

# Characterization of Siloxane Adsorbates Covalently Attached to TiO<sub>2</sub>

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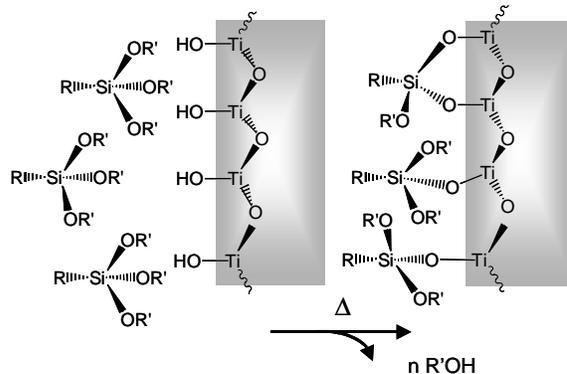
## ABSTRACT

Siloxanes with the general formula R-(CH<sub>2</sub>)<sub>n</sub>-Si-(OR')<sub>3</sub> form durable bonds with inorganic materials upon hydrolysis of labile -OR' groups, and serve as robust coupling agents between organic and inorganic materials. In the field of dye-sensitized solar cells, functionalization of TiO<sub>2</sub> thin-films with siloxane adsorbates has been shown to be useful as a surface-passivation technique that hinders recombination processes and improves the overall efficiency of light-to-electricity conversion. However, the attachment of siloxane adsorbates on TiO<sub>2</sub> surfaces still remains poorly understood at the molecular level. In this paper, we report the characterization of 3-(triethoxysilyl) propionitrile (TPS) adsorbates, covalently attached onto TiO<sub>2</sub> surfaces. We combine synthetic methods based on chemical vapor deposition, Fourier transform (FT) infrared (IR) spectroscopy and electronic structure calculations based on density functional theory (DFT). We predict that trifunctional siloxanes form only 2 covalent bonds, in a 'bridge' mode with adjacent Ti<sup>4+</sup> ions on the TiO<sub>2</sub> surface, leaving 'dangling' alkoxy groups on the surface adsorbates. Our findings are supported by the observation of a prominent fingerprint band at 1000-1100 cm<sup>-1</sup>, assigned to Si-O-C stretching modes, and by calculations of binding enthalpies at the DFT B3LYP/(LACVP/6-31G\*\*) level of theory indicating that the 'bridge' binding ( $\Delta H_b = -55$  kcal mol<sup>-1</sup>) is more stable than 'tripod' motifs ( $\Delta H_b = -45$  kcal mol<sup>-1</sup>) where siloxanes form 3 covalent bonds with the TiO<sub>2</sub> surface. The alkoxy siloxane groups are robust under heat and water treatment and are expected to be particularly relevant for analytical methods since they could be exploited for immobilizing other functionalities onto the TiO<sub>2</sub> surfaces.

**Keywords:** TiO<sub>2</sub>, solar cells, linkers, siloxanes, silanes, DFT, binding enthalpy, IR vibrational spectroscopy.

## 1. INTRODUCTION

Advancing our understanding of chemical bonding between organic and inorganic materials is essential for the development of hybrid materials suitable for a wide range of practical applications.<sup>1-7</sup> In particular, functionalization of metal oxide surfaces by covalent attachment of molecular adsorbates offers the possibility of modifying optical, electrical, magnetic and mechanical properties of semiconductor materials. For example, dye-sensitized solar cells are based on wide band-gap semiconductor electrodes (*e.g.*, TiO<sub>2</sub>) surface-modified with molecular sensitizers for photoabsorption in the visible-range of the solar spectrum.<sup>8</sup> Sensitizers are usually covalently attached to mesoporous TiO<sub>2</sub> thin-films by using Lewis base linkers that react with surface hydroxyl groups (*e.g.*, alcohols,<sup>9</sup> diols,<sup>10,11</sup> carboxylic acids,<sup>10,12,13</sup> siloxanes,<sup>14</sup> boronic acids,<sup>15</sup> and phosphonates<sup>16,17</sup>). These reactions form stable condensation products with several metal oxides (*e.g.*, TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, ZrO, Al<sub>2</sub>O<sub>3</sub>, RuO<sub>2</sub> and Pt/PtO)<sup>18-21</sup> and have been exploited for passivation of semiconductor surfaces by attachment of molecular adsorbates that protect the surface and hinder detrimental reactions. In fact, the high-efficiency of dye-sensitized solar cells is partially due to TiO<sub>2</sub> surface-passivation, preventing direct contact of the TiO<sub>2</sub> surface with redox species in solution and therefore charge carrier recombination.<sup>1</sup> All of these applications rely upon the successful grafting of adsorbate molecules onto surface oxides (see Fig. 1). However, the interfacial chemical bonding between the inorganic and organic components is often poorly understood at the molecular level.

