

Supplementary information

Straightforward solid-phase modification of TiO₂ with propylphosphonic acid via manual grinding and shaker mixing: enhancing modification degree by thermal control while improving atom economy

Kaimin Zhang^{a,b}, Jinxin Wang^{*b,c}, Nick Gys^{b,d,e,f}, Elien Derveaux^g, Nahal Ghanemnia^g, Wouter Marchal^g, Peter Adriaenssens^g, Vera Meynen^{*b,e}

^aSchool of Resources and Safety Engineering, Wuhan Institute of Technology, Wuhan 430074, China

^bLaboratory for Adsorption and Catalysis (LADCA), Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610, Wilrijk, Belgium

^cSchool of Electrical and Electronic Engineering, Hubei University of Technology, Wuhan 430068, China

^dCenter for Membrane Separations, Adsorption, Catalysis, and Spectroscopy KU Leuven, University of Leuven, Celestijnenlaan 200F, 3001, Leuven, Belgium

^eFlemish Institute for Technological research, VITO NV, Boeretang 200, 2400 Mol, Belgium

^fMaterials and Chemistry, Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050, Brussels, Belgium

^gApplied and Circular Chemistry, NMR Group, Hasselt University, Campus Diepenbeek - Gebouw D, 3590 Diepenbeek, Belgium

*Corresponding author: angjinixn@yeah.net, vera.meynen@uantwerpen.be

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Supplementary Results and Discussion

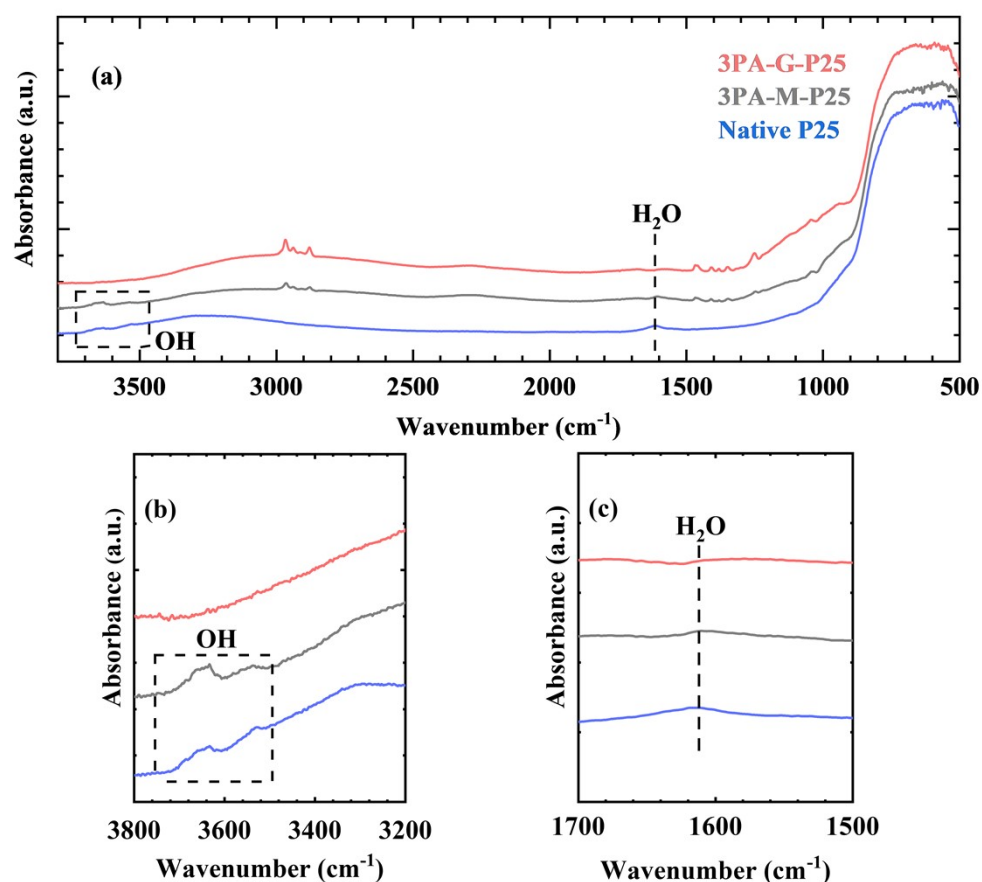


Figure S1. Normalized DRIFT spectra between 3800–500 cm⁻¹ of samples 3PA-G-P25, 3PA-M-P25, and native P25, before washing and without thermal treatment, measured as a 2 wt% dilution in KBr under an Ar flow of 50 mL/min at RT. (b), (c) are zoom-ins of (a) region between 3800–3200 cm⁻¹ and 1700–1500 cm⁻¹, respectively.

In order to semi-quantify the changes in OH groups on the surface, 3PA-G-P25, 3PA-M-P25, and native P25 were measured as 2 wt% diluted samples in KBr at RT, as shown in Figure S1. Similar conclusions were obtained: 3PA-G-P25 showed barely visible signals of OH groups in the region of 3800–3500 cm⁻¹^{1,2}, while two resolved broad bands in this region could be found for both 3PA-M-P25 and native P25. Therefore, the decreased intensity of OH groups on 3PA-G-P25 confirms that less OH groups are present on its surface as compared to 3PA-M-P25 and native P25. This can be rationalized by the fact that the grinding process promotes the grafting or the (hydrogen-bond) interactions between 3PA and the P25 titania surface, resulting in a decrease in the number of free surface OH groups, in contrast to simple shaker mixing.

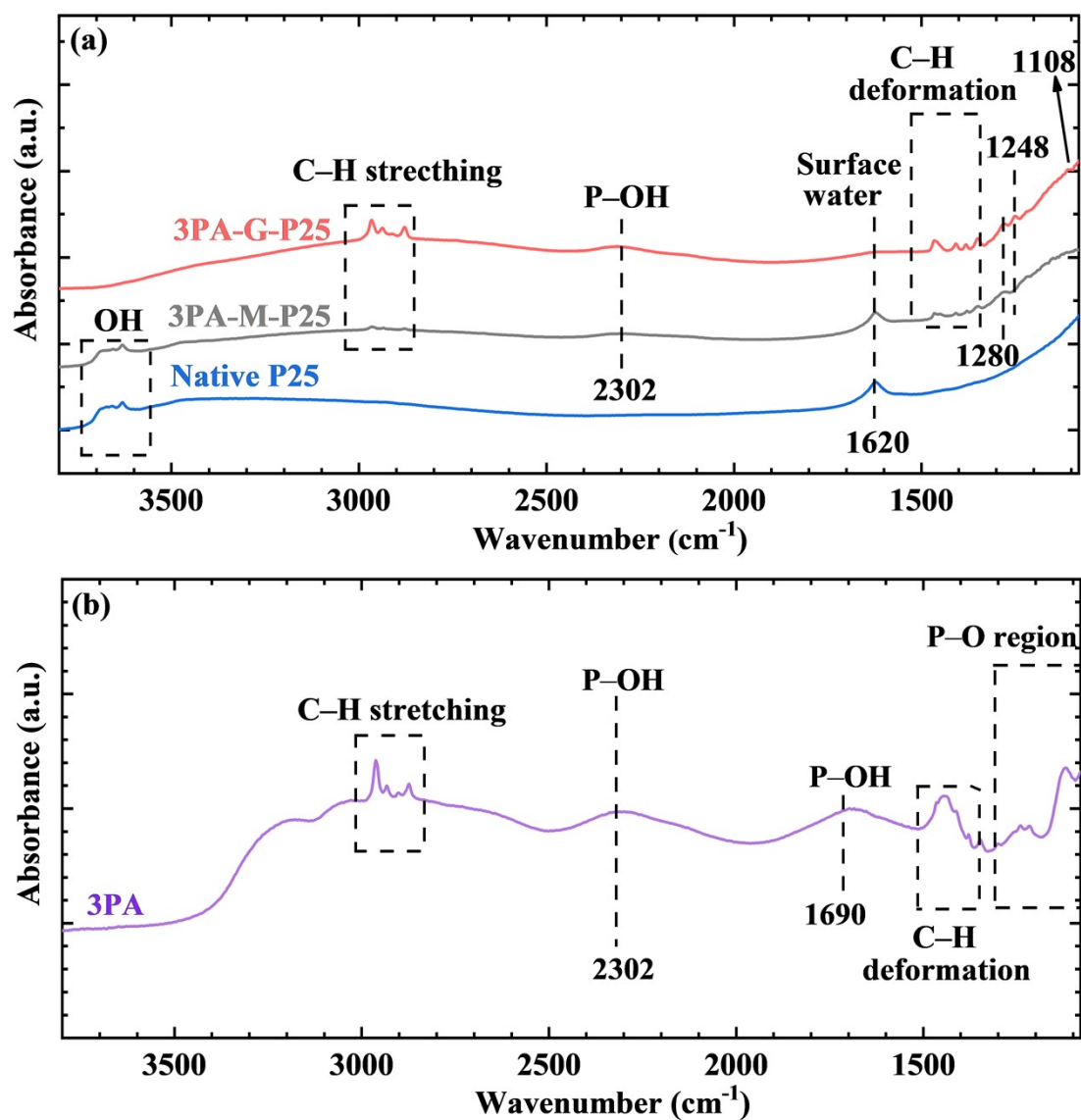


Figure S2. Unnormalized DRIFT spectra of diluted and undiluted samples were measured under an Ar flow of 50 mL/min at RT. The spectra of undiluted 3PA-G-P25, 3PA-M-P25, and native P25, before washing and without thermal treatment, are presented in (a). The spectrum of diluted 3PA (2 wt% in KBr) is shown in (b).

Table S1. Assignments of OH groups between 3750–3600 cm ⁻¹ .	
Wavenumber (cm ⁻¹)	Assignments
3630	Surface OH groups hydrogen-bonded to coordinated water ^{3,4}
3655, 3670, 3720	Surface OH groups ^{3,5}
3690	Water with dangling H located at the end of polymeric water chains adsorbed on the surface ^{3,4}

Text S1: Differences in water signal (1620 cm^{-1} or 1630 cm^{-1}) in DRFIT in Figure 1.

