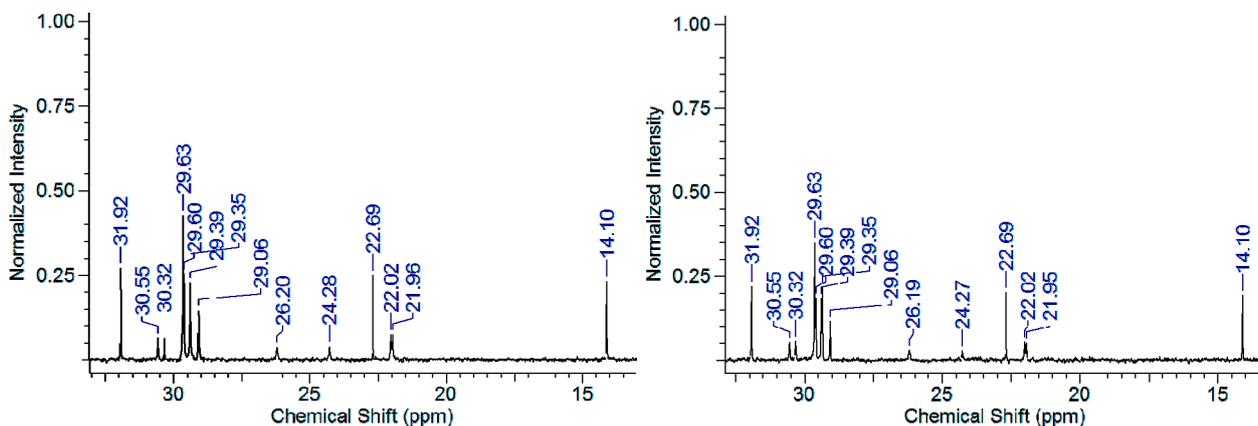


Figure S4. DPA_3: ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 14.10$ (1 C), 21.93 (1 C), 22.69 (1 C), 29.06 (1 C), 29.35 (1 C), 29.38 (1 C), 29.59 (1 C), 29.63 (1 C), 31.92 (1 C), there are some peaks missing which is due to the poor concentration of the solution (**left**) and washing solution: ^{13}C -NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 25.50$ (d, $^1J = 144.70$ Hz, 1 C), 30.50 (d, $^2J = 17.06$ Hz, 1 C), 14.10 (1 C), 22.04 (1 C), 22.11 (1 C), 22.69 (1 C), 29.10 (1 C), 29.36 (1 C), 29.42 (1 C), 29.62 (1 C), 29.65 (1 C), 31.92 (1 C) (**right**).

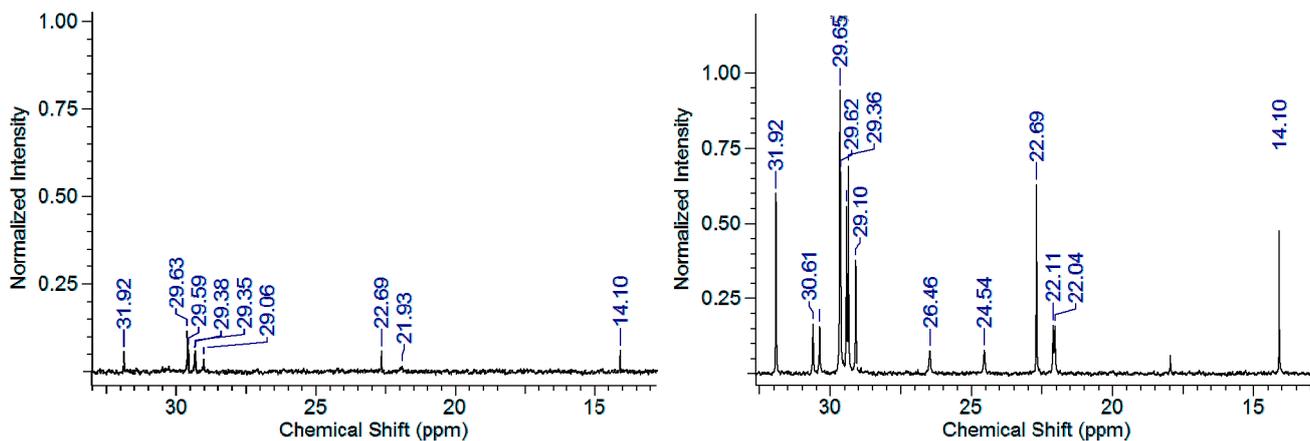


Figure S5. DPA_1: ^{31}P NMR (120 MHz, CDCl_3 , 25 °C): $\delta = 37.55$ ppm (**left**) and DPA_2: ^{31}P -NMR (120 MHz, CDCl_3 , 25 °C): $\delta = 37.65$ ppm (**right**).

