

Structural, electronic, and thermodynamic properties of TiO₂/organic clusters: performance of DFTB method with different parameter sets

Vladimir S. Naumov^{1,2}  | Anastasiia S. Loginova¹ | Alexander A. Avdoshin¹ | Stanislav K. Ignatov¹  | Alexey V. Mayorov^{3,4} | Bálint Aradi² | Thomas Frauenheim²

¹Department of Chemistry and Research Institute of Chemistry, N.I. Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia

²Bremen Center for Computational Material Studies, University of Bremen, Bremen, Germany

³Mass Spectrometry Data Center, National Institute of Standards and Technologies, Gaithersburg, Maryland

⁴A. A. Kharkevich Institute for Information Transmission Problems, Russian Academy of Sciences, Moscow, Russia

Correspondence

Vladimir S. Naumov, Department of Chemistry and Research Institute of Chemistry, N.I. Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia.
Email: vsnaumov@yandex.ru

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Abstract

The clusters of bare TiO₂ and TiO₂ with linked organic ligands modeling polyorganic composites used as photocatalytic materials were studied using the density functional based tight binding (DFTB) electronic structure method with three parameter sets (*trans3d*, *tiorg*, and *matsci*) in comparison with results of B3LYP/6-31G(d,p) calculations, semiempirical methods PM6 and PM7, and available experimental data. It was found that the highly scalable DFTB method shows results that are close to the B3LYP/6-31G(d,p) level of theory. The corrected version of the *tiorg* DFTB parameter set (*tiorg-smooth*) has better performance for the estimations of structural parameters, whereas the *trans3d* set better reproduces energies of the composite material formation in polycondensation reactions. Performance of the *matsci* set is somehow in the middle of the *tiorg-smooth* and *trans3d* sets. The *tiorg-smooth* and *matsci* sets can be used for the studies of adsorption complexes of bare TiO₂ clusters. All three DFTB parameter sets well estimate the electronic parameters of clusters (HOMO-LUMO gap, ionization potential, and dipole moment). DFTB results are closer to the estimates made with DFT (B3LYP/6-31G(d,p)) than the results of PM6 and PM7 methods. DFTB calculations of large (up to 448 atoms) bare TiO₂ and TiO₂/organic clusters (72 structures in total) confirm the robustness and computational efficiency of the method.

KEYWORDS

clusters, DFT, DFTB, HEMA, parameter sets performance, semi-empirical methods, TiO₂

1 | INTRODUCTION

Titanium oxide is one of the most widely used components of modern materials in the field of photovoltaics and photocatalysis.^[1-3] For such applications, the nanostructured TiO₂ incorporated in the porous polymeric matrices preventing nanoparticle cohesion is considered a promising photocatalytic material for oxidation reactions providing, for example, the efficient elimination of environmental organic contaminants. Its action is based on the formation of Ti³⁺ active centers during the light absorption or by the electron transfer from the neighboring metallic nanoparticles incorporated into the same matrix. This mechanism of action makes the nanomaterial open for further improvements on the basis of quantum chemical modeling of these processes with variation of the cluster size, morphology, and matrix composition. This modeling is, however, complicated by the necessity of carrying out quantum calculations for the large bulks of material with incorporated real-scale nanoparticles because the small models are not representative of the description of the processes occurring on the nano level.

The analysis of studies on the properties of the TiO₂-based nanomaterials shows that the requirements for the minimum cluster size, which would ensure a correct description of these properties, are permanently growing. For instance, one study^[4] reported (TiO₂)₆ as the cluster-reproducing band gap of bulk TiO₂. In a theoretical study,^[5] the authors conclude that (TiO₂)₆ clusters are able to estimate semiquantitatively features of electronic structure of the Ti/alizarin complexes. Later, the same authors^[6] found that (TiO₂)₁₅ is the minimal cluster that could provide a complete picture for the TiO₂/catechol system. Studies^[7,8] show that the (TiO₂)₂₄(OH)₄ cluster could be a reasonable compromise between accuracy and computational costs. One of the most recent studies^[9] systematically focused on Ti_nO_{2n+2}H₄ clusters with *n* from 14 to 54, and the main conclusion is that at least 34 titanium atoms in a cluster are necessary to provide reliable predictions for the photocatalytic and photovoltaic applications. The growth of the minimal cluster size makes DFT calculations that are routinely used for the calculations of reactions between small- and medium-size molecules impractical, and various kinds of simplified quantum chemical methods should be utilized. There are few main approaches to simulate relatively large TiO₂ models. Most of the studies explore large TiO₂ models using B3LYP^[8-17] or Perdew–Burke–Ernzerhof (PBE)^[6,13,18-21] functionals combined with simplified basis sets, including the effective core potentials approach.^[7,10-12,14,15,17] Other studies use semiempirical methods.^[16,22-24] Works using Car-Parinello calculations with plane-wave basis and ultrasoft pseudopotentials should also be noted.^[13,18-20]

Among the variety of simulation methods, the density functional tight-binding theory (DFTB) is one of the promising alternatives. It provides a very efficient estimation of different properties for many organic,^[25-28] inorganic,^[29-32] and organometallic^[33-35] species. However, its application to the TiO₂-based materials, especially in contact with metallic nanoparticles, is still restricted due to the lack of reliable atomic parameters for Ti and other metal atoms. Earlier, several parameter sets were proposed for TiO₂-based materials: *trans3d*,^[36] *tiorg*,^[37] and *matsci*.^[38-41] As noted by the authors of *trans3d* parameters,^[36] there are some known difficulties concerning the Ti–O bond and O–Ti–O angles. The *tiorg* parameter set was developed mostly for the solid-state applications and tested only with small molecular systems.^[37] The *matsci* parameters for Ti were tested mainly for systems comprising Ti, O, and H atoms^[40,41] and for rather specific cases, such as interactions of TiO₂ with phosphonic acids^[38] or DNA.^[39] Modifications of *matsci*—called *matorg* and *matorg + HBD*—should be noted as they show the results close to the DFT level for TiO₂-water systems. However, it is not completely clear how good all these parameter sets are for the description of TiO₂ nanoparticles and clusters incorporated into organic matrix, which form numerous chemical bonds with oxide atoms and modify their electronic properties.