Furthermore, in contrast to native P25, also differences in the water deformation mode between $1630\text{--}1620\text{ cm}^{-1}$ can be observed for 3PA-G-P25 and 3PA-M-P25 in Figure 1a^{3,5}. 3PA-M-P25 (1620 cm^{-1}), 3PA-G-P25 (1630 cm^{-1}), and native P25 (1620 cm^{-1}) all displayed the water deformation signal (see enlarged spectra in Figure 2). However, the signal is broader and much less resolved for 3PA-G-P25 than for 3PA-M-P25 and native P25, which could be due to a different interaction with water, causing a broadening of the 1620 cm^{-1} signal or due to a combination with the broad P–OH signal centered at 1690 cm^{-1} of pure 3PA (Figure 1c) and the surface water at 1620 cm^{-1} . The latter could suggest a promotion of the interaction between 3PA and P25 during the manual grinding process, resulting in a shift of the P–OH groups from 1690 cm^{-1} towards 1620 cm^{-1} causing an overlap with the water deformation signal. Although, the P–OH signal at 2302 cm^{-1} seems not to have shifted.

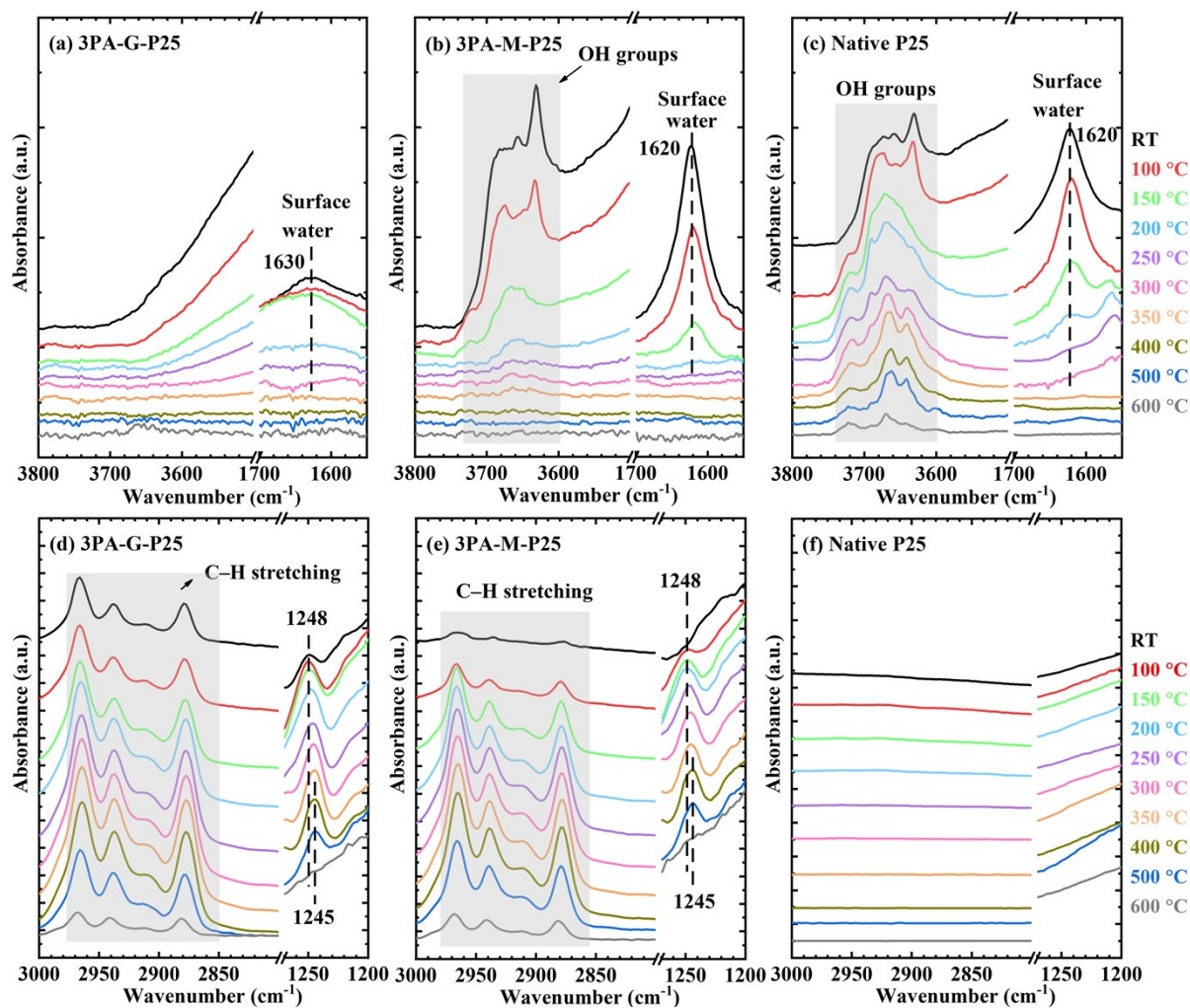


Figure S3. Unnormalized *in-situ* DRIFT spectra in function of temperature of undiluted 3PA-G-P25, 3PA-M-P25, and native P25, before washing and without thermal treatment, measured under an Ar flow of 50 mL/min from RT to 600 °C. (a-c) Spectra between $3800\text{--}3500\text{ cm}^{-1}$ and $1700\text{--}1550\text{ cm}^{-1}$, (d-f) spectra between $3000\text{--}2800\text{ cm}^{-1}$ and $1280\text{--}1200\text{ cm}^{-1}$, respectively.

Text S2: Changes in 1248 cm^{-1} and $3000\text{--}2800\text{ cm}^{-1}$ in DRFIT in Figure 2.

Interestingly, the 1248 cm^{-1} peak shifted for both 3PA-G-P25 and 3PA-M-P25 to 1245 cm^{-1} upon increasing the temperature to 400 °C, likely related to further promoted interaction between 3PA and P25 upon heating. Above 400 °C, the intensity at 1245 cm^{-1} decreases proportionally with the intensity of the C–H stretching between $3000\text{--}2800\text{ cm}^{-1}$.

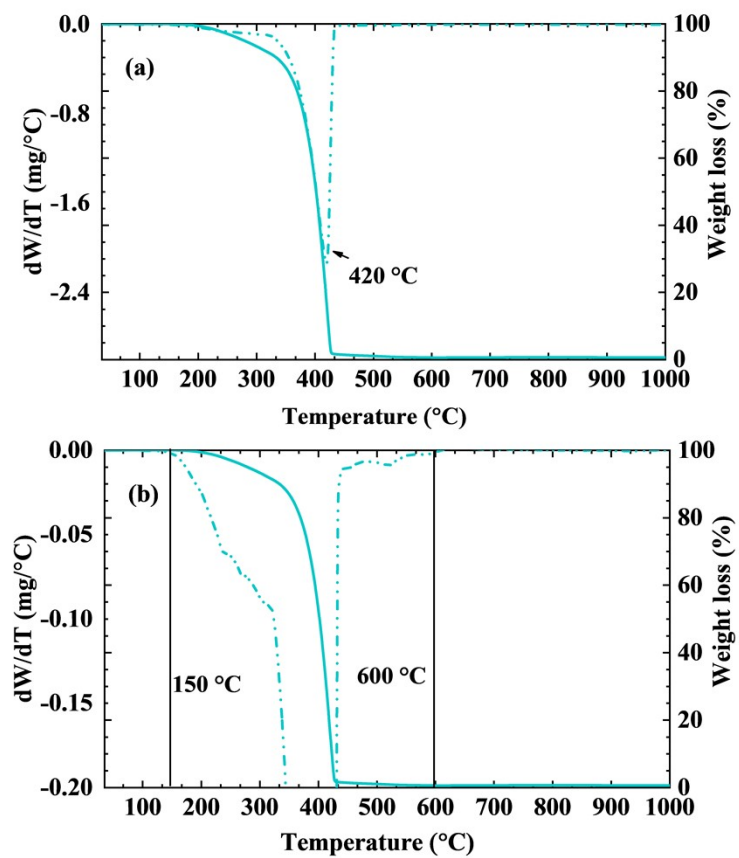


Figure S4. TG/DTG curves of pure 3PA, measured under an Ar flow of 50 mL/min from RT to 1000 °C with a heating rate of 10 °C/min (a). An enlarged DTG curve of (a) is shown in (b). The solid and dash-dot lines represent TG and DTG curves, respectively.

Table S2. Overview of (D)TG results of 3PA-G-P25, 3PA-M-P25, and native P25 in Figure 3.

	3PA-G-P25			3PA-M-P25				Native P25	
Weight loss temperature ranges (°C)	30-135	135-330	430-630	30-135	135-270	270-330	430-630	30-135	135-330
DTG maximal temperature (°C)	90	190	535	78	200	300	535	73	220
DTG maximal (mg/°C)	-0.005	-0.004	-0.029	-0.009	-0.012	-0.007	-0.019	-0.011	-0.004
Weight loss (%)	0.36	0.56	1.78	0.61	1.14	0.33	1.34	0.70	0.63

Text S3: TG and DTG results of 3PA-G-P25 and 3PA-M-P25 in Figure 3.

In contrast to native P25, 3PA-G-P25 and 3PA-M-P25 presented an additional weight loss between 430–630 °C with the DTG maximum at 535 °C. Based on the presence of hydrogen and different carbon fragments in MS (Figure 3c-d), this can be attributed to 3PA. It was found that the weight loss of pure 3PA occurred in a lower temperature range of 150–600 °C with the maximum of the DTG curve at 420 °C (Figure S4). Therefore, the shift of the weight loss and DTG maximum of 3PA in both 3PA-G-P25 and 3PA-M-P25 towards a higher temperature suggests that 3PA was grafted to or at least interacting with the surface of TiO₂. The above *in-situ* DRIFT results showed that the grafting between 3PA and P25 can be promoted during the heating process, between RT and 250 °C. The 3PA grafting on 3PA-M-P25 can thus be caused by the heating during the TGA measurement. Similarly, this grafting could also take place for 3PA-G-P25. It thus becomes challenging to differentiate manual grinding from shaker mixing with TGA-MS.

