# SUPPORTING INFORMATION

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# Organic Surface Modification and Analysis of Titania Nanoparticles for Self-Assembly in Multiple Layers

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### Procedure for the functionalization of $\text{TiO}_2$ nanoparticles with APPA and GA

A proper approach for the functionalization of commercial  $TiO_2$  P25 NPs with 3-aminopropylphosphonic acid (3APPA) was developed.

In general, 200 mg of P25 TiO<sub>2</sub> (previously calcined for 2 hours at 500 °C in oxygen) are suspended in 40 mL of the proper solvent (see below) into a two-neck round bottom flask (100 mL) equipped with a magnetic stir bar and the suspension is sonicated for 20 min at room temperature to enhance particle dispersion. A solution of APPA (48 mg) in the same solvent (10 mL) is then freshly prepared and added to the suspension. The amount of phosphonic acid was determined in order to obtain a 10-fold excess with respect to the number of Ti centers exposed on P25 {101} facets (ca. 6/nm2). Finally, 10 mL of solvent are used to wash the flask previously containing the APPA solution and added to the reaction flask obtaining a total volume of 60 mL. The reaction is then carried out at room temperature for the proper time (see below) under continuous flowing nitrogen and stirring. TiO<sub>2</sub> NPs are recovered from the reaction medium by centrifugation (10000 rpm, 20 min), washed three times with MilliQ water by re-suspension and centrifugation cycles and stored as suspension in MilliQ water in a sealed glass flask in order to avoid possible contamination.

In order to evaluate the influence of the reaction time and medium on the efficiency of phosphonic acid immobilization a series of samples were produced. In particular, pure MilliQ water and a solution of ammonia and ethylene glycol (EG) (3mM and 5% v/v, respectively) were used as solvents whereas reaction times of 16, 24 and 48 hours were tested. For each sample a correspondent negative control was prepared by the same procedure but without the addition of APPA.

### **Methods and instruments**

**Fourier transform infrared (FTIR) spectroscopy:** The structural composition of the samples was recorded by FTIR spectra using a Perkin Elmer Spectrum One spectrophotometer (scan from 4000 cm<sup>-1</sup> to 40 cm<sup>-1</sup>, resolution 8 cm<sup>-1</sup>, number of scans = 8). TiO<sub>2</sub> NPs were diluted with KBr in a volume ratio 1:9 and the mixture is placed between KBr cells for the analysis.

**X-ray photoelectron spectroscopy (XPS):** The as-received functionalized NPs have been deposited onto gold substrates attached to molybdenum plate by tantalum clips and subsequently inserted in the UHV chamber. XPS measurements were carried out with a SPECS system equipped with a hemispherical analyser. XPS spectra were taken with a non-monochromatic Al KG source with photon energy of 1486.6 eV. The chemical composition of the sample is deduced by recording a wide scan spectrum in the binding energy range between 0 and 1300 eV. For each element belonging to the TiO<sub>2</sub> NPs and to the molecules, a more detailed analysis is carried out by recording, with improved statistics, the spectrum of the core-level with the highest intensity (i.e. highest cross-section): in particular, the Ti 2p, O 1s, C 1s, Si 2s, N 1s core-levels are analysed. Noteworthy, the XPS analysis revealed a negligible content of hydrocarbons contaminants, which allows to directly associate the whole line shape of the C 1s spectra to the molecular carbon. To prove the molecular stoichiometry and to provide the molecular content relative to the TiO<sub>2</sub> NP, atomic ratios are calculated by normalizing each peak area to its characteristic cross-section and transmission function value (the tolerance range over the atomic ratios is 10%).

**Time-of-flight secondary ion mass spectrometry (ToF-SIMS):** An instrument of type ToF-SIMS IV (IONTOF GmbH, Münster, Germany) was used to probe the nanoparticles in this work. Secondary ion signals were excited bombarding the sample by 25 keV Bi<sup>3+</sup> cluster ions (beam size: ~500 nm, beam current: ~0.16 pA, pulse width: 5.9 ns, repetition rate: 10 kHz, incident angle: 45 degrees off the sample surface normal). For ToF-SIMS measurements the powder was shaped into a pellet with the help of a press. For the sample P25, it was not possible to press a pill due to the consistency/texture of the powder. Alternatively, the powder was laced between two pieces of Indium foil and the foils gently pushed together.

**Auger electron spectroscopy (AES):** AES analyses were carried out with a PHI 700 Auger Scanning Probe (ULVAC-PHI Inc.) equipped with a coaxial cylindrical mirror analyser. To evaluate the presence of the functionalized surface of the  $TiO_2$  NPs, Auger electron spectra as well as linescans corresponding to the elements of the  $TiO_2$  NPs (Ti LMM and O KLL), APTES (C KLL, N KLL, O KLL and Si KLL) and glutaraldehyde (C KLL and O KLL) were recorded. A primary electron beam of either 20 kV or 25 kV, at 1 nA, at different locations on the sample surface has been used. The specimens have been prepared for measurement as received after functionalization by dragging a conventional carbon foil coated copper TEM grid over the sample powder and then the grids have been fixed onto the sample stage.

**Energy dispersive X-ray spectrometry (EDS) with a Scanning Electron Microscope (SEM):** The morphology of the NPs was studied by means of a Zeiss Supra 40 Schottky field-emission SEM (Zeiss, Oberkochen, Germany) operated with an In-Lens SE detector to obtain high-resolution images and an SDD EDS detector (Bruker Nano GmbH, Berlin, Germany). For SEM and EDS measurements powder was rubbed with a spatula on an Aluminium sample holder, which was treated with sand paper and cleaned by sonication in ethanol before depositing the powder on it.