In the present article, we make a systematic comparison between DFTB parameter sets and compare them with the results of the DFT calculations, as well as with available experimental data and calculations performed with semiempirical methods PM6 and PM7, which were successfully used for bare TiO₂ clusters in recent studies.^[16,23,24] The goal of this study is to assess how reliable the estimates made with three DFTB parameter sets are in the small-size and medium-size organo-inorganic clusters and how effective and robust the DFTB calculations of the large-sized TiO₂ clusters are, with the organic ligands modeling real-world organo-inorganic composite materials. Among the properties of interest, we consider the structure of clusters with grafting ligands, their electronic properties (ionization potentials, electron affinities, band gaps, dipole moments), vibrational spectra, and thermodynamic parameters of the composite cluster formation because the proper prediction of these properties are most important for the design and synthesis of the photocatalytic materials.^[42] As an example of the grafting ligands, we consider here the residues of hydroxyethylmethacrylate (CH₂=C(CH₃)-C(O)-O-C₂H₄-OH, HEMA), which was used recently for the synthesis of TiO₂-based nanocomposite materials with improved photocatalytic properties.^[43-45]

2 | COMPUTATIONAL DETAILS

All DFTB calculations were carried out using the DFTB+ code^[46] and three parameter sets elaborated earlier: *trans3d*,^[36] *tiorg*,^[37] and *matsci*.^[38,39] In addition, the *tiorg* parameter set was modified in order to achieve better performance in vibrational frequency calculations of composite materials. This modification includes improved spline smoothing of the Ti-X atomic potentials (where X = C, H, O, Ti). Due to this modification, the non-realistically high vibrational frequencies, which had been found at the organic-inorganic interfaces, were eliminated. Using the modified parameter set (which will be referenced in the following as *tiorg-smooth*), calculations were performed for the whole set of structures. Because the results obtained with *tiorg* and *tiorg-smooth* parameters are essentially the same for all the properties except the vibrational frequencies, we will describe below only the results obtained with the *tiorg-smooth* parameter set. The *tiorg-smooth* parameter set is available for download on the website <http://www.qchem.unn.ru>.

The data calculated using the DFTB method were compared with DFT and semiempirical calculation results. The DFT calculations at B3LYP/6-31G(d,p), CAM-B3LYP/6-31G(d,p), and semiempirical (PM6^[47] and PM7^[48]) theory levels were performed using Gaussian03^[49] and Gaussian16^[50] programs. The DFT functional and basis sets were chosen on the basis of the previous study of the TiO₂/HEMA composites,^[44] where this level of theory was the best among the levels, well reproducing structural, energetic, and electronic parameters of small TiO₂/HEMA clusters, as well as these composites with coordinated Au atoms and clusters.

Structures 1 to 19 (Figure 1) in the DFT calculations were geometrically relaxed at the B3LYP/6-31G(d,p) theory level. For structures 20 to 27, geometries reported by Chen^[16] at the B3LYP/DZVP2 level were taken for the single-point DFT calculations. In addition, for structures 20, 21, and 22, geometry optimization were performed at the B3LYP/6-31G(d,p) level in order to estimate the discrepancies between 6-31G(d,p) and DZVP2. We consider these discrepancies negligible and predictable (see Table 1) and therefore use DZVP2 geometries in the further comparisons

between DFTB, semiempirical, and DFT methods. To estimate electronic properties, CAM-B3LYP/6-31G(d,p) and B3LYP/6-31G(d,p) single-point calculations were carried out with the geometries optimized at the B3LYP/6-31G(d,p) level for the TiO₂/organic clusters and at the B3LYP/DZVP2 level for the bare TiO₂ particles.

The cluster structures chosen for the calculations include several types of structures: (a) the bare clusters with morphology of anatase and rutile crystals, (b) the clusters found earlier to be very favorable at DFT (B3LYP/DZVP2) and PM6 levels,^[16] and (c) the clusters with linked organic ligands. Some of the TiO₂/organic clusters were generated on the basis of recently described structures of TiO₂ particles.^[51,52] Among the organic ligands, the HEMA substituents were used in the most cases as real-world polymers used for the photocatalytic composite synthesis.^[43] The bare TiO₂ structures could also be prospective for photocatalytic activity. For example, structure 25 (ti64a) was noted by the authors as having few potentially active catalytical sites due to structural specificity of surfaces.^[16] For some clusters, the H atoms were used as boundary terminators. All 72 structures were calculated using DFTB with different parameters sets, and 27 of them were studied using DFT, PM6, and PM7 levels of theory. During the geometry optimization, some of starting geometries were analogous to the structures considered in recent studies.^[16,44]

To estimate the adsorption energies of the CO molecule on TiO₂ surface, cluster structures 20 (ti10a), 24 (ti48b), and 25 (ti64a) were used. For each of these bare TiO₂ clusters, six adsorption complexes were considered (three interaction sites in combination with two orientations of