In addition, the weight loss of the 3PA-M-P25 sample (2.1 wt%) in the region of 30–330 °C is almost two and a half times higher than of 3PA-G-P25 (0.9 wt%) and one and a half times higher than of native P25 (1.3 wt%). This could be linked to i) the condensation between TiO₂ and 3PA releasing water, and ii) the presence of more physisorbed surface water, which is correlated to the hygroscopic property of unreacted/unbonded 3PA. Although the same condensation reaction between TiO₂ and 3PA might also take place for 3PA-G-P25, its lower water weight loss indicates that the hydroxyl groups of P25 have already reacted with 3PA during the manual grinding process, as also observed by DRIFT. Therefore, less condensation reactions can take place between P25 and 3PA as well as between Ti–OH groups on the surface for 3PA-G-P25 during the heating process. On the other hand, Lewis acid sites on P25 might also interact with the P=O groups of 3PA during the manual grinding process. Both these bonded 3PA molecules (either through condensation between P–OH and Ti–OH or coordination between Lewis acid sites and P=O) and decreased hydrophilic sites (P=O, P–OH, Ti–OH, etc.) on the surface reduce the tendency/ability to adsorb water, *i.e.*, decrease contribution of adsorbed surface water for 3PA-G-P25 in this temperature range. These two factors explain the lowest weight loss of water for 3PA-G-P25. All these results suggest that the grafting of 3PA on P25 occurred and can be promoted during the manual grinding process, which is in good agreement with the results obtained from the *in-situ* DRIFT measurements (Figure 1 and 2).

As an important note, 3PA-G-P25 showed a higher weight loss (1.8 wt%) in the temperature range (430–630 °C) than 3PA-M-P25 (1.4 wt%). Given that the same synthesis parameters, *i.e.*, the amount of 3PA and P25 and reaction time, were used in their preparation, the lower weight loss in 3PA-M-P25 might be caused by the inhomogeneous mixing. When a small sample amount is taken for the TGA measurement (~ 20 mg) from the larger batch of the material prepared (~ 1.0 g), it might contain somewhat less 3PA for the more inhomogeneous 3PA-M-P25 material (see later discussion about reproducibility, Figure S5).

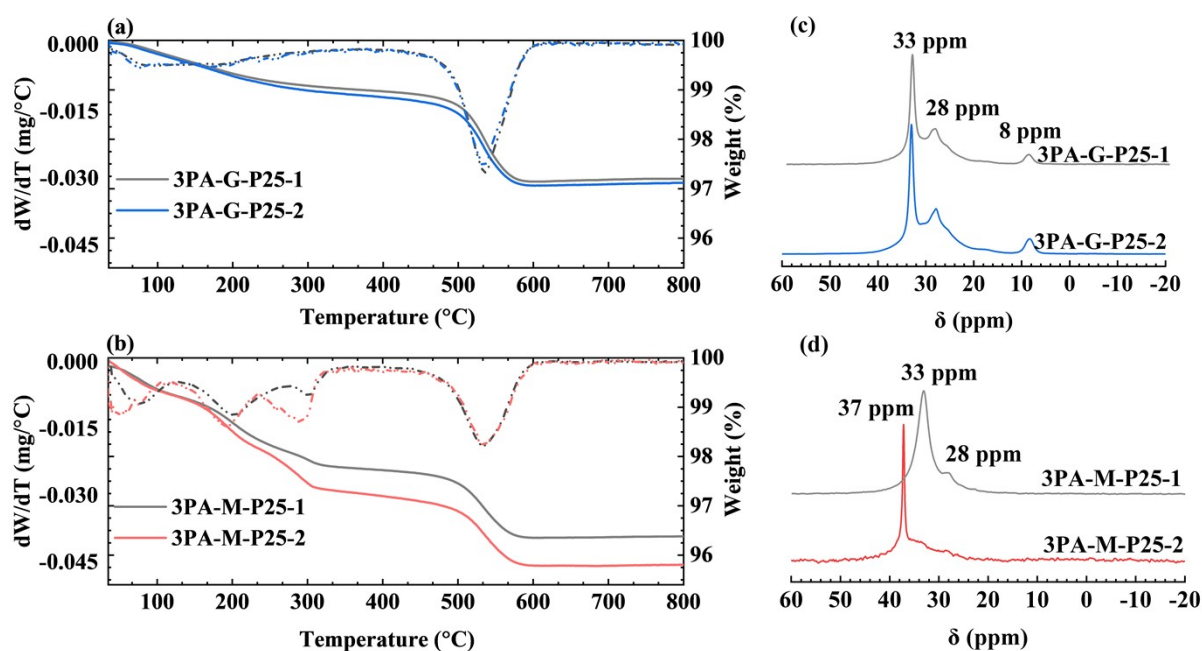


Figure S5. TG/DTG curves (a-b) and ³¹P-MAS NMR spectra (c-d) of 3PA-G-P25 and 3PA-M-P25 from two different batches. All these samples were obtained before washing and without thermal treatment. TG/DTG measurements were carried out under an Ar flow of 50 mL/min from RT to 1000 °C with a heating rate of 10 °C/min. The solid and dash-dot lines represent TG and DTG curves, respectively.

The reproducibility of shaker mixed and manually ground samples was compared as shown in Figure S5. The TG/DTG results of manual grinding samples from two different batches showed the same pattern (Figure S5a). However, differences in the DTG maxima (between RT and 330 °C) were observed for the two shaker mixed samples (Figure S5b). Consistently, the ³¹P-MAS NMR results (Figure S5c) of manually ground samples from the different produced batches were the same, *i.e.* two well resolved signals with a major contribution at 28 ppm and a sharp signal at 33 ppm, in addition to a small signal at 8 ppm. However, differences were again observed for the shaker mixed samples from two different synthetic batches. The ³¹P-MAS NMR spectrum (Figure S5d) of one of the mixed samples, 3PA-M-P25-1, also showed the two upfield resonance signals around 33 ppm and 28 ppm, but compared to the manually ground samples (3PA-G-P25 batches), the 33 ppm signal is much broader and the 28 ppm signal is displayed as a less resolved shoulder. The other batch (3PA-M-P25-2) only showed a clear signal at 37 ppm as well as a broad and unresolved band in the region of 33 ppm and 28 ppm, which was almost the same as signals from pure, unreacted 3PA (Figure 4). Therefore, the grafting of 3PA can occur during the shaker mixing process but is not reproducible or in a much less controllable way.

Text S4: Assignment of NMR peaks in Figure 4

In previous research regarding the grafting of P25 with 3PA via a liquid-phase process, the broad upfield shifted asymmetric peak around 28 ppm was assigned to a multitude of slightly different chemical environments around phosphorus nuclei that are covalently grafted to the titania via P–O–Ti condensation bonds (non-uniform binding)⁶. The broadening arises from i) slight variations in the chemical environments surrounding the phosphorus nucleus as a result of a multitude of additional weak hydrogen bonding interactions of the remaining P–OH and P=O groups with surface OH groups, adjacent P=O or P–OH groups, and even trapped water, and ii) restricted mobility due to steric constraints^{7,8}. The peak at 8 ppm could be related to the formation of titanium propylphosphonate lamellar structure via dissolution-precipitation⁶. However, the intensity of the 8 ppm signal in this study is much smaller and also broader than the one usually observed for 3PA-grafted TiO₂ prepared via a liquid-phase method, as described in our previous work⁶. As no solvent was applied (although surface adsorbed water might play a role) and the amount of 3PA used was much lower

in this study, the 8 ppm signal might also be related to other unknown species or non-assigned interactions/binding modes between 3PA and P25. For example, some researchers attributed this signal to the tridentate binding mode of grafted 3PA but no real evidence was provided⁷. The remaining resonance signal at 33 ppm can be attributed to weakly interacting 3PA on P25. Gys et al. reported the presence of a broad signal centered around 32.5 ppm for 3PA-grafted TiO₂ prepared via a liquid-phase method using a low 3PA concentration of 0.02 M, but no specific assignment was provided⁹. As the signal is sharper than the one reported by Gys et al., it might point to a less strong, more mobile bonding of 3PA. However, TG/DTG-MS did not show significant indications for a condensation between such weakly adsorbed 3PA and P25 for 3PA-G-P25 (Figure 3a). It could be that there are no bonding sites left on P25 as all OH groups seem to have interacted based on the DRIFT results, leaving only possible Lewis acid sites to interact with the P=O group, excluding release of water as observed in TG/DTG-MS. If this would be the reason, they should be removable via a washing process (see later). In all, it is evidenced that the grafting of 3PA to P25 is occurring in the manual grinding process, while is not taking place during the shaker mixing.

Text S5: Part TG/DTG analysis in Figure 5

Moreover, no significant weight loss or DTG signal was observed in the higher temperature range between 420–500 °C for 3PA-G-P25, a region in which the weight loss of titanium propylphosphonate takes place⁶. This means that the 8 ppm signal observed in the ³¹P-NMR spectrum of 3PA-G-P25 prior to washing (Figure 4) might not be originating from titanium propylphosphonate or that its relative amount in the material might be too low to be detected by TGA or it was removed by the washing (see later washing-induced changes in weight loss between 420–500 °C in Figure S9d). Furthermore, the maximum in the DTG curve of 3PA-G-P25 (325 °C) had a contribution at lower temperature than of 3PA-M-P25 (360 °C), which can be correlated with a denser grafting, and/or a more ordered grafted organic layer, and/or a higher modification degree on 3PA-G-P25, according to literature^{6,10}. Nevertheless, the DTG curve of 3PA-G-P25 between 270–420 °C also showed a (broad) shoulder at around 360 °C, which indicates a broad distribution of 3PA grafted groups with slightly different environments.