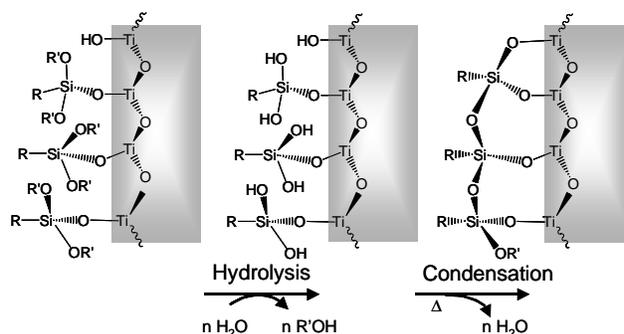


**Figure 1:** Functionalization of TiO<sub>2</sub> by anhydrous chemical vapor deposition of trifunctional siloxane adsorbates.

This paper focuses on the characterization of TiO<sub>2</sub> surfaces functionalized with siloxane adsorbates, R-(CH<sub>2</sub>)<sub>n</sub>-Si(OR')<sub>3</sub> by anhydrous chemical vapor deposition (see Fig. 1). The functionalization of metal oxides with siloxanes has been previously investigated to analyze changes in semiconductor properties due to the influence of the surface adsorbates, including changes in the flat-band potential, the apparent doping level, hole oxidation of water, and reduction processes via surface states.<sup>12,20-23</sup> However, the structural characterization of the resulting siloxane adsorbates has been difficult due to the complexity of the interfacial composite material.<sup>18,19,21,24</sup>

Unlike monofunctional adsorbates that exhibit monomolecular coverage, it is known that trifunctional siloxanes can form up to three bonds with the TiO<sub>2</sub> surface. However, it is yet to be established whether the fully coordinated adsorbates are more or less stable than adsorbates with 'dangling' alkoxy groups OR' (e.g., generated by incomplete reaction).<sup>21</sup> Furthermore, thermal curing in the presence of moisture can lead to surface polymerization, as shown in Fig. 2, forming covalent polysiloxane by cross-linking on the surface.<sup>25</sup>

In this study we analyze the covalent attachment of 3-(triethoxysilyl) propionitrile (TPS) grafted onto TiO<sub>2</sub> surfaces by chemical vapor deposition, combining Fourier transform (FT) infrared (IR) spectroscopy and electronic structure calculations based on density functional theory (DFT). We focus on structures where TPS has multiple bonds with the surface since the attachment with a single Si-O-Ti bond is expected to be less stable. We also limit our analysis to pristine TiO<sub>2</sub> [101] anatase surfaces, although we acknowledge that Lewis base adsorbates might bind more strongly to surface defects where Ti<sup>4+</sup> has a lower coordination number (e.g., oxygen vacancies).<sup>26</sup> The combination of gas-phase synthetic methods, spectroscopy and computational modeling builds upon our recent studies of TiO<sub>2</sub> surfaces functionalized with catechol moieties,<sup>27,28</sup> and Mn-complexes covalently attached with catechol,<sup>7</sup> or acetylacetonate linkers.<sup>26</sup> The reported findings provide fundamental understanding of the nature of siloxane-TiO<sub>2</sub> covalent bonding, bypassing the intrinsic difficulties associated with the characterization of polysiloxane adsorbates.



**Figure 2:** Polymerization of trifunctional siloxanes, induced by hydrolysis and condensation reactions, when adsorbed onto TiO<sub>2</sub>.