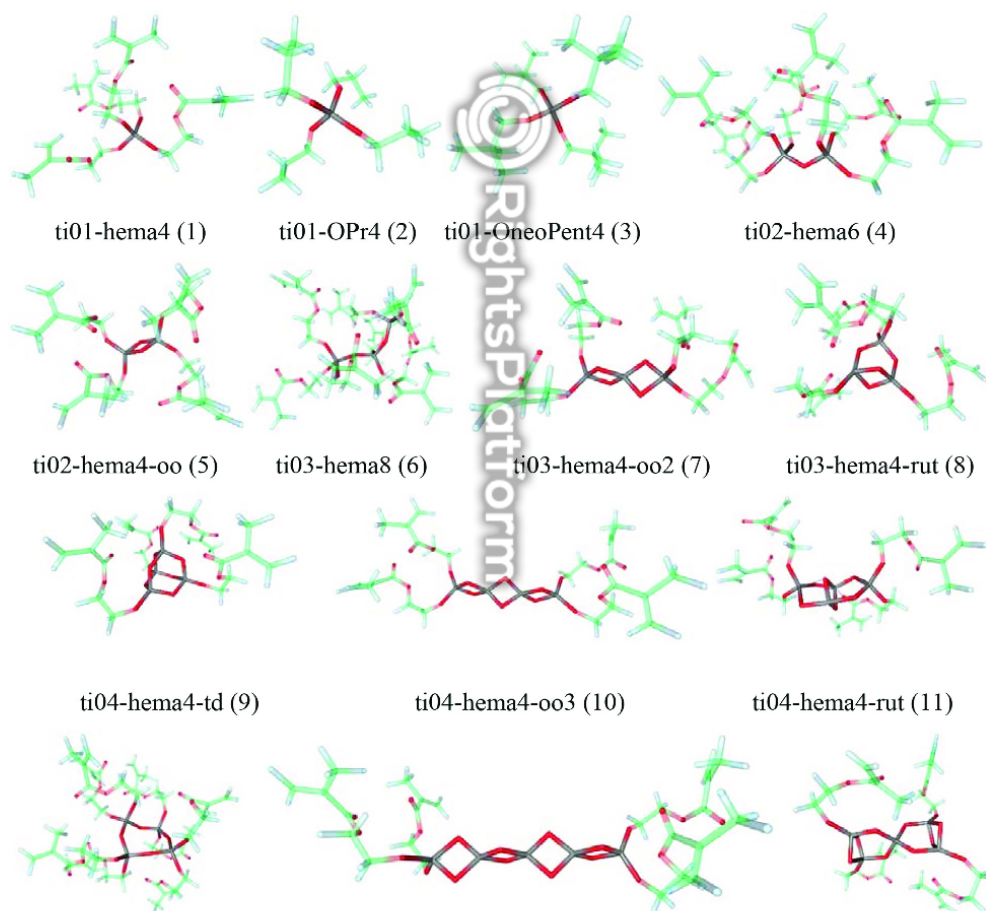
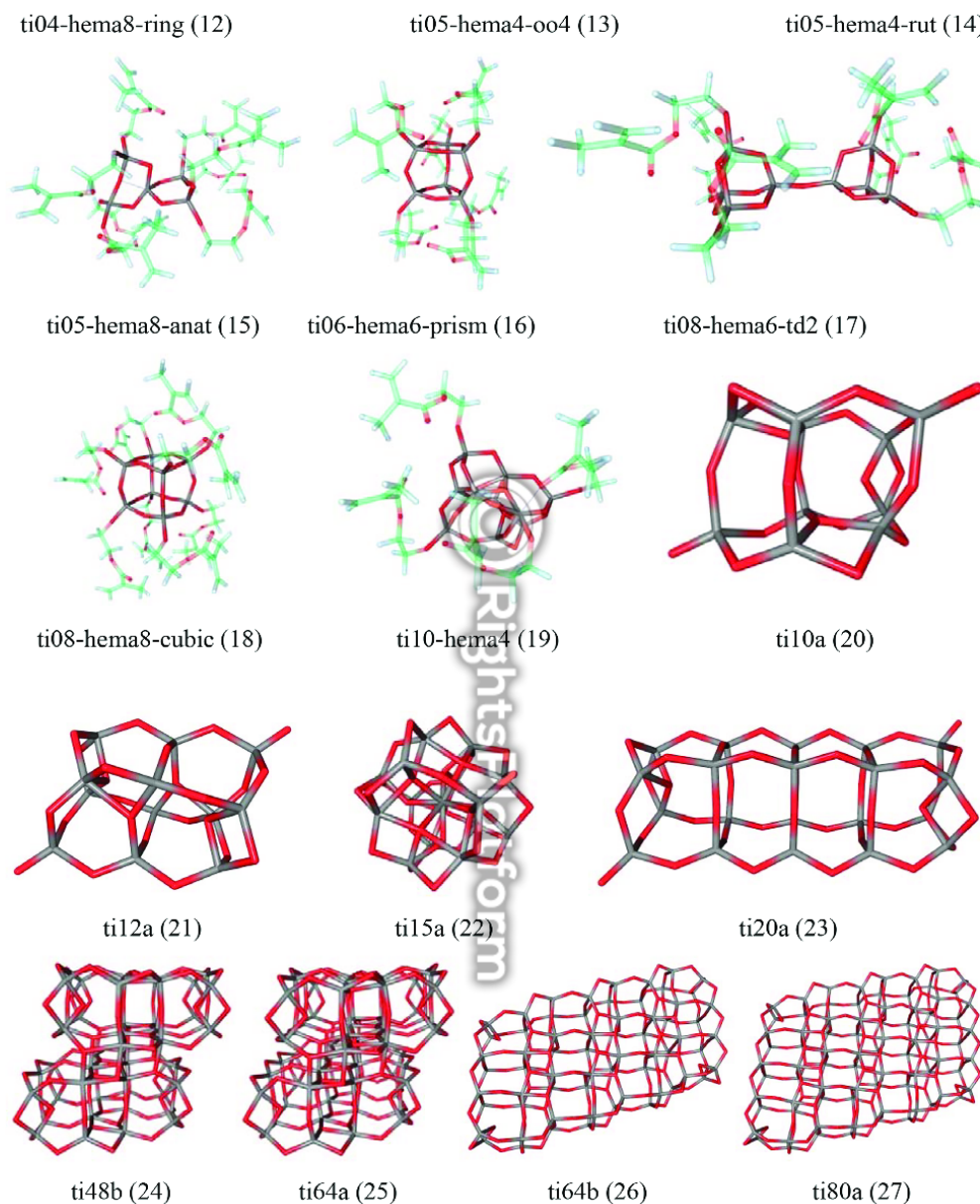