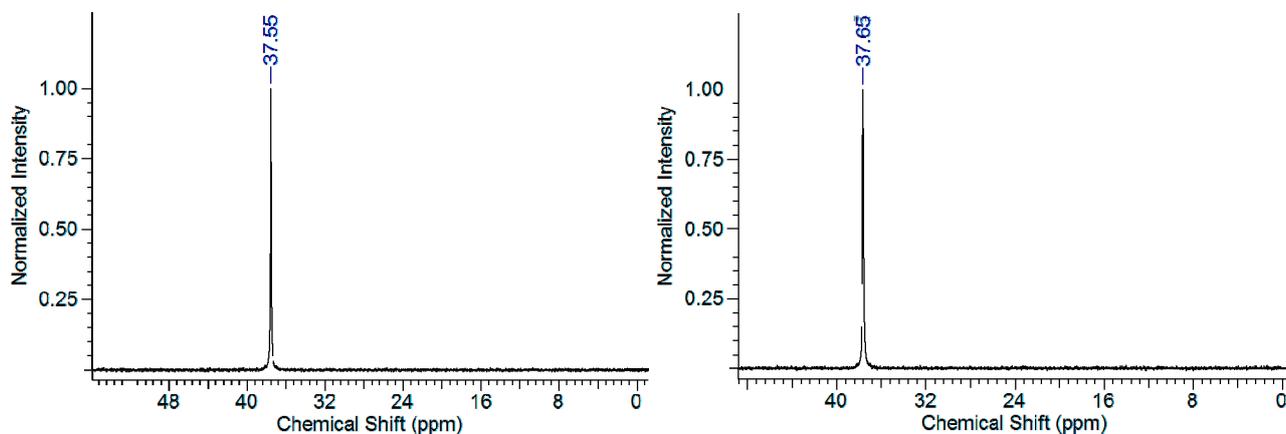


Figure S6. DPA_3: ^{31}P -NMR (120 MHz, CDCl_3 , 25 °C): $\delta = 38.07$ ppm (**left**) and washing solution: ^{31}P -NMR (120 MHz, CDCl_3 , 25 °C): $\delta = 36.70$ ppm (**right**).

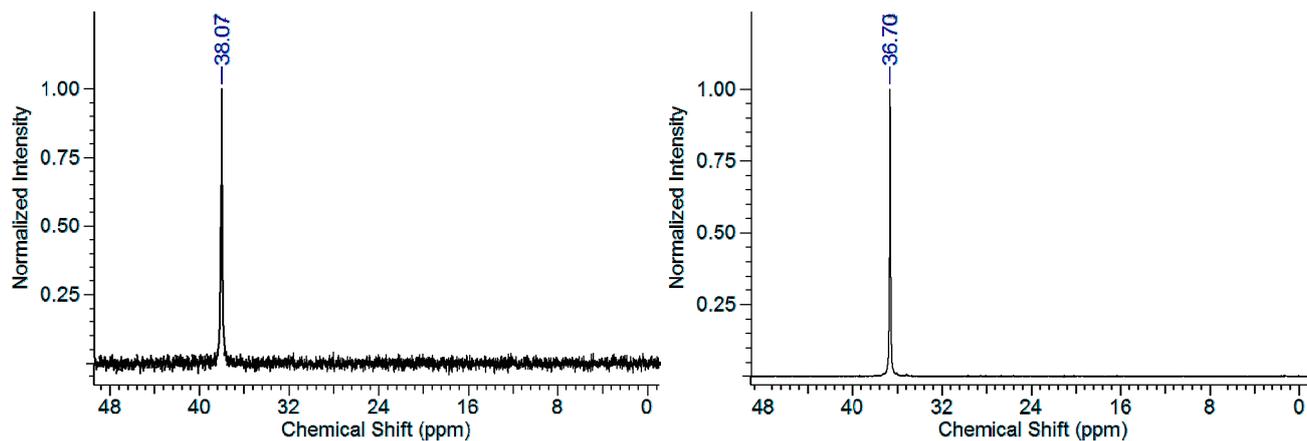


Figure S7. FTIR-spectra of the starting material titania, coupling agent dedecylphosphonic acid (DDPA) and samples after the milling process at 200 rpm; surface modification has taken place after the milling process, which is indicated by the characteristic bands for the C–H oscillation (1440 cm^{-1} and 2900 cm^{-1}) and the wide band at 1000 cm^{-1} (P–O region).