## 2. METHODS

### 2.1. Experimental Procedures

All studies were carried out using commercially available Degussa P25 TiO<sub>2</sub> nanoparticles. The nanoparticles were silanized by using TPS purchased from Aldrich and used as received.

#### 2.1.1. Siloxane Coating

Thin mesoporous films of the Degussa P25 nanoparticles were used in the coating process and prepared as previously described.<sup>7</sup> Up to five thin film samples were placed upright within the second chamber of a two chamber vapor deposition apparatus. The second chamber of the apparatus was then sealed and flame dried while under vacuum. The vacuum was maintained for two hours after heating to ensure that as much water as possible was removed and then filled with an anhydrous nitrogen atmosphere. Simultaneous to the second chamber vacuum treatment the first chamber of the apparatus was loaded with 2 mL of TPS and subjected to three cycles of quick evacuation followed by house nitrogen.

Once the vapor deposition apparatus was prepared, a slow flow of nitrogen was applied to the first chamber across the TPS into the second chamber, and finally exiting the second chamber through an oil bubbler. The slow flow of nitrogen was maintained for 1 hour. After vapor deposition the two chambers of the apparatus were sealed and the second chamber containing the TiO<sub>2</sub> thin films was evacuated for another two hours to ensure that all residual vapor was removed. After the two-hour evacuation the slides were exposed to air and used as necessary.

### 2.1.2. Infrared spectroscopy

Diffuse reflectance IR spectroscopy was carried out using a Thermo Electron Corporation Nicolet 6700 FT-IR equipped with a Thermo FT-IR DRIFTS accessory. Samples were prepared by removing TPS coated TiO<sub>2</sub> thin films from their glass support and mixing 1 part TPS coated TiO<sub>2</sub> with 9 parts KBr by weight with a mortar and pestle. The spectrum of TPS was collected neat with a NaCl salt plate.

## 2.2. Computational Methods

This section describes the construction of computational structural models of TiO<sub>2</sub> nanoparticles functionalized with TPS adsorbates for calculations of binding enthalpies and simulations of IR vibrational spectra.

### 2.2.1. Precursor Structural Models

Precursor structural models of TiO<sub>2</sub> anatase nanoparticles, functionalized with TPS monomers, were obtained by DFT geometry optimization, starting with the crystal structure of bulk anatase. Model nanoparticles, composed of TPS adsorbed on the (101) surface of anatase, were described by 32 [TiO<sub>2</sub>] units with dimensions 1.0 × 1.5 × 3.1 nm along the [-101], [010] and [101] directions, respectively. Periodic boundary conditions were imposed with a vacuum spacer between slabs, making negligible the interaction between distinct surfaces in the infinitely periodic model system. The surface dangling bonds were saturated with capping hydrogen atoms, in order to quench the formation of surface states<sup>29</sup> and avoid unphysical low coordination numbers. The DFT geometry relaxation was performed by using the Vienna Ab-initio Simulation Package (VASP/VAMP)<sup>30,32</sup> implementing the PW91/GGA<sup>33</sup> approximation in a plane-wave basis ultrasoft Vanderbilt pseudopotentials<sup>34</sup> to describe the ionic interactions. A wavefunction cutoff of 400 eV was used in all calculations as well as a single Gamma point k-point sampling due to the large size of the supercell. The Kohn-Sham (KS) Hamiltonian was projected onto a plane-wave basis set and high-efficiency iterative methods were implemented to obtain the KS eigenstates and eigenvalues. Self-consistency was accelerated by means of efficient charge density mixing schemes.

