




Organic surface modification and analysis of titania nanoparticles for self-assembly in multiple layers

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The characteristics of TiO₂ coatings can greatly influence their final performance in large-scale applications. In the present study, self-assembly of TiO₂ nanoparticles (NPs) in multiple layers was selected as a deposition procedure on various substrates. For this, the main prerequisite constitutes the surface modification of both NPs and substrate with, for example, silane coupling agents. A set of functionalized TiO₂ NPs has been produced by reaction with either (3-aminopropyl)triethoxysilane (APTES) or (3-aminopropyl)phosphonic acid (APPA) to functionalize the NP surface with free amino-groups. Then, the complementary functionalized NP set can be obtained from an aliquot of the first one, through the conversion of free surface amino groups to aldehydes by reaction with glutaraldehyde (GA). Several types of TiO₂ NPs differing in size, shape, and specific surface area have been functionalized. Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), SEM/energy-dispersive X-ray spectroscopy (EDS), XPS, Auger electron spectroscopy (AES), and Time-of-Flight (ToF)-SIMS analyses have been carried out to evaluate the degree of functionalization, all the analytical methods employed demonstrating successful functionalization of TiO₂ NP surface with APTES or APPA and GA.

KEYWORDS

(3-aminopropyl)triethoxysilane, (3-aminopropyl)phosphonic acid, glutaraldehyde, layer-by-layer deposition, surface functionalization, TiO₂ nanoparticles

1 | INTRODUCTION

The final performance of coated materials designed for large-scale applications such as photocatalysis, prosthesis, cell cultures, or dye-sensitized solar cells may be greatly influenced by the physico-chemical parameters of the respective coatings. For the deposition of mesoporous TiO₂ films with defined and homogeneous chemical composition and thickness on supports of interest various procedures such as PVD, sol-gel techniques, screen printing, dip, or spray coating

can be employed.¹⁻³ In the present study, self-assembly, layer-by-layer (LbL) deposition⁴ of TiO₂ nanoparticles (NPs) was selected as a method to fabricate homogeneous mesoporous layers by alternating layers of oppositely charged/functionalized titania NPs based on (i) molecules ending with amino groups, either (3-aminopropyl)triethoxysilane ("APTES") or (3-aminopropyl)phosphonic acid ("APPA"), and (ii) a cross-linking agent, glutaraldehyde ("GA"), as reported in different recent studies in literature.⁵⁻⁹ Hence, in a first step, the NPs should be functionalized with amino groups, which then, in a second

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step, can react with carbonyl group of GA; see Figure 1. The present paper is dedicated to the systematic analysis of the functionalization of TiO₂ NPs by the two routes described above, that is, (i) APTES + GA and (ii) APPA + GA. For this, a well-defined set of different types of TiO₂ NPs has been selected for investigations (see Section 2.1—Materials). The surface sensitive methods FTIR, TGA, SEM, SEM/EDS, XPS, Auger electron spectroscopy (AES), and ToF-SIMS have been applied to analyze the degree of functionalization of the particles on a complementary basis. Because of the large amount of characterization data, we have decided to include in this paper the results of the complete characterization of one set of NPs, namely, the commercial P25 TiO₂ (Evonik) and one route of functionalization, that is, that with APTES + GA. Relevant information, additionally obtained to these data, have been included in the supplementary information.

The LbL deposition technique as a simple and inexpensive means for film preparation offers an easy control over the film thickness and requires also a proper functionalization of the supports. This aims at promoting the adhesion of the film to the substrates by interaction of the functional groups on the substrates with the functional groups of the functionalized TiO₂ NPs deposited on them. Detailed results on the surface functionalization of different types of substrates as the counterpart of the layer with functionalized NPs have been recently published in Rades et al.⁹ The optimization of the quality of the LbL deposition of the functionalized TiO₂ NPs on the functionalized substrates is object of further investigations.

