Supporting information

A relationship among structural, electronic order-disorder effects and optical properties in crystalline TiO_2 nanomaterials

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A. Rietveld refinements

Table S1. Planes, d-spacing, diffraction peaks position and intensity of the XRD patterns indexed from Rietveld refinements using the GSAS program.

Planes - phase	2θ (°)	d-spacing (Å)	Intensity	
			Counts Rate	Relative (%)
TiO_2 NPs – 2 minutes				
(101) - anatase	25.32	3.5137	2844	100
(121) - brookite	30.65	2.9145	82	2.83
(004) - anatase	37.92	2.3705	669	23.52
(200) - anatase	48.09	1.8905	802	28.20
(105) – anatase or (320) - brookite	53.99	1.6970	547	19.23
(211) - anatase	55.18	1.6630	508	17.86
(204) - anatase	62.75	1.4801	389	15.63
(116) – anatase or (400) – brookite	68.78	1.3633	169	5.94
(215) – anatase	75.23	1.2622	250	8.79
(224)-anatase or (312) - anatase	82.86	1.1639	176	6.18
(217) - anatase	95.04	1.081	94	3.31
(109) - anatase	98.50	1.016	60	2.11
(316) – anatase or (125)/(372)/(254) - brookite	107.78	0.9539	90	3.16

TiO_2 NPs – 8 minutes				
(101) - anatase	25.36	3.5079	2984	100
(121) - brookite	30.89	2.8923	76	2.55
(004) - anatase	37.97	2.3678	701	23.49
(200) - anatase	48.13	1.8891	808	27.08
(105) – anatase or (320) - brookite	53.99	1.6970	567	19
(211) - anatase	55.23	1.6617	527	26.56
(204) - anatase	62.75	1.4794	429	14.38
(116) – anatase or (400) – brookite	68.84	1.3628	191	6.40

(215) – anatase	75.31	1.2623	257	12.95
(224)-anatase or (312) - anatase	82.89	1.1638	190	6.37
(217) - anatase	94.83	1.0462	101	3.38
(109) - anatase	98.52	1.0166	66	2.21
(316) – anatase or (125)/(372)/(254) - brookite	107.63	0.9544	95	3.18

TiO_2 NPs – 32 minutes				
(101) - anatase	25.28	3.5198	2639	100
(121) - brookite	30.45	2.9336	106	4.02
(004) - anatase	37.89	2.3728	642	24.32
(200) - anatase	48.03	1.8928	749	28.38
(105) – anatase or (320) - brookite	54.01	1.6964	530	20.08
(211) - anatase	55.06	1.6666	517	19.59
(204) - anatase	62.67	1.4812	381	14.44
(116) – anatase or (400) – brookite	68.79	1.3636	179	6.78
(215) – anatase	75.17	1.2628	254	9.62
(224)-anatase or (312) - anatase	82.79	1.1649	167	6.33
(217) - anatase	94.73	1.0470	108	4.09
(109) - anatase	98.57	1.0163	68	2.58
(316) – anatase or (125)/(372)/(254) - brookite	107.60	0.9545	95	3.60

B. Optical *band gap* energy

The optical *band gap* energy of the semiconductors can be calculated experimentally thought of the absorption coefficient α(λ), and subsequent issuance of the quantum energy associated to electronics states within $E_{gap,}$ which the electronics transitions occur [S1]. So, for a thin film the absorption coefficient is given by the equation (1):

$$\alpha(\lambda) = 2.303\left(\frac{A}{t}\right) \qquad (1)$$

where *A* is the absorbance and *t* the sample thickness. Therefore, the optical *band gap* energy and absorption coefficient of semiconductor oxides [S2], to parabolic band structure, can be calculated by following equation (2):

$$\alpha h\nu = K^{'}(h\nu - E_{gap})^{n} \qquad (2)$$

where α is the linear absorption coefficient of the material, $h\nu$ is the photon energy, K' is a proportionality constant, E_{gap} is the optical *band gap* and n is a constant associated to the different kinds of electronic transitions. The kind of electronic transition, which is related to n constant, should be considered for better interpretation of the *band gap* optical energy. However, in reflectance diffuse mode, the sample thickness depending of factors related to deep beam penetration such as, package density, particle size and amount of absorbent material in the sample [S3]. The absorption coefficient (α) is related to reflectance (R) by means of equation (3):

$$\alpha = F(R).\left(\frac{s}{2V_R}\right) \qquad (3)$$

where s is the scattering coefficient, V_R is the volumetric fraction of the absorbents species and $F(R)$ is the Kubelka-Munk function [S3], defined by:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \qquad (4)$$

