Supporting information

Influence of Morphology and Crystallinity on Surface Reactivity of Nanosized Anatase TiO$_2$ Studied by Adsorption Techniques: II. Solid-Liquid Interface

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1. TDIS MODELING AND THE LANGMUIR-FREUNDLICH EQUATION

When working with real solids, the assumption of true homogeneous patches must be moderated by a distribution term. To this end, a quasi-gaussian distribution can be used, as developed by Bradley [1] and used by Koopal et al. [2] or Bersillon et al. [3]. The amount of hydroxyls consumed, N_{ads}, is desribed then by the so-called Langmuir-Freundlich equation:

$$\theta = \frac{K[H^+]^m}{1 + K[H^+]^m} \quad (1) \quad \text{and its derivative is:} \quad \frac{d\theta}{d\,ln[H^+]} = m\theta(1-\theta) \text{ or}$$

$$\frac{d\theta}{dpH} = -2.3\,m\theta(1-\theta) \quad (2)$$

The term m takes a value between 0 and 1 and represents the broadening of the affinity constant K around its mean value. It has been shown that the gaussian term m also expresses the cooperative effect due to lateral interaction between the adsorbed species. However, lateral interactions are better described by the Bragg-Williams-Temkin isotherm. Introducing $a = \omega/kT$ (ω the lateral interactions), equations (1) and (2) become then:

$$\theta = \frac{K\,exp(a\theta)[H^+]}{1 + K\,exp(a\theta)[H^+]} \quad (3) \text{ and its derivative is: } \frac{d\theta}{d\,ln[H^+]} = \frac{\theta(1-\theta)}{1 - a\theta(1-\theta)} \quad (4)$$

In fact, as well as the gaussian parameter m, the term ω is a combination of lateral interaction and local heterogeneity [3]. In the present study, the Bragg-Williams-Temkin expression is used to calculate energy distributions both at the solid/gas interface and at the solid/electrolyte interface.

The local derivatives are characterized by a maximum, which corresponds to the pK of the protonation reaction, a surface area which gives the amount of the surface groups under consideration, and a broadening parameter which can be interpreted as a local pK distribution or interaction between the adsorbed ions.

2. PRINCIPLES OF THE DIS MODELING AND RECOMPOSITION OF PROTON AFFINITY DISTRIBUTION.

On the basis of a comparison between the shapes of the experimental and calculated derived isotherms, various parameters of the local isotherm are added to the model until a satisfactory shape is obtained. This recomposition is based on the Ocham razor principle, which considers that a new energetic domain is added only when it is necessary for the quality of the fitted curve. This means that a minimum of peaks are used. The most acidic and the most basic peak are first chosen (acid pK and basic pK). Then the most intense domain is located. The curve modeling is finally improved by adjusting the height and the broadening (w) of peaks, together with light displacement of the position (pK) if necessary. The pK positions are determined by considering the complete set of samples of this study, and their proton affinity distribution (PAD), the objective being to get a common set of pK compatible for all samples. In all cases, five local derivative isotherms fixed at pK 4.0; 5.5; 7.0; 8.3 and 10.0, were necessary to model experimental PAD.

These uncertainties were obtained by repeating the measurements at least two consecutive times on the same sample. The uncertainty of measurement on the domain 1 is estimated at 5% (due to the dispersion of experimental data points), whereas the uncertainty is only 2% for the other domains.

3. CHARACTERIZATION OF THE AN-RIEDEL SAMPLE

In the end, a commercial sample of anatase produced by Riedel-de Haën, named An-Riedel, used to examine the evolution of the adsorption energy in a size ranged from 4 to 50 nm. Since the synthesis conditions of this solid was not well controlled as done for the other samples of this study, the results obtained on this material are shown in Supporting Information.