With respect to other studies reported in the literature, stable surface charges on the surface of metal oxide NPs have been introduced successfully by functionalization with organophosphorus coupling agents that bear a phosphonic acid as an anchor group

and a charged functional group.¹⁰ Functionalization and stabilization of P25 TiO₂ NPs have been realized by Burger et al.¹¹ by means of N1,N7-bis(3-(4-tert-butyl-pyridium-methyl)phenyl)-4-(3-(3-(4-tert-butyl-pyridinium-methyl)phenylamino)-3-oxopropyl)-4-(3,4-dihydroxybenzamido)heptanediamide tribromide (1). A one-step, low-temperature, nonhydrolytic approach has been applied by Hu et al.¹² to in situ synthesis of amino-functionalized TiO₂ NPs to enhance the power conversion efficiency (PCE) of perovskite solar cells over 21%. Functionalization agent induced oriented attachment as the origin of the elongation of the TiO₂ NPs has been reported in Dalod et al.¹³ Hydrophilic TiO₂ NPs could be converted into hydrophobic ones by silylation of their surface hydroxyl groups.¹⁴ Synthesis of identical, highly crystalline anatase NPs differing only in size and surface composition, with control over the density of the functional surface groups, has been attained as reported in Kotsoskechagia et al.¹⁵ Controlled functionalization of TiO₂ NPs with an organic chromophore was demonstrated as an efficient procedure to enable the visualization of the NPs within cells.¹⁶

2 | MATERIALS AND METHODS

2.1 | Materials

Four types of TiO₂ NPs differing in size, shape, surface area, and structure have been undergone to same functionalization procedures: (i) commercially available P25 (Evonik), (ii) NPs with high specific surface area, that is, >150 m²/g, (iii) NPs with low size, that is, <20 nm, and (iv) bipyramidal NPs. The last three types of TiO₂ NPs have been

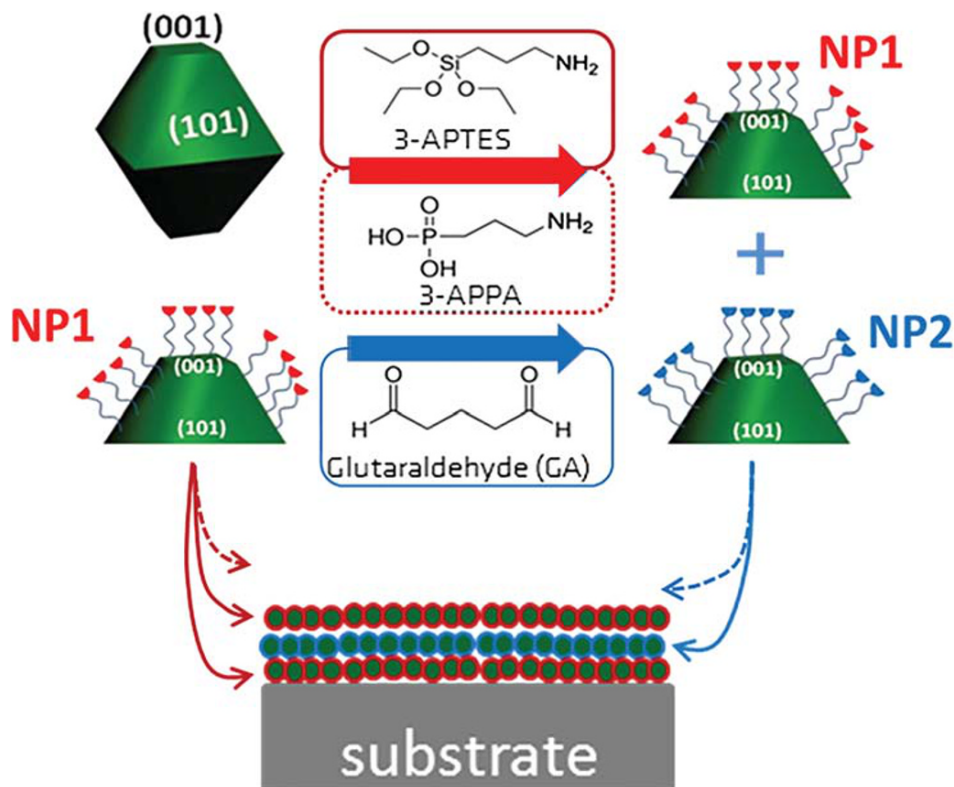


FIGURE 1 Illustration of the alternating sequence of layer-by-layer deposition of differently functionalized TiO₂ NPs

developed in the frame of the large EU/FP7 project SETNanoMetro¹⁷ with the systematic characterization of their morphology being published elsewhere.¹⁸

Regarding the substrate material, following selection has been made based on materials employed for large-scale applications: conductive (FTO) glass, silica glass, and titanium alloy.⁹

Because of space limitations, in the following, results on a single type of TiO₂ NPs, namely, P25, are presented and discussed in detail. The similarities and differences to the other three types of TiO₂ NPs will be highlighted at the corresponding place.