where k is the molar absorption coefficient. The coefficients k and s are features intrinsic of the material, being that real scattering and absorption coefficients, α_ν and σ_ν, for certain frequency (ν), are related to k and s according:

$$\propto_\nu = \eta k \qquad (5)$$

$$\sigma_\nu = \chi s \qquad (6)$$

The χ and η values are taken in the limit of the small absorptions, so them admit the values of 1/2 and 4/3, respectively. For small absorption $\eta = 2$ and $k = 2\alpha_\nu$ and the ratio k/s = 0-3[S4]. Therefore, the Kubelka-Munk function will be:

$$F(R) = \frac{(1-R)^2.\eta}{2R.\chi} = \frac{\propto_\nu}{\sigma_\nu} \qquad (7)$$

Experimentally, the reflectance measured in diffuse mode, the R value in the Kubelka-Munk function will be:

$$R = \frac{R_{sample}}{R_{standard}} \qquad (8)$$

The reflectance measured in (8) assumes that thickness of the sample is infinitely thick and $R_{standard}$ is a material that exhibit absolute reflectance such as, MgO or $\alpha\text{–}Al_2O_3$. Finally, the optical band gap energy will can be calculated from reflectance diffuse mode according:

$$F(R).h\nu = C.(h\nu - E_{gap})^n \qquad (9)$$

where C a proportionality constant and n is a constant associated to the different kinds of electronic transitions. . The semiconductors present transitions: direct allowed (n = 0.5), indirect allowed (n = 2), direct forbidden (n=1.5), and indirect forbidden (n=3) [S2]. According to literature both theoretical and experimental data [S5, S6, S7] TiO_2 is a semiconductor characterized by an indirect allowed electronic transition between valence bad and conduct band, thus the n constant adopted for its electronic transition is n = 2. Through of a simple mathematical artifice is easy to show that $F(R).h\nu \propto (h\nu - E_{gap})^n$ or $[F(R).h\nu]^{1/n} \propto (h\nu - E_{gap})$ in the equation (9). So, finding the $F(R)$ value from equation (9) and plotting a graph of $[F(R).h\nu]^{1/2}$ versus $h\nu$, admitting that TiO_2 has an indirect electronic transition (n=2), it was possible determine the E_{gap} of TiO_2 NPs extrapolating the linear portion of the reflectance curve, plotted with photon energy on the x-axis, in the condition in which the reflectance is zero. In this work, the optical band gap energy of the TiO_2 NPs was obtained from UV-vis absorption spectroscopy technique in diffuse reflectance mode and calculated by Kubelka-Munk method [S4].

C. XPS analysis

Table. S2. XPS survey analysis and Ti:O ratio for the TiO_2 NPs processed in 2, 8 and 32 minutes.

TiO_2 NPs	**Position (eV)**	**FWHM**	**Area**	**Atom content %^{a}**
	O 1s			
2 minutes	529.95	2.296	180022.2	51.41
8 minutes	529.95	2.304	158151.0	51.16
32 minutes	529.85	2.337	177068.0	51.09

TiO_2 NPs	**Position (eV)**	**FWHM**	**Area**	**Atom content %^{a}**
	Ti 2p			
2 minutes	458.70	2.079	201150.7	20.72
8 minutes	458.70	2.060	177100.2	20.67
32 minutes	458.60	2.082	192810.6	20.07

TiO_2 NPs	**Position (eV)**	**FWHM**	**Area**	**Atom content %^{a}**
	C 1s			
2 minutes	285.20	2.566	34243.4	27.87
8 minutes	284.95	2.476	30556.0	28.17
32 minutes	284.85	2.500	35074.8	28.84

O:Ti^b		
TiO_2 NPs		
2 minutes	**8 minutes**	**32 minutes**

2.48	2.47	2.55

Atom content %^{a}: element analysis considering the C 1s XPS signal.
O:Ti^b : stoichiometric ratio considering the C 1s XPS signal;

Table. S3. XPS analysis of the Ti 2p$_{1/2}$, Ti 2p$_{3/2}$, O 1s and C 1s signals for the TiO$_2$ NPs processed in 2, 8 and 32 minutes.