FIGURE 1 Structures of the clusters studied at the DFTB and DFT levels. Structures correspond to the DFT calculation results. The cluster designations represent structure type: numbers after "ti" correspond to the number of Ti atoms, and numbers after "hema"/"OPr"/"OneoPent" correspond to the number of organic residues. In addition, some structural and geometrical motifs in structures 1 to 19 are designated as "oo" for the double-O bridges, "anat" for the anatase motifs, "rut" for the rutile motifs, "cubic", "prism", and "td" (tetrahedron). Designations of structures 20 to 27 are the same as in^[16]

**FIGURE 1** (Continued)

CO molecule). Calculations were performed for the on-top complexes when CO is coordinated on a single Ti atom. The initial Ti...C/O distances were about 2 Å. All the adsorption calculations were performed using three DFTB parameter sets: *trans3d*, *tiorg-smooth*, and *matsci*. Some small adsorption complexes were also studied at the B3LYP/6-31G(d,p) level. Some structures optimized with the *tiorg-smooth* parameter set are represented in Figure 2. In addition, combined DFTB calculations with *tiorg-smooth* geometrical preoptimization and further optimization with *trans3d* were performed to estimate the performance of the parameter sets (see further details in the Results section).

TABLE 1 Structural and electronic parameters of the bare TiO₂ clusters at different DFT theory levels

Property	DFT Basis	Structures (Figure 1)		
		10a (20)	12a (21)	15a (22)
Structural properties				
Ti–O, Å (averaged values)	DZVP2 ^a	1.858	1.849	1.899
	6-31G(d,p)	1.843	1.844	1.857
O–Ti–O, ° (averaged values)	DZVP2 ^a	107.3	108.0	106.3
	6-31G(d,p)	107.4	107.8	107.0
Electronic properties				
IP (–E _{HOMO}), eV	DZVP2 ^a	8.75	8.90	8.94
	6-31G(d,p) // DZVP2 ^b	8.51	8.70	8.77
	6-31G(d,p)	8.62	8.80	8.63
EA (–E _{LUMO}), eV	DZVP2 ^a	4.42	4.37	4.41
	6-31G(d,p) // DZVP2 ^b	4.15	4.13	4.23
	6-31G(d,p)	4.05	4.02	3.76
BG, eV	DZVP2 ^a	4.33	4.53	4.54
	6-31G(d,p) // DZVP2 ^b	4.36	4.57	4.54
	6-31G(d,p)	4.57	4.78	4.87

^aData from Reference 16.

^bSingle-point B3LYP/6-31G(d,p) calculations for the geometries from Reference 16.

3 | RESULTS

3.1 | Structural properties

Structures of the clusters calculated at DFT, DFTB, and semiempirical levels are shown in Figure 1. The remaining clusters studied at the DFTB level only within three parameter sets are presented in Figure S1 of Supporting Information. Averaged values of bonds, valence angles, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, and band gaps are represented in Table 2. The data are collected into three groups: (a) the average values among all the structures, (b) the values averaged only among TiO₂/organic clusters, and (c) those only among bare TiO₂ clusters.

According to the available experimental data, average Ti–O bond lengths between the nearest atoms inside the 30 Å nanoparticles are about 1.84 Å for the surface bonds and 1.99 Å for the internal ones.^[51] When the size of the nanoparticles decreases to 19 Å, the average Ti–O bond length reduces to 1.77 Å (surface bonds) and 1.94 Å (internal bonds).^[53] The average Ti–O bond length of bulk TiO₂ crystalline phases is 1.96 Å.^[54,55] As is evident from Table 2, the B3LYP-calculated values are in agreement with experimental data, and the B3LYP values are rather reliable in describing the structure of titanium dioxide.

Statistical analysis of bond lengths and valence angles demonstrates rather significant discrepancies between *trans3d*, *tiorg-smooth*, *mtsc*, DFT, and semiempirical calculated structural parameters. Figure 3 shows the comparison between the mean values of the Ti–O bond lengths, including separate analysis of different types of such bonds: Ti–O_{ino} for oxygen atoms inside the inorganic part of cluster (connected with two titanium atoms) and Ti–O_{org} for oxygen atoms that are connected to titanium and carbon.

Figure 3 shows that calculated bond lengths obtained with DFTB are typically closer to the DFT results than that obtained by the PM6 and PM7 methods. Typical mean absolute deviation (MAD) between DFT and semiempirical levels is up to 0.07 Å. The *trans3d* parameters tend to slightly overestimate the Ti–O bond lengths relative to DFT, especially in the case of Ti–O_{org} moieties (MAD is 0.031 Å). The *tiorg-smooth* parameter set underestimates Ti–O bond lengths by only about 0.001 to 0.003 Å on average, and MAD is up to 0.023 Å and is larger for the TiO₂/organic clusters. In geometries obtained by calculations with *matsci* parameters, the Ti–O bond is overestimated by about 0.021 Å for Ti–O_{ino} (MAD is 0.023 Å); in the case of bonds between organic and inorganic parts, average overestimation is 0.048 Å. Table 3 gives the complete statistical analysis for the discrepancies between DFTB *tiorg-smooth*, DFTB *trans3d*, DFTB *matsci*, PM6, and PM7 in comparison with DFT theory, along with different properties including structural, electronic, and thermodynamic characteristics.

Figure 4 demonstrates the deviations of the O–Ti–O average angles calculated at the DFT, semiempirical, and DFTB levels with *trans3d*, *tiorg-smooth*, and *matsci* parameters. All the methods give quite close results, and MAD from the DFT level is not larger than 1.68°. There are some noticeable exceptions—few structures show the deviations from DFT by about 2 to 3°, which is still a very accurate result. The closest to B3LYP results were obtained by DFTB *tiorg-smooth* (typical MAD value is 0.31°).