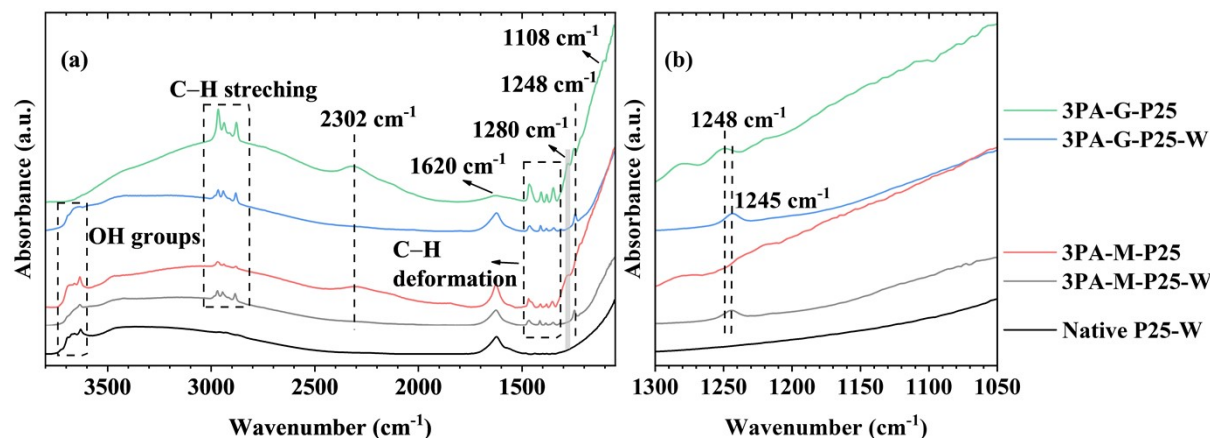


Figure S6. Normalized *In-situ* DRIFT spectra between 3800–1050 cm⁻¹ of unwashed (3PA-G-P25, 3PA-M-P25) and washed samples (3PA-G-P25-W, 3PA-M-P25-W, and native P25-W), measured using undiluted samples under an Ar flow of 50 mL/min at RT. (b) is a zoom-in of (a) between 1300–1050 cm⁻¹. All the unwashed samples were not thermally treated, while washed samples were dried at 60 °C in an oven overnight.

To understand the effect of the washing step, *in-situ* DRIFT measurements were carried out on washed samples (followed by oven drying at 60 °C overnight) of 3PA-G-P25, 3PA-M-P25, and native P25. The *in-situ* DRIFT spectra were acquired using undiluted samples under an Ar flow at RT (Figure S6). For ease of comparison, unwashed 3PA-G-P25 and 3PA-M-P25, measured under the same conditions, were also displayed in Figure S6.

Compared to unwashed 3PA-G-P25 (3PA-G-P25), the spectrum of washed 3PA-G-P25 (3PA-G-P25-W) showed that the C–H stretching and deformation signals between 3000–2800 cm^{-1} and 1500–1300 cm^{-1} , respectively, still remained on its surface but with lower intensities. The signal at 1248 cm^{-1} related to phosphoryl vibration (P=O) slightly downshifted to 1245 cm^{-1} and became sharper/more resolved (Figure S6b). However, the signals at 2302 cm^{-1} , 1280 cm^{-1} and 1108 cm^{-1} , which were attributed to P–OH groups, P–O bands, and PO_3 stretching, respectively, disappeared. These findings indicate that only chemically bonded 3PA remained present on the surface of 3PA-G-P25-W, while the weakly adsorbed and/or unreacted 3PA molecules were removed or at least reduced to amounts below the detection limit of the DRIFT. This is in line with the decreased weight loss in TG/DTG (see later in Figure S9). Moreover, 3PA-G-P25-W showed that its OH groups stretching between 3750–3600 cm^{-1} became partly visible and resolved again, and that the surface water band at 1620 cm^{-1} became sharper, compared to those for the unwashed sample. This change can be related to the removal of the weakly interacting in contact with the surface OH-groups.

Also in the spectra of 3PA-M-P25 before (3PA-M-P25) vs. after (3PA-M-P25-W) washing, the C–H stretching (3000–2800 cm^{-1}) and deformation signals (1500–1300 cm^{-1}) remained present on the surface of 3PA-M-P25-W. Also the peak at 1245 cm^{-1} related to phosphoryl vibration (P=O) was visible. All these absorptions indicate the grafting of 3PA. As the results of the sample before washing obtained from ^{31}P -MAS NMR (Figure 4) and *in-situ* DRIFT (Figures 1–2) indicates that grafting of 3PA by simple shaker mixing is limited and less controllable (Figure S5), the limited degree of grafting observed for 3PA-M-P25-W is expected to occur during the washing step which creates a short liquid phase grafting condition, and subsequent drying overnight at 60 °C. The signals at 2302 cm^{-1} and 1280 cm^{-1} , which were attributed to P–OH and P–O bands, respectively, became invisible after washing, indicating the removal of unreacted 3PA molecules (consistent with a decreased weight loss in TG/DTG as shown later in Figure S9). In addition, the broad bands of OH stretching located between 3750–3600 cm^{-1} became less resolved and changed shape for 3PA-M-P25-W compared to the unwashed sample. In 3PA-M-P25-W, the peak at 3630 cm^{-1} , associated to the surface hydroxyl groups hydrogen-bonded to coordinated water ³, were less resolved. To rule out the effect of washing on the changes in OH groups between 3750–3600 cm^{-1} , the native P25 was treated by the same washing step as applied to 3PA-M-P25-W. The results showed that the signals of the OH groups on the surface of 3PA-M-P25-W were still less resolved compared to those on washed P25. Therefore, the changes in OH groups can most likely be related to the consumption due to the 3PA grafting, occurring during washing and subsequent drying.

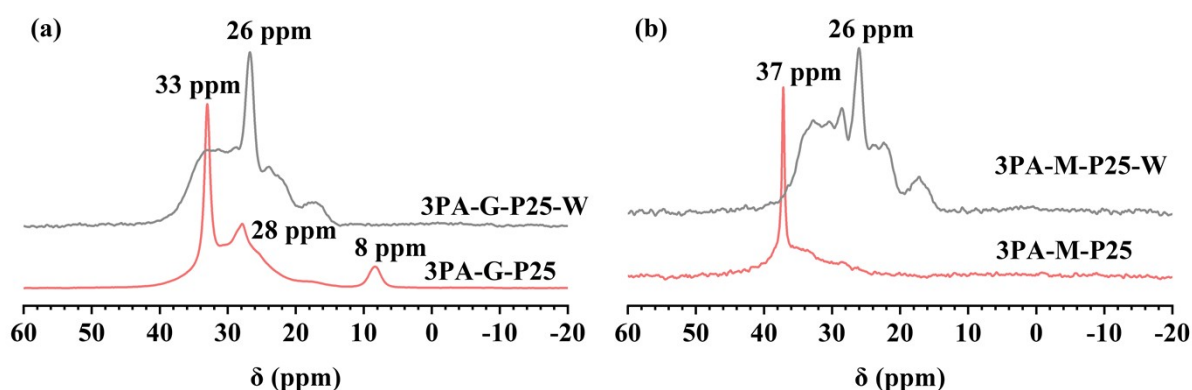


Figure S7. ^{31}P -MAS NMR spectra of washed (grey line) and unwashed (red line) 3PA-G-P25 (a) and 3PA-M-P25 (b). The unwashed samples were not thermally treated, while washed samples were dried at 60 °C overnight.

To obtain further insight into the effect of the washing step, solid-state ^{31}P -MAS NMR spectra were taken to reveal the changes in surface bonding between 3PA and P25. The spectra of washed and unwashed 3PA-G-P25 and 3PA-M-P25 are shown in Figure S7. After washing, the sharp resonance signal at 33 ppm was absent for 3PA-G-P25, indicating the

removal of weakly interacting 3PA. This is in agreement with the results obtained from DRIFT (Figure S6) and TGA-MS (Figure 3, 5). The signal at 8 ppm, uncertain in assignment, disappeared as well. The underlying reasons remains unknown. Moreover, the broad upfield-shifted peak around 28 ppm became sharper and shifted further upfield to around 26 ppm, showing broad shoulders at two sides. The upfield-shift from 28 ppm to 26 ppm corresponds well with the peak shift from 1248 cm^{-1} to 1245 cm^{-1} after washing (Figure S6). Hence, clear changes induced by washing could be observed.

Figure S7b shows the ^{31}P -MAS NMR spectra of 3PA-M-P25 before and after washing. The sharp resonance signal at 37 ppm of 3PA-M-P25 also disappeared after washing, indicating the removal of unreacted 3PA molecules. Moreover, the washed 3PA-M-P25 displayed an upfield main resonance signal around 26 ppm, with broad shoulder signals at two sides, a pattern quite similar to this of washed 3PA-G-P25. This confirms that some grafting of 3PA on 3PA-M-P25 was caused by the washing step which creates a short liquid phase grafting condition, and the subsequent overnight drying at $60\text{ }^{\circ}\text{C}$. This is consistent with the DRIFT (Figure S6) and TGA-MS results (Figure 3, 5).