The Figure 1 displays the surface charge behavior, shows that the An Riedel exhibits PZC=7. There is quite no influence of ionic strength on the surface charge. One explanation could be that the sample is contaminated by reagents used during synthesis. Indeed XPS measurements have detected the presence of small amount of sulfate. Nevertheless, the ions analysis of the supernatant does not show any release of sulfate or other ions (chloride or nitrate). Because the synthesis conditions are not perfectly known for commercial samples, the surface properties can not be controlled, and this results remains unexplained.
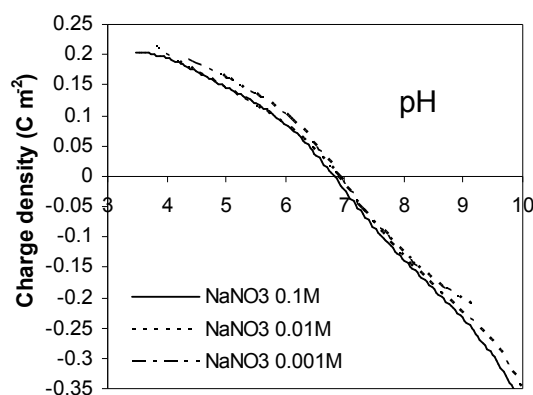
Figure 1-SI. *Surface charge density of anatase as function of pH for the NaNO$_3$ electrolyte concentrations of 10^{-1}, 10^{-2}, and 10^{-3} mol.L^{-1} for An Riedel.*
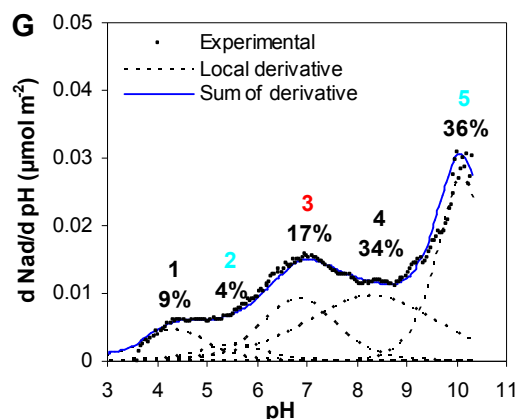
Figure 2-SI. *Proton affinity distribution using TDIS procedure in 0.1 mol.L^{-1} NaNO$_3$, expressed as the derivative adsorption isotherm of OH$^-$ versus pH for An Riedel.*

The Proton affinity distribution using TDIS procedure are shown on the Figure 2. As observed for the other samples, the domain 1 exhibits a contribution lower than 14% and consequently, it was attributed to both {101} and {001} faces by the MUSIC model. The proportion of domain 4 (34%) obtained from the *TDIS* results of An-Riedel sample is similar to that observed for OA (37%). This leads to the conclusion that the An-Riedel sample displays the {100} face. The {101} and {001} faces are also present for this solid, and their relative proportions can be evaluated from domains 2+5 and domain 3 respectively.

Finally, the *TDIS* distribution of An-Riedel shows smaller contributions of domains 2 (strong acid sites) and 3 (medium acid sites), and higher contribution of domain 5 (weak acid sites) compared to those of OA sample. Therefore, the PZC of An-Riedel is shifted to 7.0.

4. DETAILS ON ANATASE HYDRATED SURFACE MODELIZATION

Calculations are carried out in the the framework of the density functional theory (DFT) implemented in the Vienna *Ab initio* Simulation Package code (VASP 4.6)[24-25]. In this program, the Kohn–Sham equations are solved with the generalized gradient approximation

(GGA) proposed by Perdew and Wang [26]. The eigenstates of the electron wave functions are expanded on a plane-wave basis set, with pseudopotentials used to describe the electron–ion interaction within the projector augmented-wave approach (PAW) [27] and a cut-off energy of 400 eV. The Brillouin zone integrations have been performed using a Monkhoorst–Pack grid [28]. Accurate bulk properties were obtained with a 5x5x5 grid which provided a good compromise between calculation accuracy and computational cost. Then, the grid size was adapted accordingly to the periodic cells used: 4x4x1 for the cells used for water adsorption study and 2x2x1 for larger cells for the stepped surface study.

The geometry optimization at 0 K is performed by using a conjugate gradient algorithm, and by determining the exact Hellman-Feynman forces acting on the ions for each optimization step. A full relaxation of all atomic positions in the cell was performed.