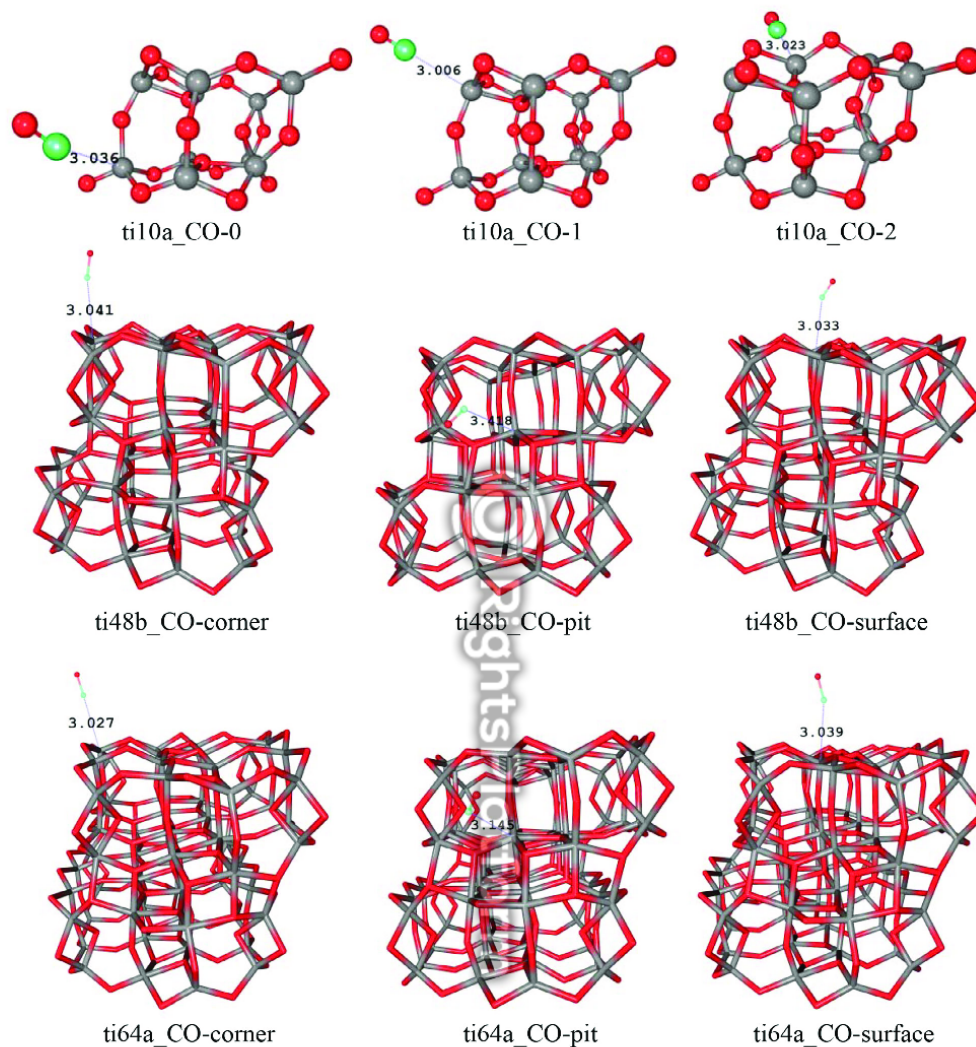


FIGURE 2 Structures of adsorption complexes of carbon monoxide on bare TiO_2 clusters with $\text{Ti} \cdots \text{C}$ interactions optimized at DFTB *tiorg-smooth* level

The comparison between Ti-O-C angles calculated with different theory levels is shown in Figure 5. As is seen, there are crucial differences between the results of DFT, DFTB, and semiempirical methods. The *tiorg-smooth* demonstrates only negligible deviation from the DFT values (about 140°), whereas other DFTB parameter sets and semiempirical methods give quite unrealistic values of Ti-O-C valence angles of about 115° and 175° , respectively, for all the compounds. These results lead to a significant difference in the MADs as is evident from Table 3: 3.4° for *tiorg-smooth*; 13.9° for *matsci*; and about 30° for *trans3d*, *PM6*, and *PM7*.

Based on the results obtained, we conclude that *tiorg-smooth* parameters better describe the bond lengths in the clusters of interests and coincide much better with the DFT values of Ti-O-C valence angles in the organic ligands linked to the TiO_2 surface. All DFTB parameter sets demonstrate good agreement with DFT for O-Ti-O angles. In general, the DFTB method is superior in describing the structure of TiO_2 /organic clusters than semiempirical methods.

TABLE 2 Structural and electronic parameters of TiO₂/organic clusters calculated with different quantum chemical methods. Data represent the values averaged among all clusters, among TiO₂/organic clusters (in parentheses), and among bare TiO₂ clusters [in brackets]

Property	DFT	PM6	PM7	DFTB (<i>tos</i>)	DFTB (<i>t3d</i>)	DFTB (<i>mtsc</i>)	Experiment	Exp. Ref.
Structural properties								
Ti–O, Å	1.833 (1.818) [1.869 ^a]	1.874 (1.859) [1.908]	1.869 (1.858) [1.893]	1.831 (1.816) [1.866]	1.849 (1.836) [1.877]	1.859 (1.852) [1.875]	–	
Ti–O _{ino} , Å	1.844 (1.831) [1.869 ^a]	1.897 (1.889) [1.913]	1.900 (1.902) [1.896]	1.841 (1.829) [1.866]	1.852 (1.840) [1.877]	1.865 (1.854) [1.887]	1.959 1.84 / 1.99 1.77 / 1.95	[54,55] [51] [53]
Ti–O _{org} , Å	(1.803) 108.4	(1.814) 109.2	(1.797) 108.5	(1.802) 108.6	(1.834) 109.0	(1.851) 108.4	–	
O–Ti–O, °	(108.8) [107.4 ^a]	(109.2) [109.0]	(108.6) [108.3]	(109.0) [107.4]	(109.0) [109.1]	(108.6) [107.7]	81.12 108.0	[54] [55]
Ti–O–C, °	(143.8)	(176.4)	(172.5)	(141.1)	(112.3)	(129.9)	–	
Electronic properties								
IP (– ϵ_{HOMO}), eV	7.34 ^b /8.97 ^c (6.84 ^b /8.45 ^c) [8.52 ^a /10.19 ^c]	10.65 (10.42) [11.22]	9.70 (9.69) [9.71]	5.78 (5.67) [6.04]	5.91 (5.72) [6.38]	5.99 (5.94) [6.11]	7.96 ^d 7.40 ^e 7.2 ^f 5.17 ^f	[56] [56] [27,57] [58]
EA (– ϵ_{LUMO}), eV	2.48 ^b /1.19 ^c (1.79 ^b /0.47 ^c) [4.12 ^a /2.90 ^c]	1.85 (1.58) [2.49]	1.26 (0.83) [2.29]	2.29 (2.04) [2.90]	2.76 (2.55) [3.31]	2.65 (2.53) [2.95]	4.0 ^f 1.5 ... 3.3 ^g 3.00 ... 3.6 ^g	[57] [59] [4]
BG, eV	4.86 ^b /7.78 ^c (5.05 ^b /7.98 ^c) [4.41 ^a /7.30 ^c]	8.80 (8.84) [8.72]	8.44 (8.86) [7.43]	3.48 (3.63) [3.14]	3.14 (3.17) [3.06]	3.34 (3.42) [3.16]	3.2 ^f 3.23 ^d >3.40 ^d 3.13 ^d 3.06 ^e	[57,58] [60] [60] [61] [61]