2.2 | Procedure for the functionalization of TiO₂ NPs with APTES and GA

For the functionalization of all types of TiO₂ NPs with APTES, following procedure has been developed: Generally, 1 g of TiO₂ NPs is suspended in an ethanol:water mixture in a volume ratio of 95:5 acidified with acetic acid until pH = 5 into a two-neck round bottom flask (100 mL) equipped with a magnetic stir bar. The dispersion is sonicated for 30 min at room temperature in an ultrasonic bath (Elmasonic S30, 280 W) to enhance particle dispersion. Then, 10 mL of APTES (Aldrich) is added to the dispersion, and the mixture is maintained for 24 h under continuous flowing nitrogen and stirring. Then, the TiO₂ NPs are recovered from the reaction medium by vacuum filtering and washing twice with ethanol. Finally, the NPs are dried in a vacuum oven for 24 h at 40°C. After the APTES functionalization, a dispersion with 8 g/L of NPs in deionized water is prepared in a 100-mL double-neck round bottom flask and is sonicated for 30 min in an ultrasonic bath. Then, the flask is equipped with a magnetic stir bar, and 25 mL of a GA (solution 0.5M in deionized water) is added to the dispersion. The mixture is maintained for 24 h at room temperature under continuous stirring and flowing nitrogen.

The functionalization route with APPA and GA is described in SI.

2.3 | Methods and instruments

In order to evaluate the degree of functionalization of all types of TiO₂ NPs, Fourier-transform infrared spectroscopy (FTIR), SEM/energy-dispersive X-ray spectroscopy (EDS), XPS, Auger electron spectroscopy (AES), and Time-of-Flight (ToF)-SIMS as surface-sensitive techniques and SEM/EDS and TGA analysis as bulk techniques have been used. A detailed description of the measurement conditions is given in SI.

3 | RESULTS AND DISCUSSION

The SEM micrographs in Figure 2 show the morphology of the TiO₂ NPs of type P25 before and after the two-step functionalization via both routes APTES + GA and APPA + GA. No significant differences were observed between the morphologies and sizes of the NPs as before and after the two routes of functionalization with respect to an additional, visible coating. The size distribution of the particles remains broad, and the particle shape remains irregular. This suggests that the functionalization layer is ultrathin (likely sub-nm), and for its detection, other more sensitive methods are necessary; see below.

The FTIR spectroscopy analysis of the P25 TiO₂ NPs as before and after the two functionalization steps, with APTES, and then with GA, can be summarized with the help of the FTIR spectra in Figure 3 (left). The characteristic bands are identified and commented in detail in Tables S1–S3. For the NPs functionalized with APTES, the signals due to surface OH groups not involved in H-bond (at 3600 cm⁻¹) in pristine P25 NPs do not appear, this indicating that surface moieties were consumed by reaction with the functionalizing molecules.