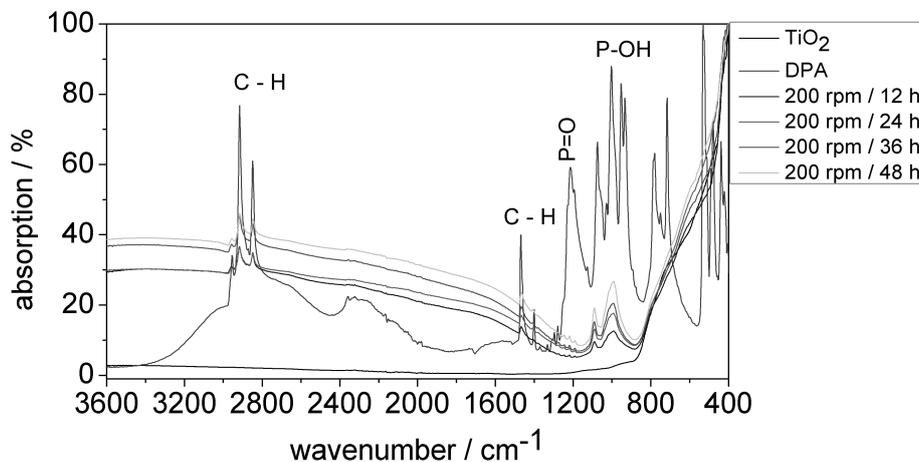


Figure S8. FTIR-spectra of the starting material titania, coupling agent dedecylphosphonic acid and samples after the milling process at 250 rpm; surface modification has taken place after the milling process, which is indicated by the characteristic bands for the C–H oscillation (1440 cm^{-1} and 2900 cm^{-1}) and the wide band at 1000 cm^{-1} (P–O region).

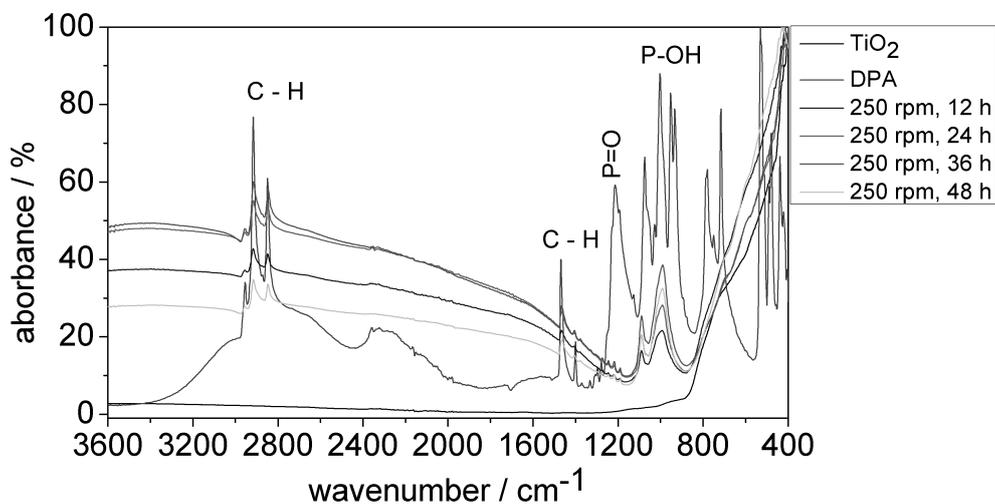


Figure S9. ^{13}C CP-MAS NMR spectrum, titania milled with dodecylphosphonic acid at 300 rpm for 12 h.

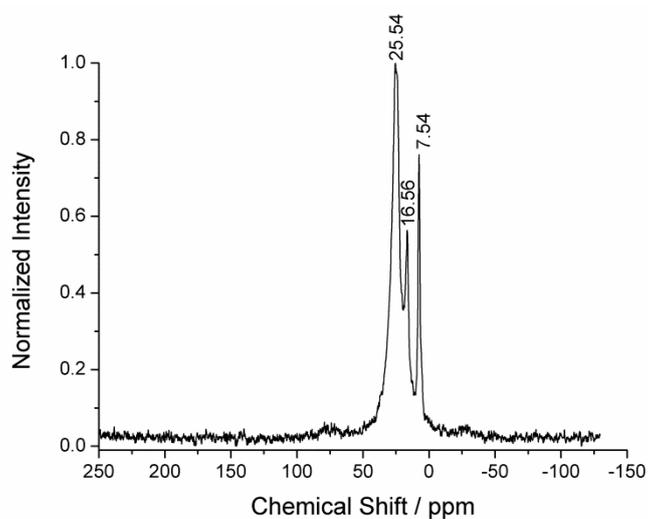


Figure S10. ^{31}P CP-MAS NMR spectrum, titania milled with dodecylphosphonic acid at 300 rpm for 12 h