Abbreviations: *tos*, *tiorg-smooth* parameter set; *t3d*, *trans3d* parameter set; *mtsc*, *matsci* parameter set.

^aSingle-point B3LYP/6-31G(d,p) with the geometries from Reference 16.

^bB3LYP/6-31G(d,p).

^cCAM-B3LYP/6-31G(d,p).^[69]

^dAnatase.

^eRutile.

^fAmorphous, mixed, or nonspecified phase.

^gTiO₂ clusters.

3.2 | Electronic properties

The main electronic properties regarding the photocatalytic applications are ionization potentials (IPs), electron affinities (EAs), and HOMO-LUMO band gaps (BGs). The latter parameter influences the photoexcitation abilities of the material, whereas the two others affect the ability to accept or donate electrons from/to the “antenna” nanoparticles (of Au, Ag, or other metals) during their photoexcitation. Typically, the Au or other metallic nanoparticles embedded into the composite material enhance the light absorptions due to their plasmon resonance ability and donate electrons to the neighboring TiO₂ particles forming the Ti³⁺ centers.

Although the accurate estimation of vertical ionization potentials and, especially, the electron affinities is a rather complicated task, these properties could be crudely estimated using the Koopmans theorem. Therefore, in this study, we estimated the IP, EA, and BG values using the approximate expressions:

$$IP = -\epsilon_{\text{HOMO}}, \quad EA = -\epsilon_{\text{LUMO}}, \quad BG = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}.$$

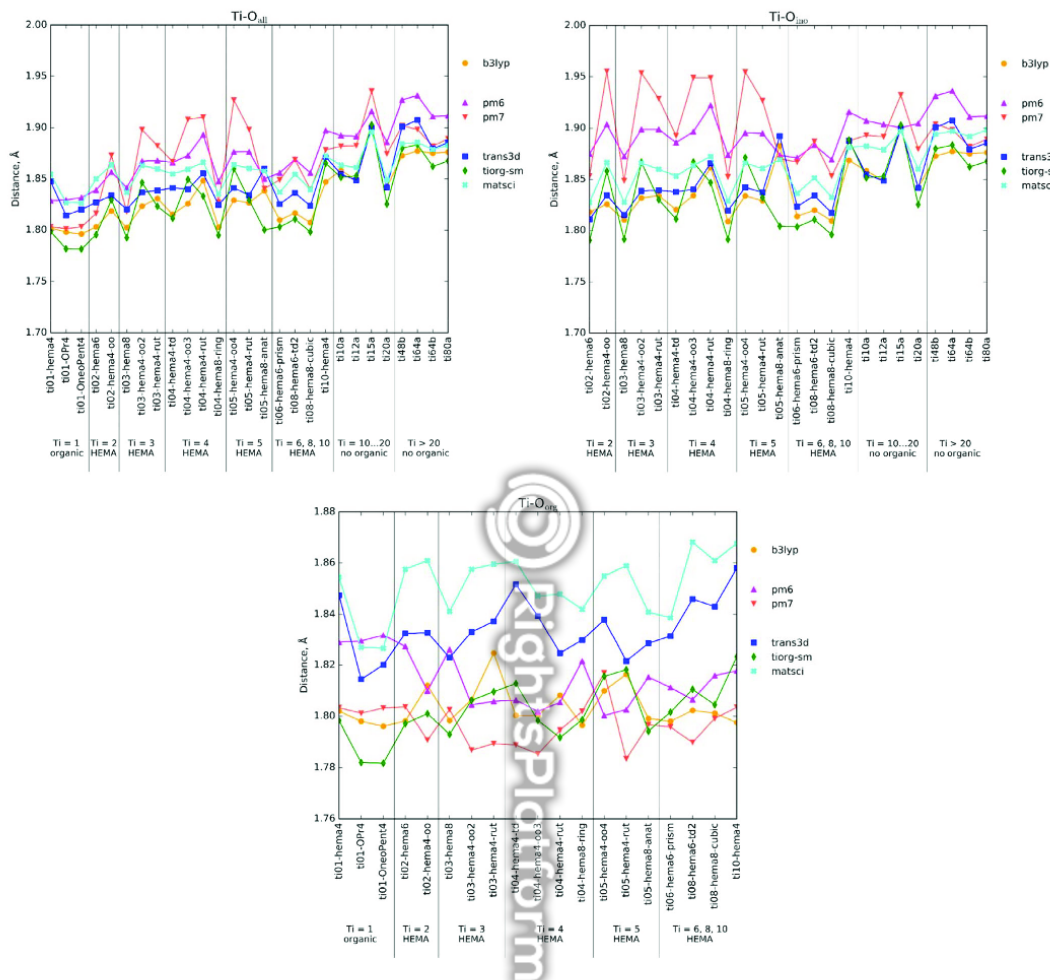


FIGURE 3 The Ti–O bond length values calculated with DFTB and semiempirical methods in comparison with DFT results

One of the most recent studies^[57] discusses the positions of conduction band and oxygen vacancy, and the authors conclude that the earlier^[58] reported value of the ionization potential is not correct due to oxygen vacancy level within the BG. Nevertheless, the value of 5.17 eV reported in^[58] is considered one of the reliable ones. According to some experimental data, including studies of electronic properties of (TiO₂)_n (where *n* is up to 10),^[4,59] clusters larger than (TiO₂)₆ could represent electronic properties of bulk titanium dioxide.^[4] At the same time, one theoretical study^[9] reports the Ti₃₄O₇₀H₄ cluster as the smallest one, which could reproduce features of electronic properties. Unfortunately, the computational costs of B3LYP/6-31G(d,p) calculations (TiO₂)_n/HEMA clusters with *n* > 10 make such calculations impractical.