### 2.2.2. Binding Enthalpies and IR Spectra

DFT calculations of binding energies and simulations of IR vibrational spectra are based on reduced models of TiO<sub>2</sub> NPs functionalized with TPS, constructed from the fully optimized configurations of the precursor structural models described in Sec. 2.2.1. The reduced models included TPS adsorbed onto 6[TiO<sub>2</sub>] units and capped with terminal OH fragments, where the position of the O atoms in the capping fragments were constrained to their corresponding positions in the 32 [TiO<sub>2</sub>] unit precursor structure. The reduced models were fully relaxed by energy minimization at the DFT level, using the Becke-3-Lee-Yang-Parr (B3LYP) hybrid density functional,<sup>35</sup> as implemented in Gaussian 03,<sup>36</sup> subject to the constraints of fixed OH capping fragments. A combination of basis sets was chosen to optimize accuracy and efficiency, including the LACVP basis set considering non-relativistic electron core potentials (ECPs) for Ti, and the 6-31G\*\* basis set for the rest of the atoms (*i.e.*, C, H, Si and O) in the model. Calculations with smaller basis sets, including LACVP/3-21G, 6-31G and 6-31G\* were also performed to investigate convergence.

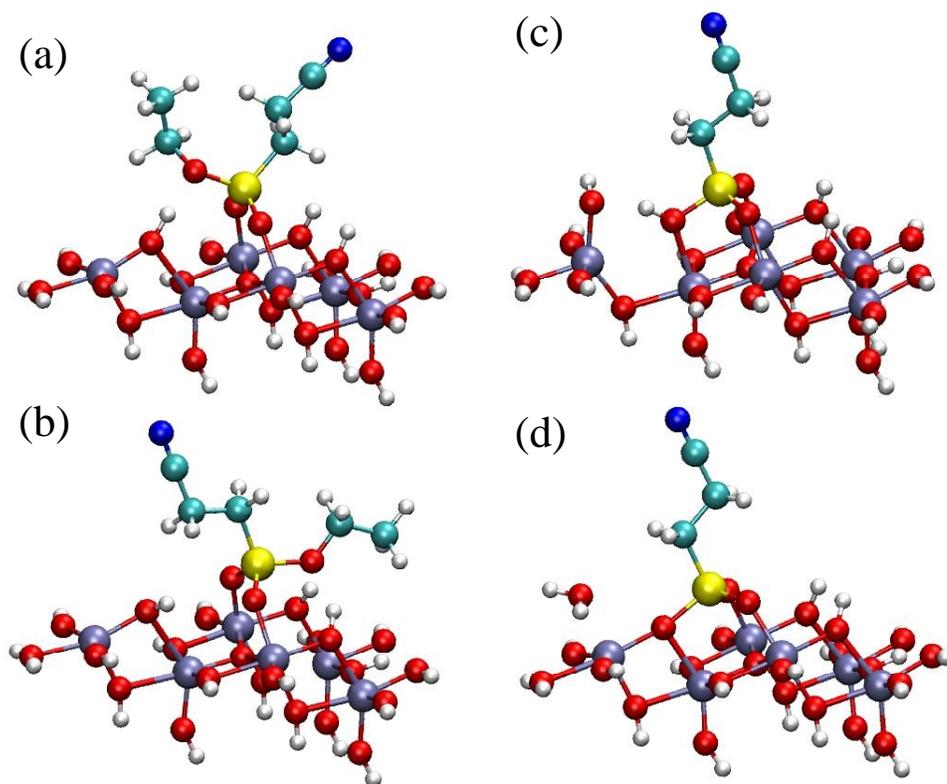
## 3. RESULTS

### 3.1. Binding Energies

A Figure 3 shows relaxed configurations of TiO<sub>2</sub>-anatase nanostructures, functionalized with TPS, after fully optimizing the energy of the system with respect to the geometry of the adsorbate and the atoms in the TiO<sub>2</sub> surface subject to the constraint of fixed terminal OH fragments, as described in Sec. 2.2.2. Four binding modes are compared, including structures (a) and (b), where TPS is covalently attached to the TiO<sub>2</sub> surface according to two alternative 'bridge' binding modes (*e.g.*, simultaneously ligating two Ti<sup>4+</sup> ions on the [101] surface), and structures (c) and (d) where TPS is covalently attached to the TiO<sub>2</sub> surface according to a 'tripod' motif (*e.g.*, simultaneously ligating three Ti<sup>4+</sup> ions on the [101] surface). The main differences between 'bridge' and 'tripod' motifs are the hydrogen-bonding interactions between the surface and the adsorbate in the 'bridge' configuration, not present in 'tripod' motif, and the Si-O-C modes in the 'bridge' structures, leading to differences in binding energies and distinct vibrational spectra (*vide infra*).