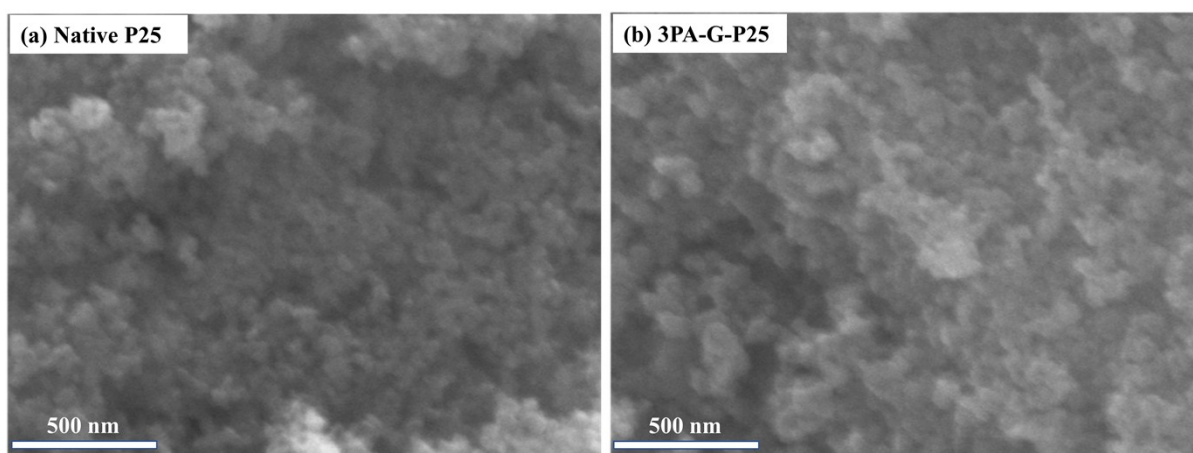


Figure S8. SEM images of native P25 (a) and 3PA-G-P25 (b). 3PA-G-P25 was obtained after washing and drying at $60\text{ }^{\circ}\text{C}$ overnight.

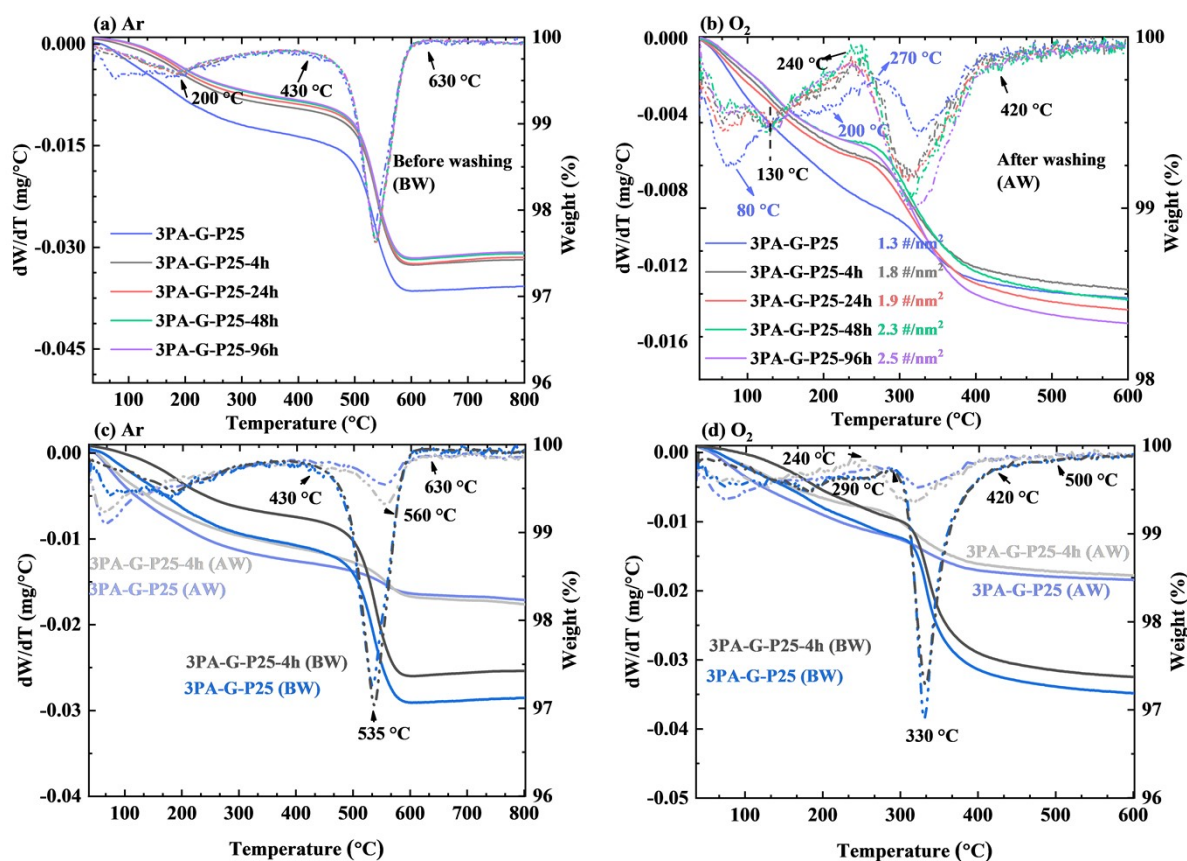


Figure S9. TG and DTG of 3PA-G-P25 prepared without and with different thermal durations (4–96 h) at 90 °C, measured under an Ar flow of 50 mL/min from 30 °C to 800 °C (a, c) and under an O₂ flow of 80 mL/min from 30 °C to 600 °C (b, d). The heating rate is 10 °C/min for both Ar and O₂ measurements. The results shown in (a) and (b) are from samples before and after washing, respectively. Two samples from (a-b), both before and after washing, were compared in Ar (c) and O₂ (d) atmosphere. The washed samples were dried at 60 °C overnight. The experimental error on the calculation of the modification degree is 0.1 #/nm², based on five repeated TG/DTG measurements of different batches of samples. The solid and dash-dot lines are for TG and DTG curves, respectively.

These samples without and with thermal treatment were measured under Ar and O₂. Samples prior to washing were measured under Ar, preventing the burning of 3PA molecules (Figure S9a); washed samples were measured under O₂ to calculate the modification degree (Figure S9b). Prior to washing (Figure S9a), all samples (with and without thermal treatment) exhibited a similar weight loss and DTG profile between 430–630 °C under an Ar flow, corresponding to thermolysis/thermal decomposition of 3PA molecules. Note that TG/DTG is unable to indicate the type of bonding or interaction as the condensation reaction could take place during the TG/DTG measurement, as observed before. In general, similar weight loss is expected for all samples since the same amount of 3PA was applied. However, 3PA-G-P25 (without thermal treatment) exhibited an additional weight loss between 30–200 °C, which is assigned to physisorbed- and structural water (condensation of TiO₂ surface OH groups). Given that these samples were measured immediately after the synthesis, the lower weight loss observed between 30–200 °C for all thermally treated samples might result from the more extensively dried surface due to the thermal treatment at 90 °C.

Subsequently, these samples were washed to remove unreacted and weakly interacting 3PA molecules and dried at 60 °C overnight. These samples were then measured under an oxygen flow to determine their modification degrees, as shown in Figure S9b. It can be observed that the onset temperatures where the propyl group is burned off is shifted to lower temperature (240 °C) for the thermally treated samples compared to the sample without thermal treatment (3PA-G-P25, 270 °C). This might be related to a higher modification degree, and/or a more ordered or more densely grafted organic layer, similar to previous reports in the literature^{6,10}. Moreover, a clear increase in weight loss, assigned to the

burning of the grafted organic groups (between 240–420 °C or 270–420 °C), was observed with increasing duration of the thermal treatment. This corresponds to an increase in modification degree from 1.3 #/nm² (3PA-G-P25, *i.e.*, without heating), to 1.8 #/nm² (3PA-G-P25-4h) and to 2.5 #/nm² (3PA-G-P25-96h), caused by an enhanced amount of strongly grafted 3PA with increasing thermal treatment, which remains after washing.

Apart from the oxidative decomposition of grafted propyl groups, the loss of water, assigned to physisorbed and structural water (partial condensation of TiO₂ surface OH groups), occurred in a multiple steps for all samples. 3PA-G-P25 showed multiple, not fully resolved DTG maxima at 80 °C, 130 °C and 200 °C. After the thermal treatment, the DTG signal at 130 °C became more resolved while the DTG signal at 200 °C became less resolved. Furthermore, the total weight loss of physisorbed- and structural water between 30–270 °C for 3PA-G-P25 without thermal treatment is 2.7 wt% while it decreased to 1.7–1.9 wt% for samples after the thermal process (between 30–240 °C). This points to the more hydrophobic nature of the thermally treated samples and/or the evaporated water during the thermal treatment at 90 °C. All these variations further supports the observation that the thermal treatment seems to promotes further condensation reaction between 3PA and TiO₂ (undetectable by TGA), lowering the concentration of hydroxyl groups at the TiO₂ surface and coinciding with the increasing modification degree. Therefore, although hydrophilic interaction sites (unbound P–OH, P=O, Ti–OH) might remain available, the large number of organic groups can influence the interaction with surface water. Moreover, samples without thermal treatment and with 4-hour thermal treatment, both before and after washing, were selected to compare in both Ar and O₂ (Figure S9c-d). However, it is challenging to reflect the effect of thermal treatment on grafting by TGA measurements, a thermal technique. Therefore, these two unwashed (excluding the impact of washing step) samples without thermal treatment and with 4-hour thermal treatment were further analyzed by solid-state ³¹P-MAS NMR to investigate the effect of thermal treatment, as seen in Figure S10.

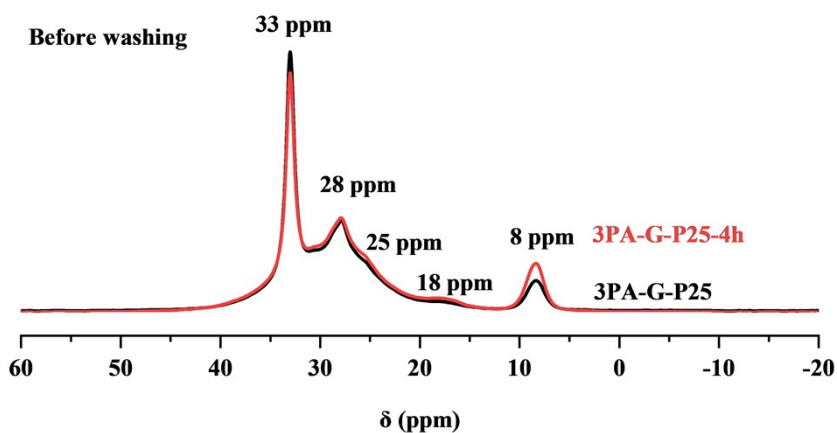


Figure S10. ³¹P-MAS NMR spectra of 3PA-G-P25 obtained without thermal treatment vs. with thermal treatment of 4h at 90 °C.