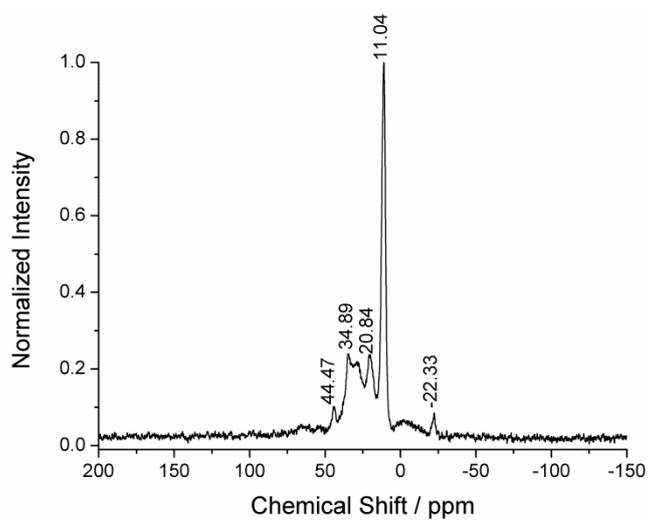


Figure S11. ^{13}C CP-MAS NMR spectrum, titania milled with dodecylphosphonic acid at 300 rpm for 48 h.

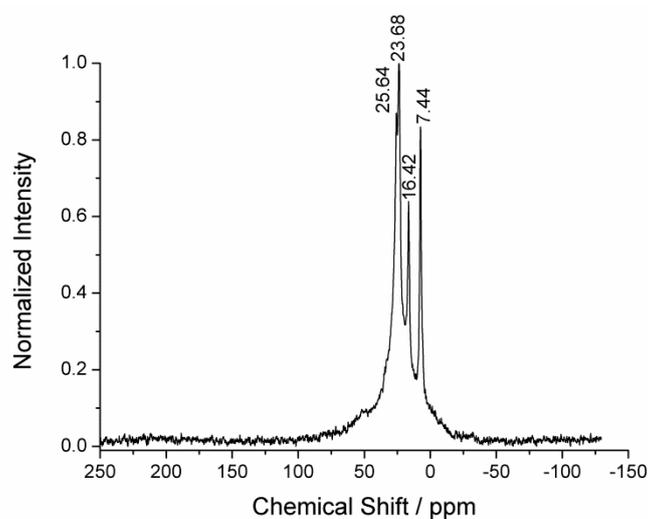


Figure S12. ^{31}P CP-MAS NMR spectrum, titania milled with dodecylphosphonic acid at 300 rpm for 48h.

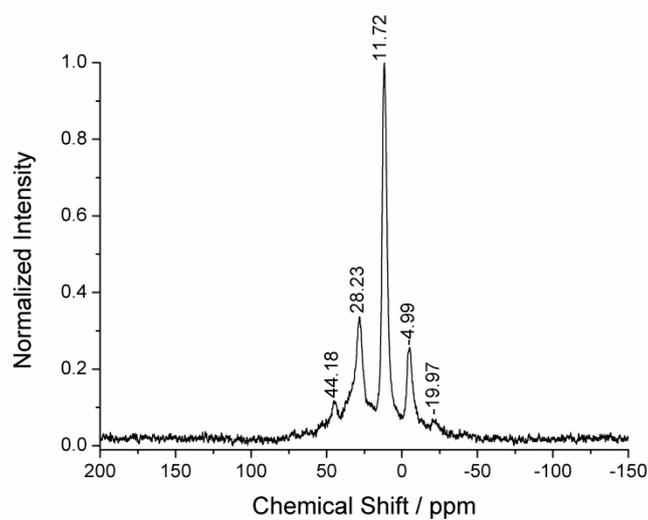


Figure S13. XRD patterns of the starting material anatase and the samples after milling with dedecylphosphonic acid (DDPA) at 200 rpm with different durations. After the milling the presence of high pressure TiO₂ ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.