Figure 3 also illustrates that binding of siloxane onto anatase induces local conformational changes in the TiO<sub>2</sub> structure, including small geometry rearrangements of the Ti<sup>4+</sup> and O<sup>2-</sup> ions next to the molecular adsorbate. The Ti<sup>4+</sup>

ions anchoring the siloxane molecule are displaced 0.02 Å inward relative to the (101) plane of the crystal in structures (a), (b), and (c), while it is displaced 0.02 Å outward in structure (d). Both in bridge mode and the three-legged



**Figure 3.** Comparison of relaxed configurations of model anatase nanostructures sensitized with 3-(Triethoxysilyl) propionitrile (TPS) anchored to the [101] surface in bridging modes, panels (a) and (b) (e.g., simultaneously ligating two different  $\text{Ti}^{4+}$  ions); and covalently attached as a tripod panels (c) and (d) (e.g., simultaneously ligating three different  $\text{Ti}^{4+}$  ions). Color key: Si (yellow), C(light-blue), O(red), Ti (purple), H (white) and N(blue).

attachment, the 3-fold coordinated  $\text{O}^{2-}$  ions connected to both of these  $\text{Ti}^{4+}$  ions are displaced significantly inward relative to the [101] plane of the crystal. Contrary to the understanding that this rearrangement places  $\text{O}^{2-}$  ions to remain at an equidistant position relative to its three nearest  $\text{Ti}^{4+}$  ions, the distance between  $\text{O}^{2-}$  ion and the nearest  $\text{Ti}^{4+}$  ions are about 1.75 Å, 2.1 Å, and 2.1 Å. Our computations have allowed for substantial surface relaxation that takes place, with the minimum-geometry structures being significantly different from the initial configuration where the corresponding bond distances are 1.98 Å (hexacoordinate Ti-O) and 1.93 Å (for both pentacoordinate Ti-O). These structural changes are important within the context of interfacial electron transfer since the  $\text{Ti}^{4+}$  ions directly attached to the molecular adsorbate and the hexacoordinated  $\text{Ti}^{4+}$  ion next to the adsorbate often play a crucial role in the interfacial electron transfer mechanisms.<sup>51, 53</sup>

Table 1 compares the binding enthalpies  $\Delta H_b(0 \text{ K})$  of TPS grafted onto pristine [101]  $\text{TiO}_2$ -anatase surfaces as described by the minimum energy structures (a)–(d) depicted in Fig. 3. All binding enthalpies were

**Table 1:** Binding energies  $\Delta H_b(0 \text{ K})$ , in kcal mol<sup>-1</sup>, for 3-(triethoxysilyl) propionitrile (TPS) moieties anchored onto the [101] surface of  $\text{TiO}_2$ -anatase nanostructures, as described by models (a)–(d), shown in Fig. 3, in their hydrolyzed forms. Calculations are reported at the DFT B3LYP/ LACVP level of theory, with various basis sets for O, H, C and Si, including 3-21G, 6-31G, 6-31G\* and 6-31G\*\*.

1.1	3-21G	6-31G	6-31G*	6-31G**
(a)	107	79	53	54
(b)	102	71	52	52
(c)	96	64	43	43
(d)	97	71	45	45

computed as the total energy difference for the model system with the adsorbate attached and detached from the surface, and corrected with the zero-point energies obtained from the vibrational analysis. The results obtained at various levels of basis sets indicate the importance of polarization functions for a proper description of surface-adsorbate interactions, due to the strong influence of covalent bonding interactions on the Si-O-Ti and O-Si-O- bending angles. The binding energies obtained at the DFT B3LYP/(LACVP, 6-31G\*\*) level of theory are 54, 52, 43 and 45 kcal/mol, for structures (a)–(d), respectively, indicating that the ‘bridge’ mode binding is more stable than the ‘tripod’ motif. Binding with three covalent bonds onto the TiO<sub>2</sub> surface is approximately 10 kcal mol<sup>-1</sup> less stable than when forming only 2 covalent bonds in ‘bridge’ mode configurations, due to the resulting strained attachment of the third covalent bond onto the surface and the resulting conformational changes induced by binding in the TiO<sub>2</sub> anchoring site.