Figure S10 shows that the intensity ratio of the 33 ppm chemical shift to the 28 ppm signal slightly decreases after 4-hours of thermal treatment, indicating that weakly interacting 3PA is being converted into covalently, stronger bonded 3PA on P25. Moreover, the relative contributions of other upfield signals at 25 ppm and 18 ppm, arising from other binding modes, also slightly increase accordingly, *i.e.*, relative contributions of strong bonded 3PA slightly increase. The 8 ppm signal increases as well, but no further assignment is provided as its assignment is unclear and disappears after washing (see Figure S7). In all, at least the increases in upfield signals, including 28 ppm, 25 ppm, 18 ppm, and the intensity decrease at 33 ppm suggest the positive effect of the thermal treatment on improving the relative amount of strongly bonded 3PA. This is in good agreement with the increased modification degrees after thermal treatment and subsequent washing.

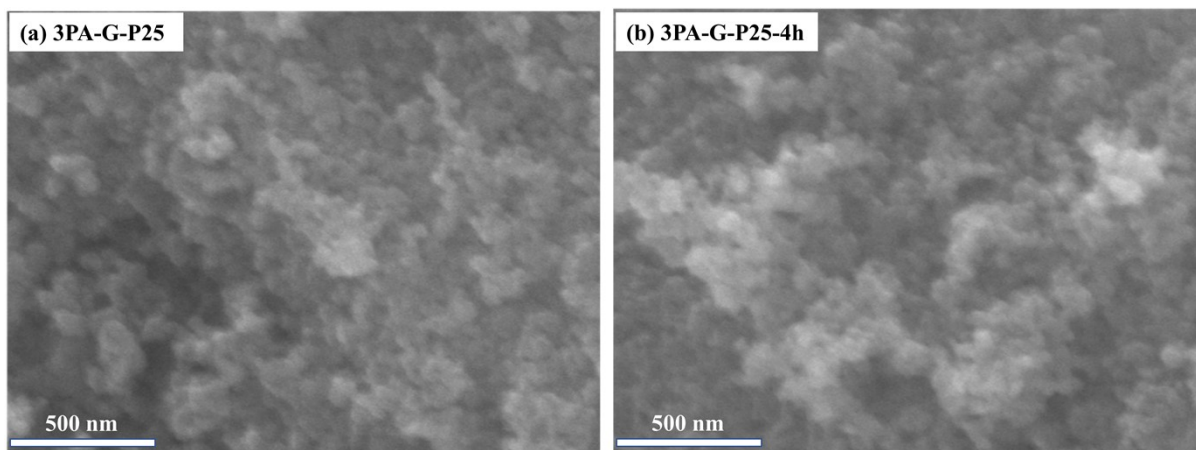


Figure S11. SEM images of 3PA-G-P25 obtained without thermal treatment (a) vs. with thermal treatment of 4h at 90 °C (b). Samples were obtained after washing and drying at 60 °C overnight.

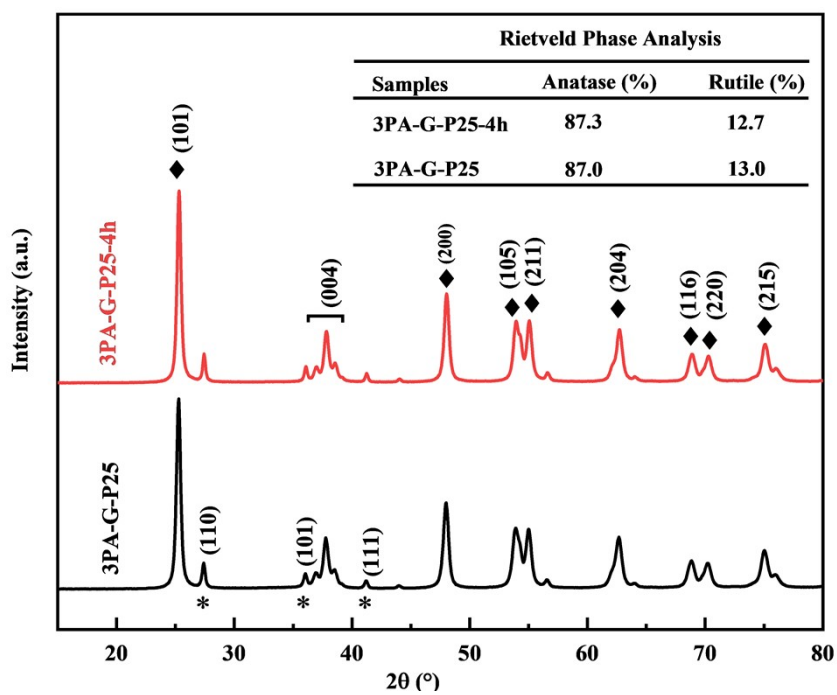


Figure S12. XRD patterns of 3PA-G-P25 (without thermal treatment) and 3PA-G-P25-4h (with thermal treatment of 4h at 90 °C). ♦ is for anatase, * is for rutile. The inserted table is the phase composition of 3PA-G-P25 and 3PA-G-P25-4h based on a Rietveld analysis. Samples were obtained after washing and drying at 60 °C overnight.

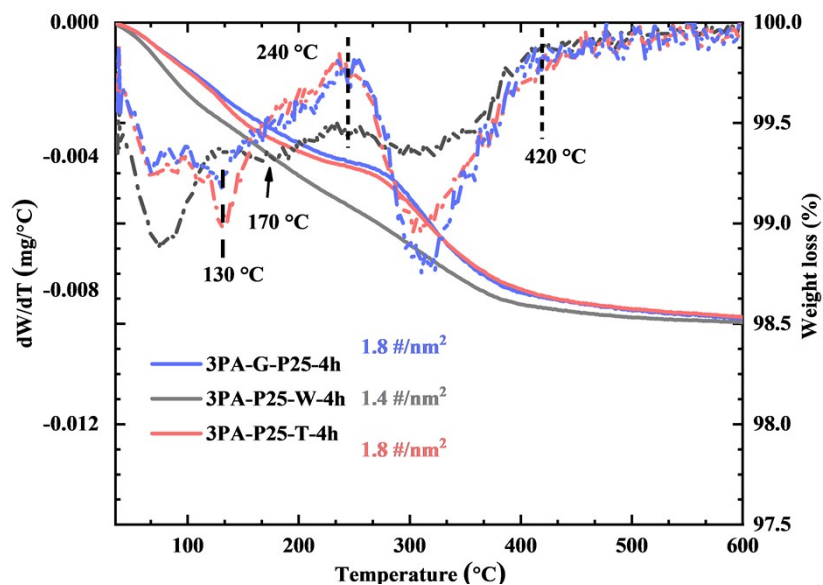


Figure S13. TG/DTG results of 3PA-modified P25 after washing and drying at 60 °C overnight. Samples were synthesized by the solid-phase (3PA-G-P25-4h) method, and the liquid-phase method performed in water (3PA-P25-W-4h) and toluene (3PA-P25-T-4h). The reaction temperature and time were 90 °C and 4 h, respectively. The TG/DTG measurements were performed under an oxygen flow of 80 mL/min from RT to 600 °C with a ramping rate of 10 °C/min, and the solid and dash-dot lines are for TG and DTG curves, correspondingly. The experimental error is 0.1 #/nm², based on five repeated TG/DTG measurements of different batches of samples.

In the region of 30–240 °C (Figure S13), ascribed to the physisorbed- and structural (*i.e.*, by condensation of Ti–OH groups) water, a DTG maximum at 130 °C was observed for 3PA-P25-T-4h and 3PA-G-P25-4h while was at 170 °C for the 3PA-P25-W-4h sample. This indicates a difference in surfaces water interactions and/or the loss of structure water for 3PA-P25-T-4h and 3PA-G-P25-4h as compared to 3PA-P25-W-4h, which is in line with their higher modification degree. This was also observed for the above thermally treated samples (Figure S9b), *i.e.*, the DTG maxima was at a lower temperature for samples with higher modification degree (≥ 1.8 #/nm²).

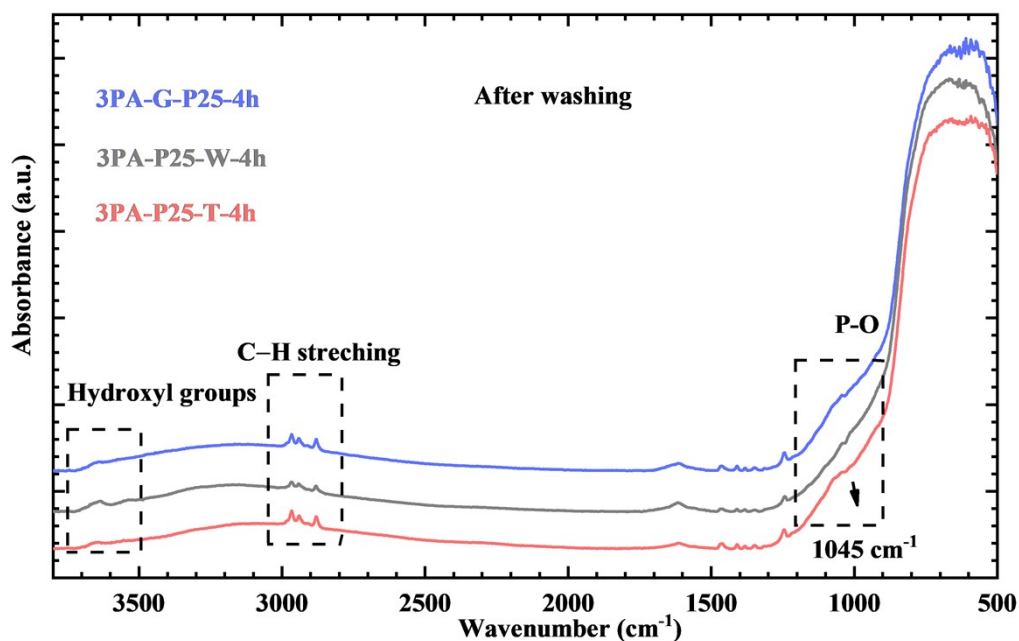


Figure S14. Normalized DRIFT spectra between 3800–800 cm^{-1} of modified samples prepared by the solid-phase method (3PA-G-P25-4h), and the liquid-phase method performed in water (3PA-P25-W-4h) and toluene (3PA-P25-T-4h), measured with 2 wt% diluted samples in KBr at RT under an Ar flow of 50 mL/min. These samples were obtained after washing and drying at 60 °C overnight.