TiO$_2$ NPs	**Ti 2p**					
	Binding Energy (eV)		FWHM		% Area	
	Ti 2p$_{3/2}$	Ti 2p$_{1/2}$	Ti 2p$_{3/2}$	Ti 2p$_{1/2}$	Ti 2p$_{3/2}$	Ti 2p$_{1/2}$
2 minutes	458.78	464.53	1.223	2.064	67.08	32.92
8 minutes	458.78	464.52	1.228	2.066	67.17	32.83
32 minutes	458.74	464.49	1.228	2.080	66.94	33.06

TiO$_2$ NPs	**O 1s**								
	Binding Energy (eV)			FWHM			% Area		
	TiO$_2$	-OH	O-C	TiO$_2$	-OH	O-C	TiO$_2$	-OH	O-C
2 minutes	530.07	531.47	532.31	1.329	1.800	1.800	79.51	13.48	7.01
8 minutes	530.06	531.54	532.42	1.324	1.800	1.800	79.64	14.77	5.58
32 minutes	530.04	531.26	532.26	1.330	1.800	1.800	78.90	12.66	8.45

TiO$_2$ NPs	**C 1s**								
	Binding Energy (eV)			FWHM			% Area		
	CC-H	C-O	O-C=O	CC-H	C-O	O-C=O	CC-H	C-O	O-C=O
2 minutes	284.95	286.40	288.86	1.459	1.616	1.358	70.65	22.07	7.28
8 minutes	284.96	286.50	288.85	1.538	1.447	1.451	75.52	16.88	7.61
32 minutes	284.95	286.44	288.81	1.473	1.527	1.504	71.62	20.00	8.38

TiO$_2$ NPs	**Atom content %^{c}**	
	O 1s	**Ti 2p**
2 minutes	69.4	30.6
8 minutes	68.8	31.2
32 minutes	68.8	31.2

O:Ti^d		
TiO$_2$ NPs		
2 minutes	**8 minutes**	**32 minutes**
2.26	2.21	2.21

Atom content %^{c}: element analysis disconsidering the C 1s XPS signal and the O 1s XPS signals related to oxygen vacancies and hydroxyl groups (–OH).
O:Ti^d : stoichiometric ratio disconsidering the C 1s XPS signal and the O 1s XPS signals related to oxygen vacancies and hydroxyl groups (–OH).

D. Distances and angles bonds

The bond lengths and bond angles between titanium and oxygen atoms, makers TiO$_2$ NPs lattice, from the atomic coordinates obtained by Rietveld refinements results, are displayed in the Table S1. The values were calculated through Visualization for Electronic and Structural Analysis (version 3 for Windows) [S8] and the unit cell parameters of the TiO$_2$ anatase-bulk (ICDS n° 24276) and brookite-bulk (ICDS n° 31122), were used to compare the observed and theoretical values. The results shows that clusters [TiO$_6$] are slightly distorted into cell unit, the values of the bond lengths (Ti-O$_n$ ($n = 1,\ldots,6$)) and bond angles formed between two oxygen atoms and each titanium atom (ψ, ϕ, φ, ε, γ and δ) on the TiO$_2$ lattice, presented a slighth variation compared to values encountered in the ICSD n° 24276 and 31122 for anatase-bulk and arookite-bulk, respectively. The values calculated for bond lengths and bond angles between titanium and oxygen atoms, are represented by distorted cluster [TiO_6] in the Figure S1.

The unit cell structure of the anatase-bulk has a lattice formed by octahedral clusters less distorted compared to brookite-bulk due to bond lengths are shorter, resulting in a lower variation in the bond lengths (1.91-1.95Å), between Ti and O atoms, against about to (1.87-2.04 Å) for brookite [S9, S10]. As can be observed in the Table S1, from values of bond lengths and bond angles that form clusters [TiO_6], the TiO_2 NPs lattice composed by clusters [TiO_6] ascribe anatase showed a variation in all bond lengths and slight distortions on the bond angles. While for brookite phase, the clusters makers the TiO_2 NPs lattice presented a variation slightly larger about to values of bond lengths and bond angles between titanium and oxygen atoms, as expected and reported in the literature, once the unit cell parameters for tetragonal structure, assigned to anatase, is most symmetric than orthorhombic structure lies in the brookite phase.

Table S4. Bond lengths (Ti-O) and bond angles (ψ, ϕ, φ, ε, γ and δ) between of O-Ti-O.