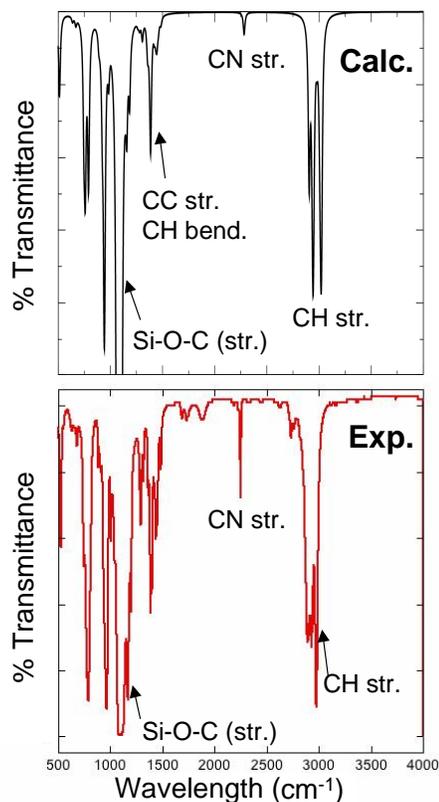
### 3.1. Vibrational Analysis

Figure 4 shows the comparison of calculated and experimental IR spectra of neat TPS. The calculated spectrum, obtained at the B3LYP/(LACVP, 6-31G\*\*) level of theory, is reported with frequencies scaled with a factor  $f=0.965$  to facilitate the comparison with experimental data. The favorable comparison between theory and experiment, shown in Fig. 4, allows the unambiguous assignment of spectroscopic features, including the fingerprint vibrational bands associated with the Si-O-C stretching modes at 1000–1100 cm<sup>-1</sup>, the adsorbate C-C stretching and C-H bending modes in the 1300–1500 cm<sup>-1</sup> range, the characteristic C≡N stretch at 2300 cm<sup>-1</sup>, and the C-H stretching modes at 2900–3100 cm<sup>-1</sup>.

Figure 5 shows the experimental FT-IR DRIFTS spectra of various TiO<sub>2</sub> samples, including untreated Degussa P25 NPs; NPs coated with TSP by chemical vapor deposition; NPs coated with TPS and then treated with heat [overnight 120 °C] (green), H<sub>2</sub>O [30 min. RT] (dark blue), and both heat and water (light blue) to test the durability of the resulting adsorbate complex. These experimental spectra can be assigned in terms of the vibrational analysis of the computational models (a)–(d), shown in Fig. 3, and the comparison with the spectrum of neat TPS, shown in Fig. 4.

Many of the spectroscopic features observed in the experimental difference spectra corresponding to *functionalized-minus-bare* NPs (Fig. 6, right) are common to the spectrum of neat TPS, including the Si-O-C stretching modes at 1000–1100 cm<sup>-1</sup>, the C-C stretching and C-H bending modes in the 1300–1500 cm<sup>-1</sup> range, the characteristic C≡N stretch at 2300 cm<sup>-1</sup>, and the C-H stretching modes at 2900–3100 cm<sup>-1</sup>. However, the fingerprint band in the 1000–1100 cm<sup>-1</sup> range is much broader in the difference spectra than in the spectrum of neat TPS, suggesting inhomogeneous broadening due to interactions with the surfaces (e.g., hydrogen-bonding interactions of the Si-O-C fragment with the TiO<sub>2</sub> surface), or the presence of additional stretching modes of similar frequency (e.g., Si-O-Si stretching modes due to interlinked siloxane adsorbates). In addition, the observation of OH-bending at ~1600 cm<sup>-1</sup> and a broad OH-stretching band in the 3200–3500 cm<sup>-1</sup> range, suggests the presence of water on the substrate surface.