The DRIFT spectra in Figure S14 were obtained at RT under an Ar flow using KBr diluted samples for purpose of semi-quantification. 3PA-G-P25-4h and 3PA-P25-T-4h displayed a similar intensity for the stretching vibrations of hydroxyl groups, which are better resolved and with higher intensity for 3PA-P25-W-4h. This suggests that the distribution/number of OH groups are more similar for 3PA-G-P25-4h and 3PA-P25-T-4h. Moreover, in the P–O region, 3PA-G-P25-4h and 3PA-P25-T-4h exhibit a peak at 1045 cm^{-1} with a subtle shoulder, while 3PA-P25-W-4h only shows the peak at 1045 cm^{-1} . Therefore, it was confirmed that samples 3PA-G-P25-4h and 3PA-P25-T-4h show more similarities although they were synthesized by different methods.

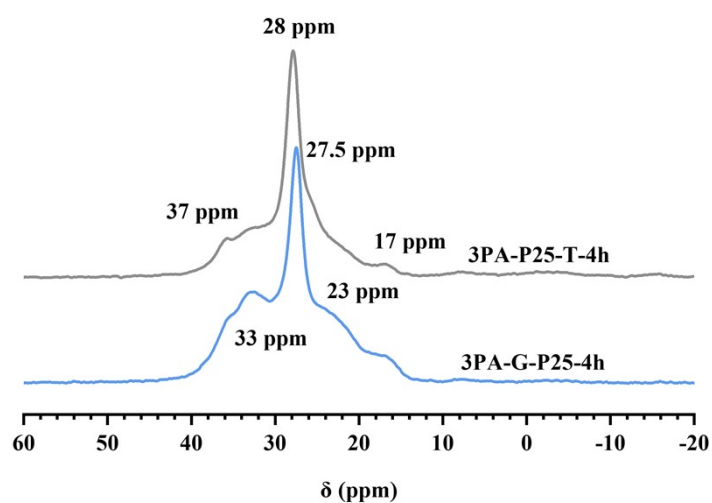


Figure S15. ^{31}P -MAS NMR spectra of 3PA-modified P25 by the solid-phase method (3PA-GP25-4h), and liquid-phase method performed in toluene (3PA-P25-T-4h). Both samples were obtained after washing and drying at 60 °C overnight.

To gain insight into the possible differences induced by the synthesis methods, samples 3PA-G-P25-4h and 3PA-P25-T-4h were further investigated by solid-state ^{31}P -MAS NMR measurements to reveal the possible differences in phosphorus environment. The ^{31}P -MAS spectra of 3PA-G-P25-4h and 3PA-P25-T-4h are displayed in Figure S15. A broad, upfield shifted asymmetric peak centered around 28 ppm was present for both 3PA-G-P25-4h and 3PA-P25-T-4h, originating from a non-uniform binding mode with minor differences in the chemical environments around the phosphorus nuclei ^{6,9}. Only slight intensity differences are observed for 3PA-G-P25-4h and 3PA-P25-T-4h around 37 ppm, 33 ppm, 23 ppm and 17 ppm, pointing to small differences in the contribution of these phosphorus environments.

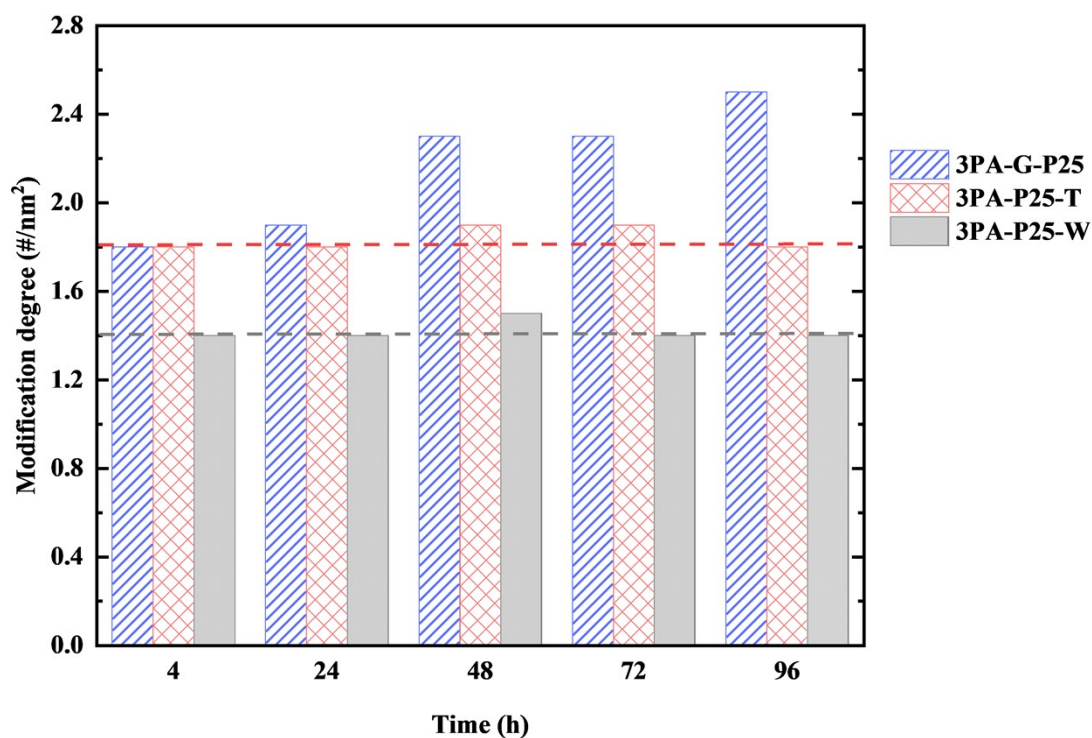


Figure S16. The impact of the reaction time on the modification degree for samples synthesized by the solid-phase method (3PA-G-P25) and the liquid-phase method performed in toluene (3PA-P25-T) and water (3PA-P25-W) at 90 °C. The experimental error is 0.1 #/nm², based on five repeated TG/DTG measurements on different batches of samples.

As discussed above, for a reaction time of 4h, the modification degree is similar for 3PA-G-P25 and 3PA-P25-T (1.8 #/nm²) and higher than 3PA-P25-W (1.4 #/nm²). Starting from a reaction time of 48 h, the modification degree of 3PA-G-P25 (2.3 #/nm²) was already pronouncedly higher than those obtained by the liquid phase method, *i.e.* 3PA-P25-T (1.9 #/nm²) and 3PA-P25-W (1.5 #/nm²), taking the experimental error into account.

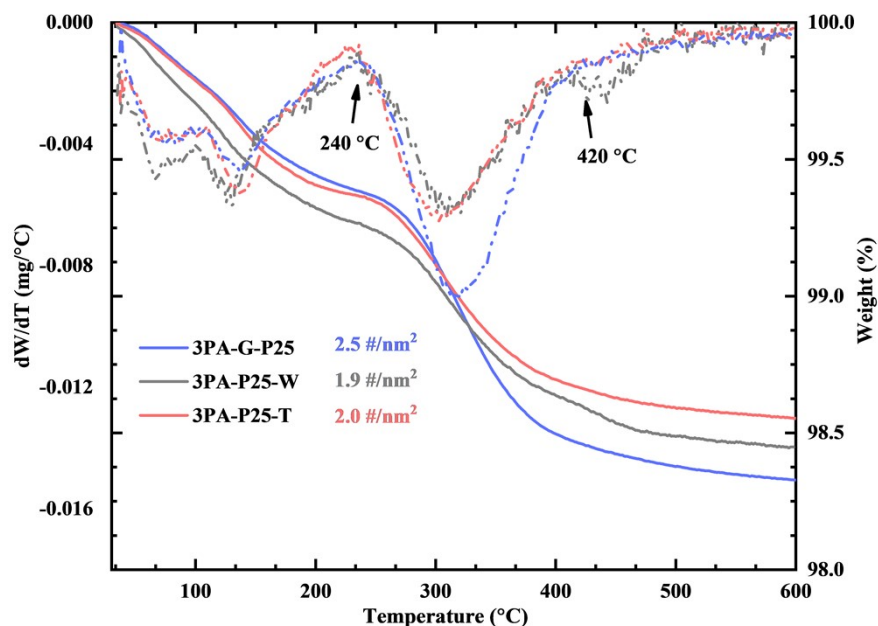


Figure S17. TG/DTG curves of 3PA-modified P25 by the solid-phase method (3PA-G-P25, 0.065 g of 3PA and 1.00 g of P25 at 90 °C for 96 h) and liquid-phase method performed in water (3PA-P25-W, 0.39 g of 3PA and 1.00 g of P25 in 20 mL of water at 90 °C for 4 h) and toluene (3PA-P25-T, 0.26 g of 3PA and 1.00 g of P25 in 20 mL of toluene at 90 °C for 4 h), measured under an oxygen flow of 80 mL/min from 30 °C to 600 °C with a heating rate of 10 °C/min. These samples were obtained after washing and drying at 60 °C overnight. The solid and dash-dot lines are for TG and DTG curves, respectively.