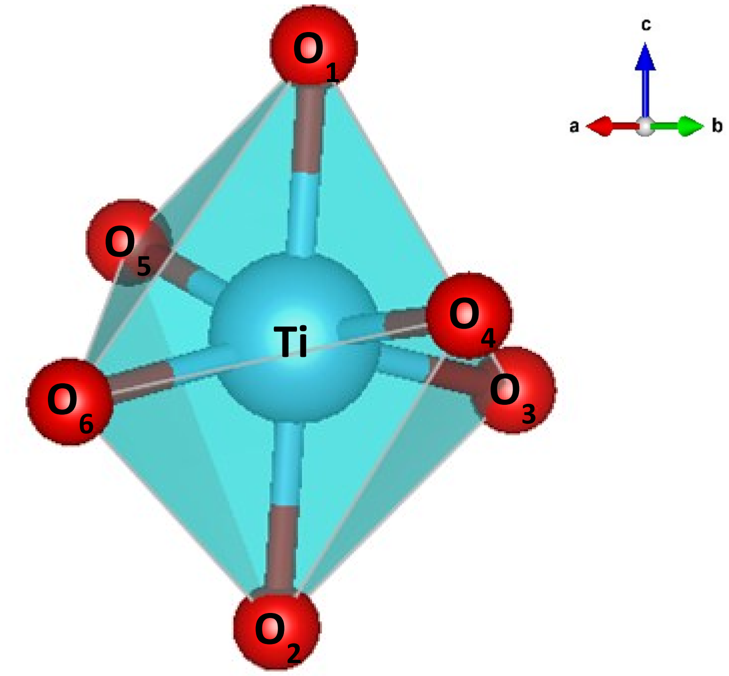
Crystallographic structure	**Bonds (Ti–O)**	**Bond lenghts (Å)**	**Bond angles (◦)**
Anatase (2 minutes)	$Ti\text{-}O_1$	1.9854(7)	$O_1\text{-}\hat{Ti}\text{-}O_2$; $\psi = 180$
	$Ti\text{-}O_2$	1.9854(7)	$O_5\text{-}\hat{Ti}\text{-}O_6$; $\phi = 92.34\ (5)$
	$Ti\text{-}O_3$	1.93268(15)	$O_3\text{-}\hat{Ti}\text{-}O_4$; $\varphi = 92.34\ (5)$
	$Ti\text{-}O_4$	1.93268(15)	$O_4\text{-}\hat{Ti}\text{-}O_6$; $\varepsilon = 92.34\ (5)$
	$Ti\text{-}O_5$	1.93268(15)	$O_5\text{-}\hat{Ti}\text{-}O_3$; $\gamma = 92.34\ (5)$
	$Ti\text{-}O_6$	1.93268(15)	$O_2\text{-}\hat{Ti}\text{-}O_1$; $\delta = 180$
Anatase (8 minutes)	$Ti\text{-}O_1$	1.9813(8)	$O_1\text{-}\hat{Ti}\text{-}O_2$; $\psi = 180$
	$Ti\text{-}O_2$	1.9813(8)	$O_5\text{-}\hat{Ti}\text{-}O_6$; $\phi = 92.39\ (5)$
	$Ti\text{-}O_3$	1.93379(17)	$O_3\text{-}\hat{Ti}\text{-}O_4$; $\varphi = 92.39\ (5)$
	$Ti\text{-}O_4$	1.93379(17)	$O_4\text{-}\hat{Ti}\text{-}O_6$; $\varepsilon = 92.39\ (5)$
	$Ti\text{-}O_5$	1.93379(17)	$O_5\text{-}\hat{Ti}\text{-}O_3$; $\gamma = 92.39\ (5)$
	$Ti\text{-}O_6$	1.93379(17)	$O_2\text{-}\hat{Ti}\text{-}O_1$; $\delta = 180$
Anatase (32 minutes)	$Ti\text{-}O_1$	1.9898(8)	$O_1\text{-}\hat{Ti}\text{-}O_2$; $\psi = 180$
	$Ti\text{-}O_2$	1.9898(8)	$O_5\text{-}\hat{Ti}\text{-}O_6$; $\phi = 92.29(5)$
	$Ti\text{-}O_3$	1.93231(16)	$O_3\text{-}\hat{Ti}\text{-}O_4$; $\varphi = 92.29(5)$
	$Ti\text{-}O_4$	1.93231(16)	$O_4\text{-}\hat{Ti}\text{-}O_6$; $\varepsilon = 92.29(5)$
	$Ti\text{-}O_5$	1.93231(16)	$O_5\text{-}\hat{Ti}\text{-}O_3$; $\gamma = 92.29(5)$
	$Ti\text{-}O_6$	1.93231(16)	$O_2\text{-}\hat{Ti}\text{-}O_1$; $\delta = 180$
Anatase (ICDS CIF n°.24276)	$Ti\text{-}O_1$	1.9731(13)	$O_1\text{-}\hat{Ti}\text{-}O_2$; $\psi = 180$
	$Ti\text{-}O_2$	1.9731(13)	$O_5\text{-}\hat{Ti}\text{-}O_6$; $\phi = 92.4434(0)$
	$Ti\text{-}O_3$	1.9296(10)	$O_3\text{-}\hat{Ti}\text{-}O_4$; $\varphi = 92.4434(0)$
	$Ti\text{-}O_4$	1.9296(10)	$O_4\text{–}\hat{Ti}\text{-}O_6$; $\varepsilon = 92.4434(0)$
	$Ti\text{-}O_5$	1.9296(10)	$O_5\text{-}\hat{Ti}\text{-}O_3$; $\gamma = 92.4434(0)$
	$Ti\text{-}O_6$	1.9296(10)	$O_2\text{-}\hat{Ti}\text{-}O_1$; $\delta = 180$
	$Ti\text{-}O_1$	1.99873(0)	$O_1\text{-}\hat{Ti}\text{-}O_2$; $\psi = 168.7661(0)$
	$Ti\text{-}O_2$	1.92326(0)	$O_5\text{-}\hat{Ti}\text{-}O_6$; $\phi = 93.7958(0)$