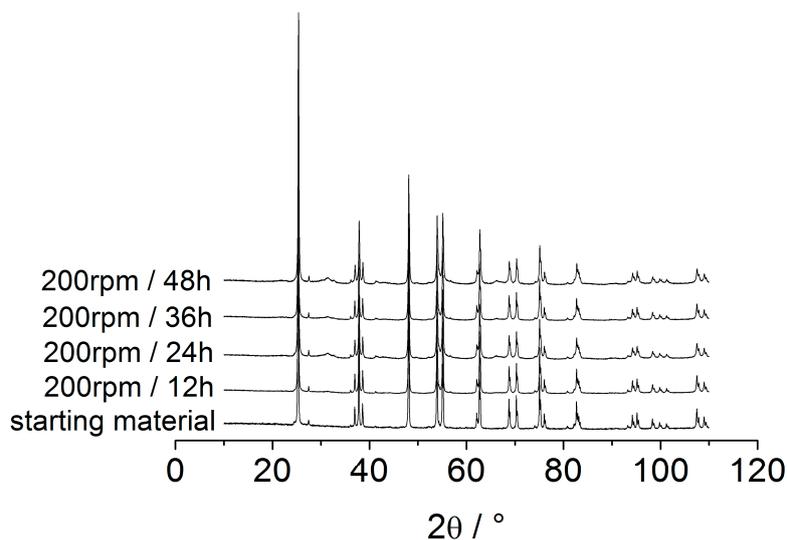


Figure S14. XRD patterns of the starting material anatase and the samples after milling with phenylphosphonic acid at 250 rpm with different durations. After the milling the presence of high pressure TiO₂ ($2\theta = 31^\circ$, 42° and 66°) and rutile ($2\theta = 27^\circ$) is indicated by additional reflections.

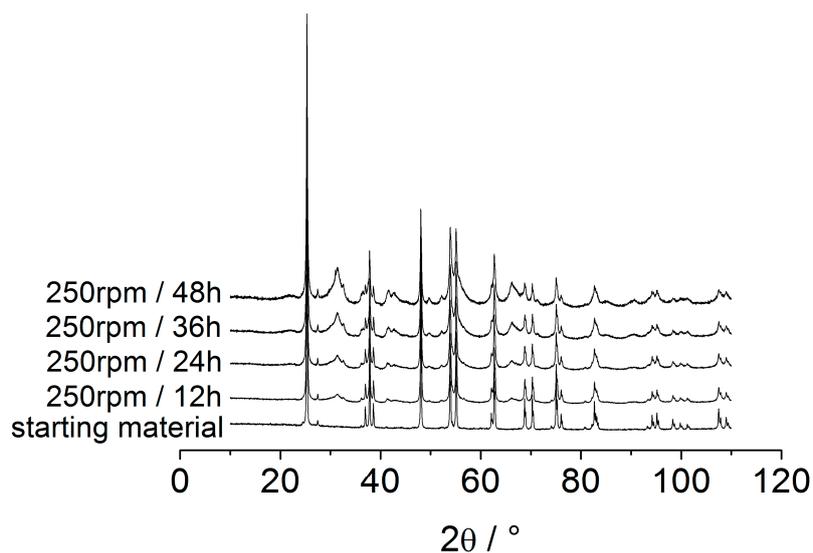


Table S1. Composition of titania milled with dodecylphosphonic acid as coupling agent at specific process parameters.

Process parameters	Anatase/wt%	Rutile/wt%	High pressure/wt%
starting material	98.2 ± 0.1	1.8 ± 0.1	0
200 rpm/12 h	91.9 ± 0.2	1.8 ± 0.1	6.3 ± 0.2
200 rpm/24 h	80.6 ± 0.2	2.4 ± 0.1	16.9 ± 0.2
200 rpm/36 h	86.8 ± 0.2	1.9 ± 0.1	11.3 ± 0.2
200 rpm/48 h	77.8 ± 0.3	2.6 ± 0.1	19.6 ± 0.3
250 rpm/12 h	73.9 ± 0.2	2.5 ± 0.1	23.6 ± 0.2
250 rpm/24 h	64.9 ± 0.2	3.0 ± 0.1	32.1 ± 0.2
250 rpm/36 h	50.8 ± 0.2	3.6 ± 0.1	45.6 ± 0.2
250 rpm/48 h	40.6 ± 0.2	3.9 ± 0.2	55.5 ± 0.2
300 rpm/12 h	66.5 ± 0.2	2.9 ± 0.1	30.6 ± 0.2
300 rpm/24 h	55.0 ± 0.2	3.5 ± 0.1	41.5 ± 0.2
300 rpm/36 h	41.3 ± 0.2	3.4 ± 0.1	55.3 ± 0.2
300 rpm/48 h	24.9 ± 0.2	3.5 ± 0.2	71.6 ± 0.2

Figure S15. 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).