Our assignment of spectroscopic bands, described in Fig. 5, is based on calculations of IR spectra at the B3LYP/(lacvp, 6-31G\*\*) level of theory of siloxane adsorbates attached onto TiO<sub>2</sub>, including the IR spectra of the four model structures (a)–(d), depicted in Fig. 3, as compared to the spectrum of the bare TiO<sub>2</sub> host substrate. Computational results are reported as *functionalized-minus-bare* TiO<sub>2</sub> IR difference spectra in order to facilitate comparison with experimental data by canceling out spectroscopic features common to TiO<sub>2</sub>.



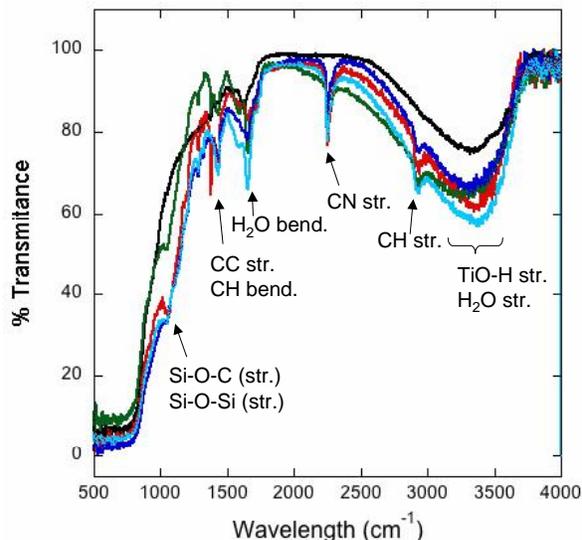
**Figure 4:** Comparison of experimental (bottom) FT-IR spectrum of neat 3-(Triethoxysilyl) propionitrile (TPS) and calculated spectrum (top) at the DFT B3LYP level as described in the text.

Figure 6 compares the calculated IR difference spectra of *functionalized-minus-bare* TiO<sub>2</sub> NPs as described by the vibrational analysis of models (b) and (d), introduced in Fig. 3, to the corresponding experimental data for TiO<sub>2</sub> NPs functionalized with TPS by chemical vapor deposition as described in Sec. 2.1.1 and subsequent treatment with heat and water. The one to one correspondence of spectroscopic features, in calculated and experimental data, supports our assignment of vibrational bands presented in Fig. 6.

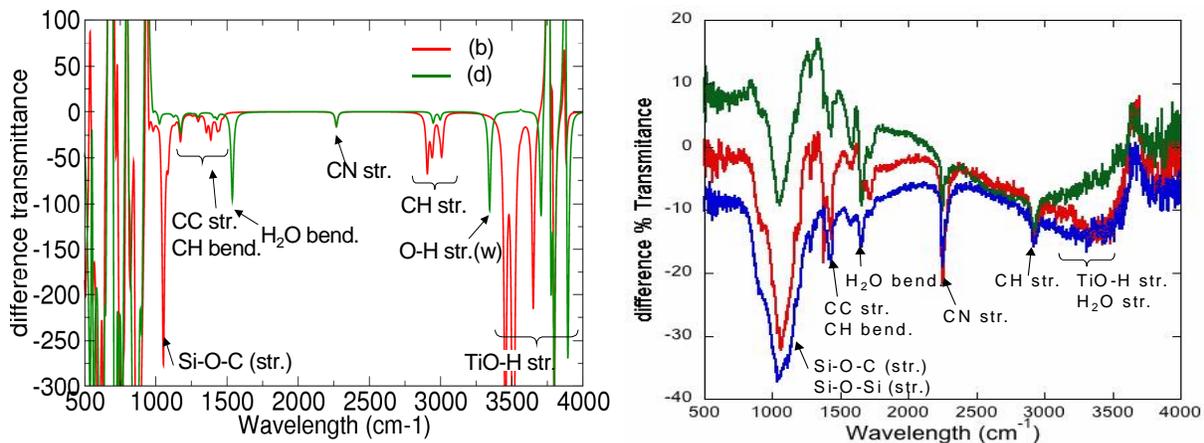
The comparison of difference spectra obtained with models (b) and (d) (see Fig. 6, left panel) shows that only siloxane monomers with ‘dangling’ alkoxy groups, such as the ethoxyl group in model (b), have a prominent band in the 1000–1100 cm<sup>-1</sup> range (due to Si-O-C stretching modes).