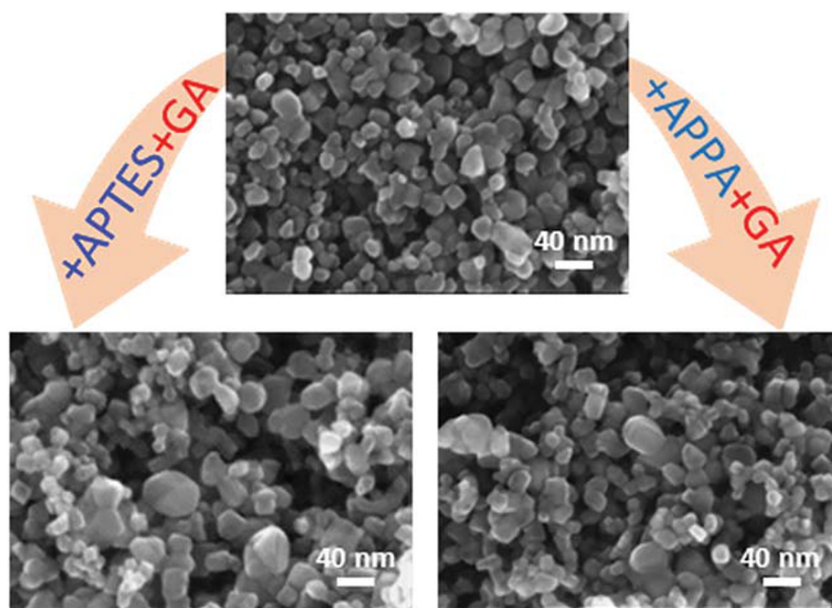


FIGURE 2 SEM In-Lens micrographs before and after the functionalization with APTES and GA (bottom left) and after functionalization with APPA and GA (bottom right)

Besides, the presence of the new bands corresponding to silane and amine groups is clearly observed, suggesting successful modification with APTES. In the GA functionalization of APTES treated TiO₂ NPs,

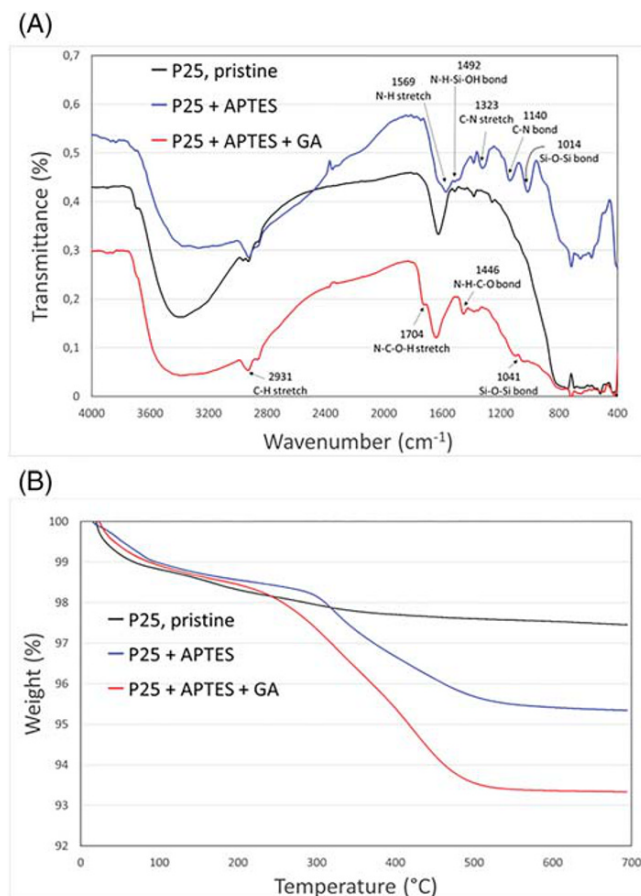


FIGURE 3 FTIR spectra (A) and TGA analysis (B) of the P25 titania NPs before and after the functionalization with APTES and GA

new functional groups appeared because of the presence of carbonylic group in the aldehyde groups, and these aldehyde groups are still available for a possible subsequent reaction with other amine groups. However, the formation of C-N or C=N linkages, as expected from the reaction of initially present amine groups and the aldehyde groups of GA, could not be clearly confirmed by FTIR.

To estimate the amount of coupling agents at the NP surface, the samples were analyzed by the TGA technique. As can be seen from the curves in Figure 3 (right), the untreated TiO₂ NPs were relatively stable in air and only slightly decomposed. Slight weight losses between 100°C and 160°C were observed for all the NPs (pristine, APTES functionalized and GA functionalized), probably because of vaporization of water physically adsorbed at the surface of TiO₂ NPs. In pristine NPs, no significant weight losses were observed indicating the lack of other compounds adsorbed on the TiO₂ surface. For the functionalized NPs, significant weight losses were observed between 200°C and 550°C corresponding to the degradation of the organic molecules on the surface of the TiO₂ NPs. The weight loss is lower for APTES functionalized NPs because of the lower amount of organic compounds on these type of NPs.