**Thermogravimetric analysis (TGA):** The samples were analysed by the TGA technique at various reaction conditions. During the analysis, the temperature was raised from room temperature to 700 °C with a heating rate of 10 °C/min in air atmosphere.

#### FTIR ANALYSIS

The pristine TiO2 P25 NPs presented the following bands.

Wavenumber (cm <sup>-1</sup> )	Band	
3600	O-H stretching of hydroxyl groups not involved in H-bonding	
3450-3200	Broad signal resulting from the overlapping of the signal due to the O-H stretching of both surface hydroxyl groups [1] and water molecules remained coordinated, through the oxygen atoms, to surface Ti(IV) sites	
2800-2950	C-H stretching of molecules adsorbed on the TiO2NPs or on KBr cells used for the analysis	
1625	band due to the deformation mode of water and O-H stretching of hydroxyl groups on the surface of $TiO_2 NP's$ [11]	
1380	band due to the deformation mode of hydroxyl groups on the surface of $TiO_2 NP's$ [11]	
700-500	Stretching vibration of Ti-O and Ti-O-Ti bonds in TiO <sub>2</sub> lattice [2]	

**TABLE S1**. Characteristics bands of  $TiO_2 P25 NPs$ 

TABLE S2. Characteristics bands of TiO $_2$  P25 NPs functionalized with APTES

Wavenumber (cm <sup>-1</sup> )	Band
3450-3200	N-H stretching modes of -NH2 groups overlapped with the signals of O-
	H stretching of both surface hydroxyl groups [1] and water molecules remained coordinated
2800-2950	C-H stretching band appeared modified in some extent, in agreement with the additional presence of asymmetrical and symmetrical stretching vibration of the C H bond in the propyl chain carried out by the functionalizing molecules
1625	band due to the deformation mode of water and O-H stretching of hydroxyl groups on the surface of $TiO_2$ NP's [1]
1577	H bending vibration of primary amines (NH <sub>2</sub> )
1492	deformation modes of the amine groups that were strongly hydrogen- bonded with the silanol groups
1380	band due to the deformation mode of hydroxyl groups on the surface of $TiO_2 NP's$ [1]
1323	C-N stretching vibration band of APTES
1140	C-N bond of primary amines [2]
1014	Si-O-Si bond indicating a possible condensation reaction between silanol groups [2]

TABLE S3. Characteristics bands of TiO<sub>2</sub> P25 NPs (ATPES functionalized) functionalized with glutaraldehyde

Wavenumber (cm <sup>-1</sup> )	Band		
3450-3200	N-H stretching modes of $-NH_2$ groups overlapped with the signals of O-H stretching of both surface hydroxyl groups [1] and water molecules		
	remained coordinated		
2800-2950	C-H stretching band appeared modified in some extent, in agreement		
	with the additional presence of the $CH_2$ and $CH_3$ groups carried out by		
	the functionalizing molecules, APTES and GA		
1725	Carbonylic moiety of aldehyde group, then available for a possible		
	subsequent reaction with amine groups		
1625	band due to the deformation mode of water and O-H stretching of		
	hydroxyl groups on the surface of TiO <sub>2</sub> NPs [1]		
1454	H bending vibration of primary amines (NH <sub>2</sub> ) which could be overlapped		
	with the presence of NHCO groups as a result of the reaction between		
	C=O groups and NH <sub>2</sub>		
1150-1000	C-N bond of primary amines and Si-O-Si bond, indicating the presence of		
	APTES excess on the functionalized NPs		

#### **EDS ANALYSIS**



**FIGURE S1** The 'marker' elements Si and P are clearly identified in the EDS spectra of all functionalized samples, here  $TiO_2 NPs$  of type P25.

#### **XPS ANALYSIS**

**Table S4:** Atomic ratios calculated from XPS spectra by normalizing each peak area to its characteristic cross-section and transmission function value (the tolerance range over the atomic ratios is 10 %)

	APTES	APTES+GA
Contaminants	Traces of Zn, Cl	Traces of Zn, Cl
Ti / O	0.48 (0.5)	0.48 (0.5)
С/Ті	1.6	3.8
N /Si	0.53 (1)	0.87 (1)
0 / Si	1.4 (2-3)	2.0 (4-5)
C / Si	2.6 (3)	19 (11)
C/O	1.9 (1-1.5)	3.1 (2.5)

**Note:** the expected values are given in parenthesis. For the O/Si ratio, only the O 1s peak area associated to molecular oxygen is considered. For the Ti/O ratio, only the O 1s peak area associated to oxygen in  $TiO_2$  is considered.

### ANALYSIS OF TIO<sub>2</sub> NANOPARTICLES OF TYPE BIPYRAMIDAL SHAPE



**FIGURE S2** a) SEM micrograph of TiO<sub>2</sub> NPs of bipyramidal shape after functionalization with APPA and Gluta; b) EDS spectrum of P K $\alpha$  for TiO<sub>2</sub> NPs in pristine form (green), after functionalization with APPA (blue), and APPA+Gluta (red); c) AES spectra of P KLL Auger peak of same sample before and after functionalization.

<sup>1</sup> Ou B, Li D, Liu Q, Zhou Z, Liao B. Functionalized TiO<sub>2</sub> nanoparticle containing isocyanate groups. *Mater Chem Phys.* 2012;135:1104-1107.

<sup>2</sup> Zhao J, Milanova M, Warmoeskerken MMCG, Dutschk V. Surface modification of TiO<sub>2</sub> nanoparticles with silane coupling agents. *Colloids Surf A*. 2012;413:273–279.