	Ti-O_3	1.93054(0)	O_3 -$\hat{Ti}$-O_4 ; φ = 87.1244(0
	Ti-O_4	2.05178(0	O_4 -$\hat{Ti}$-O_6 ; ε= 85.1473(0)
	Ti-O_5	1.86276(0)	O_5 -$\hat{Ti}$-O_3 ; γ = 95.0586(0)
	Ti-O_6	1.98987(0)	O_2 -$\hat{Ti}$-O_1 ; δ = 168.7661(0)

Brookite (8 minutes)	Ti-O_1	1.92326(0)	O_1 -$\hat{Ti}$-O_2 ; ψ= 168.7661(0)
	Ti-O_2	1.99873(0)	O_5 -$\hat{Ti}$-O_6 ; ϕ = 93.7958(0)
	Ti-O_3	1.93054(0)	O_3 -$\hat{Ti}$-O_4 ; φ = 87.1244(0)
	Ti-O_4	2.05178(0)	O_4 -$\hat{Ti}$-O_6 ; ε= 85.1473(0)
	Ti-O_5	1.86276(0)	O_5 -$\hat{Ti}$-O_3 ; γ = 95.0586(0)
	Ti-O_6	1.98987(0)	O_2 -$\hat{Ti}$-O_1 ; δ = 168.7661(0)

Brookite (32 minutes)	Ti-O_1	2.175(3)	O_1 -$\hat{Ti}$-O_2 ; ψ= 160.6149(0)
	Ti-O_2	1.622(2)	O_5 -$\hat{Ti}$-O_6 ;ϕ = 109.9986(0)
	Ti-O_3	1.8549(12)	O_3 -$\hat{Ti}$-O_4 ; φ = 84.6247(0)
	Ti-O_4	2.3043(14)	O_4 -$\hat{Ti}$-O_6 ; ε= 99.3678(0)
	Ti-O_5	1.8328(14)	O_5 -$\hat{Ti}$-O_3 ; γ = 77.1636(0)
	Ti-O_6	1.9627(13)	O_2 -$\hat{Ti}$-O_1 ; δ = 160.6149(0)

Brookite (ICDS CIF n°. 31122)	Ti-O_1	1.99488(0)	O_1 -$\hat{Ti}$-O_2 ; ψ= 168.9586(0)
	Ti-O_2	1.94937(0)	O_5 -$\hat{Ti}$-O_6 ; ϕ = 94.0637(0)
	Ti-O_3	1.93563(0)	O_3 -$\hat{Ti}$-O_4 ; φ = 87.7496(0)
	Ti-O_4	2.03185(0)	O_4 -$\hat{Ti}$-O_6 ; ε= 84.5456(0)
	Ti-O_5	1.84244(0)	O_5 -$\hat{Ti}$-O_3 ; γ = 95.2660(0)
	Ti-O_6	2.00277(0)	O_2 -$\hat{Ti}$-O_1 ; δ = 168.9586(0)



Distorted cluster [TiO_6]

Figure S1. Titanium (Ti) and oxygen (O) positions in the distorted cluster.

E. Supplementary references

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