The liquid phase method using water (3PA-P25-W, 1.9 #/nm²) has an additional drawback caused by the formation of a titanium propylphosphonate phase, visible as the extra weight loss between 420–500 °C in Figure S17. This can be explained by the occurring dissolution-precipitation side reaction, which appears at higher 3PA concentrations in water based methods, as has been thoroughly confirmed in our previous work ^{6,11}. However, no such weight loss between 420–500 °C related to titanium propylphosphonate was observed for 3PA-G-P25 although the an 8 ppm signal, previously assigned to titania propylphosphonate, was observed in its ³¹P-MAS NMR spectra (Figure S18). If the signal at 8 ppm was titanium propylphosphonate, its formation was most likely much less as no signal was present in TG/DTG, which could then be related to the absence of solvent in the manual grinding synthesis. Nevertheless, it cannot be excluded that the previous assignment of the 8 ppm signal to titanium propylphosphonate, might have to be attributed to other “difficult to form” binding modes like e.g. a tridentate binding or other, currently unknown binding modes.

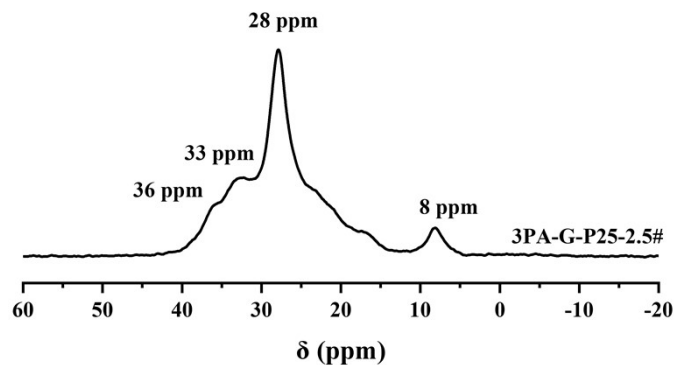


Figure S18. ^{31}P -MAS NMR spectrum of 3PA-G-P25 with the maximum modification degree. The sample was prepared after 96-hours' thermal treatment at 90 °C, followed by washing and overnight drying at 60 °C.

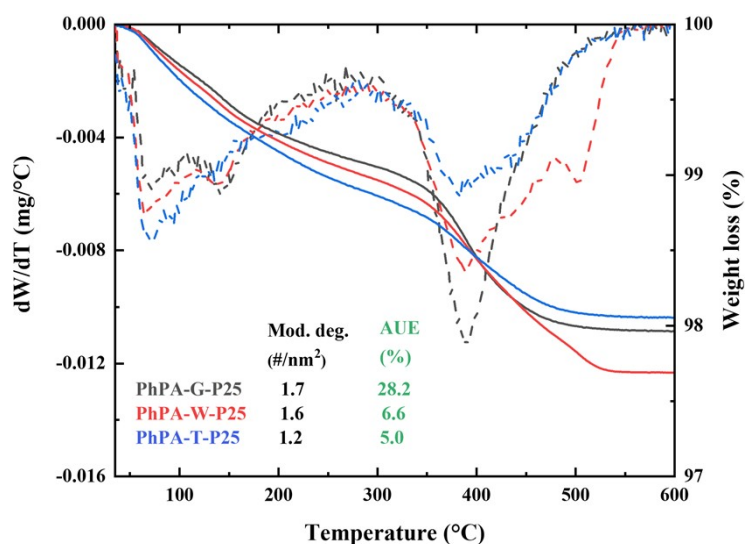


Figure S19. TG/DTG curves of PhPA-modified P25 by the solid-phase method (PhPA-G-P25, 0.079 g of PhPA and 1.00 g of P25 at 90 °C for 48 h) and liquid-phase method performed in water or toluene (PhPA-P25-W or PhPA-P25-T, 0.3162 g of PhPA and 1.00 g of P25 in 20 mL of water or toluene at 90 °C for 4 h), measured under an oxygen flow of 80 mL/min from 30 °C to 600 °C with a heating rate of 10 °C/min. These samples were obtained after washing and drying at 60 °C overnight. The solid and dash-dot lines are for TG and DTG curves, respectively. The black and green words indicate the modification degrees (calculated between 300–480 °C) and the atom utilization efficiencies (AUE), respectively.

Figure S19 shows a weight loss of 1.079 % at 300–480 °C, corresponding to the burning of the organic groups, for the solid-phase-produced sample (PhPA-G-P25-48h). This coincides with the atom utilization efficiency of 28.2 % based on Equations 1 and 2. The samples made by the liquid-phase toluene- and water-based methods shows weight losses of 0.744 % and 1.034 % at 300–480 °C, respectively, corresponding to atom utilization efficiencies of 5.0 % and 6.6 %, respectively. Moreover, the clear presence of weight loss between 480–550 °C, related to titania phosphonate formation due to a dissolution-precipitation side reaction, can be observed for the sample prepared via the liquid-phase water-based method ¹².

Table S3. A comparison of the modification degrees obtained for all samples in this work. ¹Modification degree obtained by calculating the weight loss directly from the TGA results, without corrections. ²Modification degree obtained by subtracting the weight loss of P25 in the same temperature region.

Section of main text		Samples	¹ Modification degree (#/nm ²)	² Modification degree (#/nm ²)	PA/TiO ₂		
No thermal treatment, after washing and drying		3PA-M-P25	0.9	0.1	0.065		
		3PA-G-P25	1.3	0.4			
The impact of an additional thermal treatment		3PA-G-P25-4h	1.8	1.0			
		3PA-G-P25-24h	1.9	1.1			
		3PA-G-P25-48h	2.3	1.5			
		3PA-G-P25-96h	2.5	1.7			
Solid-phase grafting vs. liquid-phase grafting	Modification degree obtained for the same reaction time of 4 h at 90 °C	3PA-P25-W-4h	1.4	0.6		0.39	
		3PA-P25-T-4h	1.8	1.0			
	Maximal modification degrees (0.150 M of 3PA in water, 0.100 M in toluene; reaction time of 4 h at 90 °C)	3PA-P25-W	1.9	1.1			0.39
		3PA-P25-T	2.0	1.2			0.26
In-depth assessment of greenness of the solid-phase method	PhPA modification on P25 by solid- and liquid-phase methods at 90 °C with 48 h and 4 h of reaction time, respectively	PhPA-G-P25-48h	1.7	1.2	0.079		
		PhPA-P25-W-4h	1.6	1.1	0.32		
		PhPA-P25-T-4h	1.2	0.8			

Note that the ¹modification degrees in Table S3 were obtained based on the weight loss that included that of P25 in the same temperature range, and therefore might be somewhat overestimated. The ²modification degrees calculated by subtracting the weight loss of P25 in the same temperature range are also summarized in Table S3, which can in turn be regarded as over-corrected since part of the OH groups have interacted with 3PA and cannot provide loss of water. Both modification degrees show the consistent trend for all samples synthesized in this paper. In the whole paper, the modification degrees without subtracting the weight loss of P25 will be used, *i.e.*, ¹modification degree.

Table S4. Overview of (D)TG results of 3PA-G-P25, 3PA-M-P25, and native P25 in Figure 5.

	3PA-G-P25			3PA-M-P25			Native P25		
Weight loss temperature ranges (°C)	30-150	150-270	270-420	30-150	150-270	270-420	30-145	145-300	300-420
DTG maximal temperature (°C)	80	198	325, 360	80	200	360	80	200	320
DTG maximal (mg/°C)	-0.007	-0.004	-0.004, -0.003	-0.007	-0.004	-0.003	-0.008	-0.005	-0.003
Weight loss (%)	0.58	0.39	0.45	0.64	0.44	0.33	0.63	0.53	0.14

References

- 1 L. F. Scatena, M. G. Brown and G. L. Richmond, *Science (80-.)*, 2001, **292**, 908–912.
- 2 N. Li, Z. Xu, S. Zheng, H. Dai, L. Wang, Y. Tian, Z. Dong and L. Jiang, *Adv. Mater.*, 2021, **33**, 1–7.
- 3 C. Morterra, *J. Chem. Soc. Faraday Trans. 1*, 1988, **84**, 1617–1637.
- 4 M. Takeuchi, L. Bertinetti, G. Martra, S. Coluccia and M. Anpo, *Appl. Catal. A Gen.*, 2006, **307**, 13–20.
- 5 M. Takeuchi, G. Martra, S. Coluccia and M. Anpo, *J. Near Infrared Spectrosc.*, 2009, **17**, 373–384.
- 6 A. Roevens, J. G. Van Dijck, M. Tassi, J. D'Haen, R. Carleer, P. Adriaensens, F. Blockhuys and V. Meynen, *Mater. Chem. Phys.*, 2016, **184**, 324–334.
- 7 H. Souma, R. Chiba and S. Hayashi, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 1267–1275.
- 8 B. Pawlak, W. Marchal, B. M. Ramesha, B. Joos, L. Calvi, J. D'Haen, B. Ruttens, A. Hardy, V. Meynen, P. Adriaensens and R. Carleer, *Microporous Mesoporous Mater.*, 2022, **341**, 112080.
- 9 N. Gys, B. Pawlak, K. Marcoen, G. Reekmans, L. F. Velasco, R. An, K. Wyns, K. Baert, K. Zhang, L. L. Lufungula, A. Piras, L. Siemons, B. Michielsens, S. Van Doorslaer, F. Blockhuys, T. Hauffman, P. Adriaensens, S. Mullens and V. Meynen, *Chempluschem*, 2023, **n/a**, e202200441.
- 10 R. Helmy and A. Y. Fadeev, *Langmuir*, 2002, **18**, 8924–8928.
- 11 R. An, L. Chukiwanka Quiñones, N. Gys, E. Derveaux, K. Baert, T. Hauffman, P. Adriaensens, F. Blockhuys and V. Meynen, *Appl. Surf. Sci.*, 2023, **639**, 158179.
- 12 A. Roevens, J. G. Van Dijck, D. Geldof, F. Blockhuys, B. Prelot, J. Zajac and V. Meynen, *Appl. Surf. Sci.*, 2017, **416**, 716–724.