The EDS analysis (see Figure S1) as a microanalysis technique could clearly identify silicon in the APTES and APTES + GA functionalized NPs and phosphorus in the APPA and APPA + GA functionalized samples.

Auger electron spectra, as those selected exemplary in Figure 4 for the case of functionalization over the APPA route, demonstrate the presence of phosphorus at the surface of the TiO₂ NPs after both functionalization steps: with APPA only and after APPA + GA. This is confirmed also by the analysis in the line scan mode¹⁹ (see Figure 4 right).

The XPS analysis on the surface of P25 TiO₂ NPs after functionalization with APTES and GA can be concluded basically relying on the spectra from Figure 5 and data in Table S4. It was found that

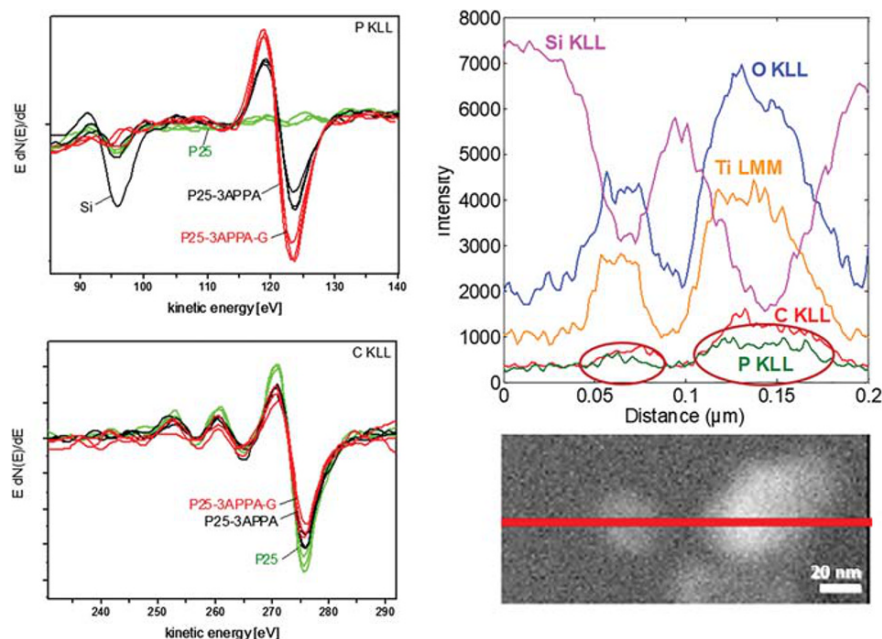


FIGURE 4 P KLL and C KLL Auger electron spectra of the P25 titania NPs before and after the functionalization with APPA and GA (left) and an Auger electrons linescan over two P25 NPs (right)

FIGURE 5 XPS analysis on the surface of P25 TiO₂ NPs after functionalization with APTES and, subsequently, with GA