Surfaces were cleaved from the optimized anatase bulk cell. This cell was optimized form the experimental one: the tetragonal phase of titanium dioxide is described by the space group I41/amd with lattice constants a=b=3.785 Å and c= 9.514 Å where Ti occupies the **a** Wyckoff positions (multiplicity 4) and O the **e** positions (multiplicity 4). In the anatase structure, TiO_6 octahedrons deviate from ideal one with axial Ti-O distances being slightly longer than equatorial ones 1.98 and 1.93 Å respectively and O-Ti-O angles varying between 78° and 102°. The anatase TiO_2 (100), (101) and (001) model surfaces were modeled as a periodic slab with 8 layers of oxide, with a vacuum between slabs of 15.7 Å. To model the interface

oxide-aqueous solution, we studied the hydration of the surface by considering first three commonly admitted modes of adsorption: dissociated, non dissociated and physisorbed. A preliminary study of each coverage step, had us chose a combination of non dissociated and physisorbed water molecule to best describe hydrated surfaces. For all surfaces, we studied the changes in the structure of the system after relaxation.

A specific concern was paid to the 001 surface where Ti with coordination 5 are found in previously reported studies. Here a coordination 6 of Ti was maintained for the final energy of the fully covered surface is lower in this case than with five coordinated Ti.

The figure 3a, b and c correspond to surface representations of the optimized hydrated surfaces structures of {100}, {101} and {001} respectively.
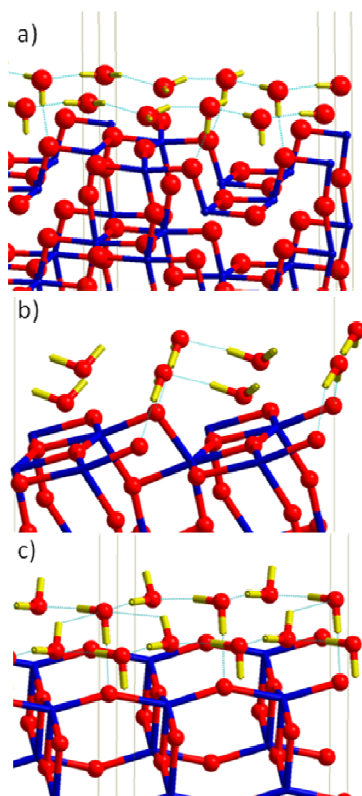
Figure 3-SI. *Schematic description of modeled fully hydrated anatase surface a) {100}, b) {101} and c) {001}. Blue balls: Ti, red balls: O and yellow balls: H. .*

Sample	N° of domain	Amount adsorbed (μmol/m²)	Proportion %
HCl-pH3	1	0.32	10
	2	0.11	3
	3	0.94	28
	4	0.56	16
	5	1.43	43
HClO4-pH4	1	0.57	14
	2	0.25	6
	3	0.86	21
	4	0.65	16
	5	1.77	43
Glu-H	1	0.46	12
	2	0.18	5
	3	0.81	21
	4	0.59	15
	5	1.78	47
HClO4-pH6	1	0.46	9
	2	0.74	13
	3	0.82	16
	4	0.83	16
	5	2.29	46
Glu-L	1	0.57	9
	2	0.89	14
	3	0.77	12
	4	0.98	15
	5	3.37	51

	1	0.68	12
	2	0.51	9
OA	3	1.32	23
	4	2.19	37
	5	1.14	19
	1	0.72	9
	2	0.35	4
An-Riedel	3	1.43	17
	4	2.78	34
	5	2.98	36

Table 1-SI. *Parameters of the decomposition of experimental curves into local derivatives of isotherms for all the TiO$_2$ samples (in NaNO$_3$ 0.1 mol.L^{-1}).*

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FIGURE CAPTION

Figure 1-SI. Surface charge density of anatase as function of pH for the NaNO$_3$ electrolyte concentrations of 10^{-1}, 10^{-2}, and 10^{-3} mol.L^{-1} for An Riedel.

Figure 2-SI. Proton affinity distribution using TDIS procedure in 0.1 mol.L^{-1} NaNO$_3$, expressed as the derivative adsorption isotherm of OH$^-$ versus pH for An Riedel.

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