Values of the HOMO and LUMO energies calculated with DFT and DFTB methods for different cluster types are shown in Figure 7 in comparison with ranges of experimental IPs and EAs. As is evident from the figure, all the methods, including all DFTB parameter sets, demonstrate similar performance for the LUMO energies and reproduce the tendency of EA growth when the cluster size increases in agreement with the results reported earlier.^[4] The common tendency is shifting up of the HOMO and LUMO energy levels in cases with the presence of organic ligands. This effect is more pronounced in the case of DFT calculations where the shift is of about 2 eV. Structures 19 (ti10-hema4) and 20 (ti10a) represent the same TiO₂ cluster structure with and without four HEMA ligands. Analysis of the differences between HOMO and LUMO levels for these structures could generally characterize the influence of organic ligands. As is evident from Figure 6, the frontier orbital shift for DFTB is remarkably lower than in the case of DFT calculations.

TABLE 3 Statistical analysis of the deviations between the results of different methods

Property	Mean deviation						Mean absolute deviation					
	CAM	PM6	PM7	DFTB (tos)	DFTB (t3d)	DFTB (mtsc)	CAM	PM6	PM7	DFTB (tos)	DFTB (t3d)	DFTB (mtsc)
Structural properties												
Ti–O, Å	–	0.041 (0.041) [0.040]	0.036 (0.040) [0.025]	–0.002 (–0.002) [–0.003]	0.015 (0.018) [0.009]	0.026 (0.034) [0.006]	–	0.041 (0.041) [0.041]	0.036 (0.040) [0.025]	0.012 (0.013) [0.008]	0.016 (0.018) [0.010]	0.026 (0.034) [0.007]
Ti–O _{ind} , Å	–	0.053 (0.058) [0.045]	0.056 (0.070) [0.028]	–0.003 (–0.003) [–0.003]	0.008 (0.008) [0.009]	0.021 (0.022) [0.019]	–	0.054 (0.059) [0.045]	0.057 (0.072) [0.028]	0.018 (0.023) [0.008]	0.009 (0.009) [0.010]	0.023 (0.024) [0.019]
Ti–O _{org} , Å	–	(0.011)	(–0.007)	(–0.001)	(0.031)	(0.048)	–	(0.016)	(0.011)	(0.008)	(0.031)	(0.048)
O–Ti–O, °	–	0.76 (0.39) [1.62]	0.08 (–0.25) [0.85]	0.16 (0.20) [0.04]	0.63 (0.19) [1.68]	–0.04 (–0.19) [0.30]	–	0.76 (0.40) [1.62]	0.60 (0.49) [0.85]	0.31 (0.35) [0.22]	0.81 (0.45) [1.68]	0.47 (0.53) [0.33]
Ti–O–C, °	–	(32.6)	(28.6)	(–2.6)	(–31.5)	(–13.9)	–	(32.6)	(28.6)	(3.4)	(31.5)	(13.9)
Electronic properties												
E _{HOMO} , eV	–1.63 (–1.61) [–1.67]	–3.32 (–3.58) [–2.69]	–2.36 (–2.85) [–1.19]	1.56 (1.17) [2.48]	1.43 (1.12) [2.14]	1.35 (0.90) [2.41]	1.63 (1.61) [1.67]	3.32 (3.58) [2.69]	2.36 (2.85) [1.19]	1.56 (1.17) [2.48]	1.43 (1.12) [2.14]	1.35 (0.90) [2.41]
E _{LUMO} , eV	1.29 (1.32) [1.22]	0.63 (0.21) [1.62]	1.22 (0.96) [1.83]	0.19 (–0.25) [1.21]	–0.30 (–0.76) [0.80]	–0.17 (–0.74) [1.17]	1.29 (1.32) [1.22]	0.66 (0.25) [1.62]	1.23 (0.98) [1.83]	0.62 (0.38) [1.21]	0.78 (0.77) [0.80]	0.87 (0.74) [1.17]
BG, eV	2.92 (2.93) [2.89]	3.94 (3.79) [4.32]	3.58 (3.81) [3.02]	–1.38 (–1.42) [–1.27]	–1.72 (–1.88) [–1.34]	–1.52 (–1.63) [–1.24]	2.92 (2.93) [2.89]	3.94 (3.79) [4.32]	3.58 (3.81) [3.02]	1.38 (1.42) [1.27]	1.72 (1.88) [1.34]	1.52 (1.63) [1.24]
μ, D	–	(0.96)	(2.11)	(0.22)	(0.21)	(0.23)	–	(3.57)	(3.20)	(1.51)	(1.88)	(1.92)
Thermodynamic properties												
Δ _r E, kcal/mol	–	(109.6)	(30.0)	(19.5)	(–3.1)	(11.3)	–	(109.6)	(30.0)	(19.5)	(7.4)	(11.3)
Δ _r E per Ti–O bond, kcal/mol	–	(8.8)	(2.0)	(1.3)	(–0.3)	(0.7)	–	(8.8)	(2.0)	(1.3)	(0.6)	(0.7)

Note: Data represent values averaged among all clusters, among TiO₂/organic clusters (in parentheses), and among bare TiO₂ clusters [in brackets]. The least deviations marked with bold font. The reference method is B3LYP/6-31G(d,p). The reference geometries for bare TiO₂ clusters are taken from Reference 16, calculated at B3LYP/DZVP2 level.