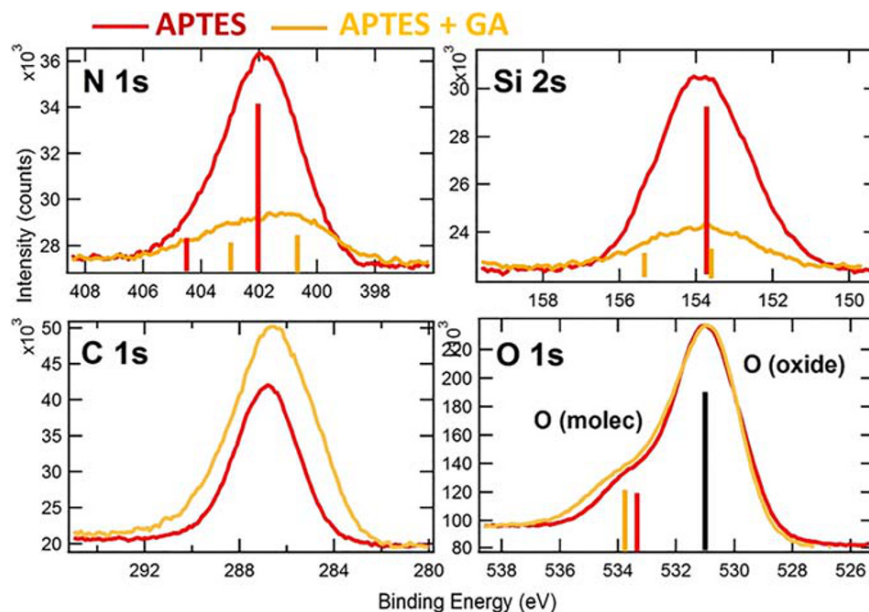


TABLE 1 ToF-SIMS results of P25 TiO₂ NPs before and after the functionalization with APTES and GA with selected positive and negative secondary ions having tendencies in intensity changes marked with arrows

ToF-SIMS	Area normalized by total ion intensity		
	P25	P25 + APTES	P25 + APTES + GA
Positive SIs			
Si ⁺	2E-4	↑0.02	↓0.01
Ti ⁺	0.2	↓0.08	0.09
TiO ⁺	0.2	↓0.05	0.04
TiO ₂ ⁺	3E-3	arrow downN.D.	N.D.
SiC ₃ H ₈ NO ₂ ⁺	N.D.	arrow up1E-4	N.D.
Negative SIs			
P25			
Si ⁻	N.D.	↑1031	arrow down6E-4
SiO ⁻	3E-5	↑48	↓2E-4
SiO ₂ ⁻	4E-4	arrow up2955	arrow down9E-3
TiO ⁻	9E-4	↓N.D.	N.D.
TiO ₂ ⁻	6E-3	↓N.D.	N.D.
SiC ₃ H ₈ NO ₂ ⁻	3E-5	arrow up12	↓9E-05
C ₁₅ H ₂₂ O ₄ ⁻	N.D.	N.D.	↑3E-05

Abbreviations: APTES, (3-aminopropyl)triethoxysilane; GA, glutaraldehyde; NPs, nanoparticles; ToF, Time-of-Flight.

the stoichiometry of TiO₂ NPs of type P25 is as expected. Regarding the integrity of APTES before GA functionalization, the molecule contains about half of the expected N (see N/Si ratio), indicating that the functionalization process removes half of the lateral NH₂ groups. The C/Si and O/Si ratios are slightly below expectations, suggesting that the molecule is not intact. In particular, the C/O

ratio indicates that the major deficiency is from O. Both N 1s and Si 2s are composed of basically one component. After the subsequent GA functionalization step, the absolute intensity of Si and N strongly decreases, suggesting that part of the APTES is washed out. In particular, the atomic ratio N/Si increases, indicating that the molecular core (Si) is lost. The line shape of Si 2s is now asymmetric on the high binding energy side, further suggesting that the APTES molecule is significantly damaged.

The ToF-SIMS analysis can be summarized with the results in Table 1. All TiX^{+/-} ion signals decrease after the APTES functionalization. In contrast, the SiX^{+/-} ion intensities increase after APTES functionalization but further decrease after the GA functionalization.

Selected results indicating the successful functionalization of P25 TiO₂ NPs. Similar results have been obtained for other NPs. As an example, results for TiO₂ NPs of type bipyramidal shape are presented in Figure S2.

4 | CONCLUSIONS

FTIR, TGA, SEM, EDS, AES, XPS, and ToF-SIMS analyses demonstrate successful functionalization of surface of TiO₂ NPs of type P25 with APTES and subsequently with GA. Evidence of similar functionalization figures has been found for other three types of TiO₂ NPs of different size, shape, surface area, and structure but is not reported here on a systematical basis because of space limitations. Selected results providing relevant evidence of functionalization of the P25 TiO₂ NPs via the alternative functionalization route APPA and GA are also presented (see SI). First attempts to prepare self-assembled TiO₂ NP coatings on functionalized substrates indicate that the functionalized NPs adhere to the substrates, even if inhomogeneous and agglomerating.⁹

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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