The observation of that frequency band in the experimental data (Fig. 6, right panel), therefore, rules out the possibility of having attachment of TPS adsorbates exclusively by ‘tripod’ motifs, as in structure (d). These results are consistent with the energetic analysis of binding enthalpies, discussed in Sec. 3.1, that favored ‘bridge’ binding over ‘tripod’ configurations.

Another possibility would be to assign the broad band, in the 1000–1100 cm<sup>-1</sup> range, to Si-O-Si stretching modes associated with cross-linked siloxane adsorbates. Such a spectroscopic assignment, however, is discredited by the observation that the band becomes less prominent by treatment with heat, and remains almost unchanged by treatment with water and heat. Both of these observations are inconsistent with the assignment of the band to Si-O-Si stretching modes, since cross-linking of siloxane adsorbates is favored by such conditions (see Fig. 2) and therefore the band would be more prominent upon treatment with heat and water. In contrast, the assignment to Si-O-C stretching modes is consistent with the intensity attenuation upon heat treatment, since such treatment under anhydrous conditions might expel R'OH to yield siloxane bridges form by condensation reactions.



**Figure 5:** (Top): Experimental diffuse reflectance FT-IR spectra of TiO<sub>2</sub> samples in KBr, 1:10 by weight. Color key: **Black:** Untreated Degusa P25 nanoparticles (NPs). **Red:** NPs coated with 3-(Triethoxysilyl) propionitrile (TPS) by vapor diffusion (NPs/TPS). **Green:** NPs/TPS treated with heat [overnight 120 °C]. **Dark blue:** NPs/TPS treated with H<sub>2</sub>O [30 min. RT], **Light blue:** NPs/TPS treated with heat and H<sub>2</sub>O.



**Figure 6:** Comparison of calculated (left panel) and experimental (right panel) difference IR spectra, corresponding to *functionalized-minus-bare* NPs. Color key: (left panel) **Red:** IR difference spectra obtained with model (b), shown in Fig. 3, where TPS is attached in a ‘bridge’ mode with an unreacted ‘dangling’ ethoxy group. **Green:** IR difference spectra obtained with model (d), shown in Fig. 3, where TPS is attached in a ‘tripod’ motif. (right panel) The spectra are offset to facilitate easier comparison. **Red:** NPs/TPS prepared by vapor diffusion. **Green:** NPs/TPS treated with heat [overnight, 120 °C]. **Blue:** NPs/TPS treated with heat and H<sub>2</sub>O.

## 4. CONCLUSIONS

In this paper we have characterized the grafting of TPS moieties onto TiO<sub>2</sub> thin-films by anhydrous chemical vapor deposition, using a combination of FT-IR spectroscopy and DFT molecular modeling. Calculations of binding enthalpies and simulations of IR vibrational spectra, validated by direct comparisons with experimental data, lead to the development of a bonding model of TPS onto TiO<sub>2</sub> surfaces. We conclude that TPS, and probably most trifunctional siloxane molecules with the general formula R-(CH<sub>2</sub>)<sub>n</sub>-Si-(OR')<sub>3</sub>, must bind by forming only two Ti-O-Si covalent bonds per adsorbate, with adjacent Ti<sup>4+</sup> ions, leaving 'dangling' alkoxy siloxane groups on the surface. Exclusive binding by forming three Ti-O-Si covalent bonds with adjacent Ti<sup>4+</sup> ions (*e.g.*, 'tripod' motifs) can be ruled out by the observation of a fingerprint band in the 1000–1100 cm<sup>-1</sup> range, assigned to Si-O-C stretching modes, and by the unfavorable binding enthalpies when compared to 'bridge' configurations. We anticipate that the 'dangling' alkoxy groups could be exploited for immobilizing other functionalities onto TiO<sub>2</sub> surface complexes. Such surface adsorbates should be robust to heat and water treatment and could be designed for practical applications (*e.g.*, analytical methods to quantify surface coverage, or to detect chemical species that might react with immobilized functionalities).

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