Abbreviations: *tos*, *tiorg-smooth* parameter set; *t3d*, *trans3d* parameter set; *mtsc*, *matsci* parameter set; CAM, CAM-B3LYP/6-31G(d,p); μ, dipole moment; Δ_rE, energies of reaction (1).

HOMO energies obtained by DFTB are typically higher than the B3LYP values, and absolute deviations are in ranges of 0.90 to 1.17 eV (TiO₂/organic) and 2.14 to 2.48 eV (bare TiO₂). The *matsci* set shows values closest to the B3LYP average values along all the structures (MAD is 1.35 eV). While DFTB and DFT methods reproduce experimental values quite well, semiempirical methods obviously underestimate the HOMO energies. PM6 typically deviates from DFT by of 2.69 to 3.58 eV depending on the presence of organic ligands (the deviation is lower for the bare TiO₂ clusters). Results obtained with PM7 are closer to the experiment and DFT/DFTB methods than for PM6, but HOMO energy remains underestimated. It should also be noted that, in the case of the bare TiO₂ clusters, PM7 (MAD is 1.19 eV) is closer to B3LYP than DFTB calculations (MAD is in range from 2.14 to 2.48 eV).

Semiempirical methods tend to overestimate LUMO energy. It was found that the older PM6 method is somewhat better in describing this property than PM7. The mean deviation from DFT is different for clusters with and without organic ligands and is larger for the last ones (up to 1.83 eV in case of PM7 calculations). All DFTB parameter sets are closer to B3LYP than the semiempirical methods, and *tiorg-smooth* gives the closest values to the B3LYP result among all the methods (MAD along all the structures is 0.62 eV). It should be noted that most of the LUMO energies obtained by DFTB falls into the range of experimental data, while many of the values obtained by other methods go over the experimental region, especially in the cases of PM7 and CAM-B3LYP for the TiO₂/organic clusters.

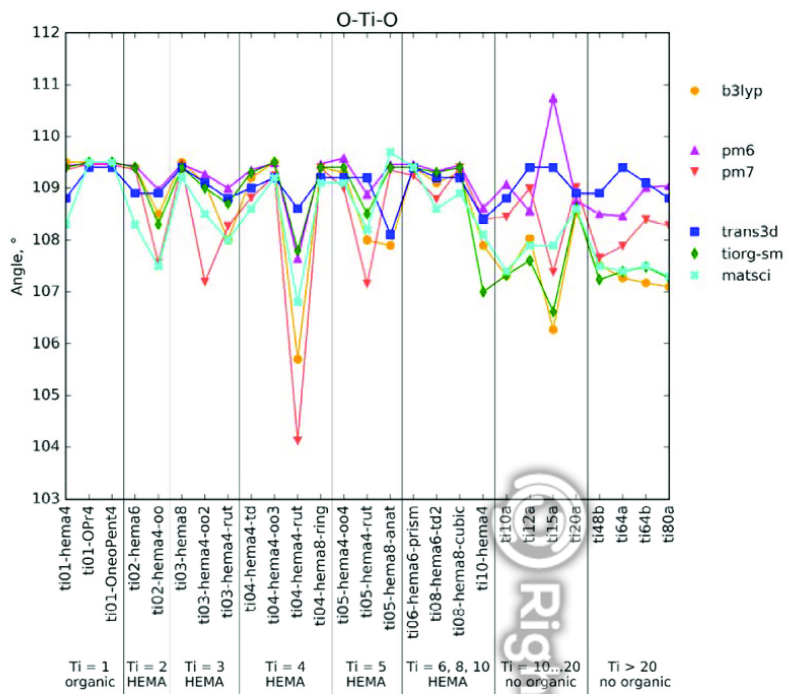


FIGURE 4 The average O-Ti-O valence angles calculated with DFTB and semiempirical methods in comparison with the DFT calculated values

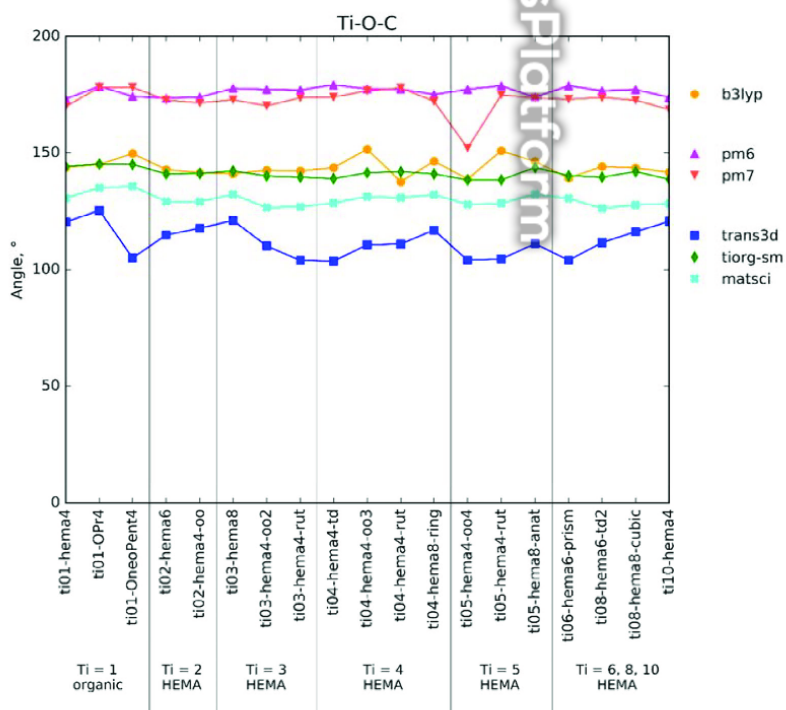


FIGURE 5 The Ti-O-C valence angles calculated with DFTB and semiempirical methods in comparison with the DFT calculated values