Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Surface Science 600 (2006) 2040–2050

SURFACE SCIENCE

www.elsevier.com/locate/susc

Simulation of the interface of (1 0 0) rutile with aqueous ionic solution

S. Köppen, W. Langel *

Institut für Chemie und Biochemie, Universität Greifswald, Soldmannstraße 23, 17489 Greifswald, Germany

Received 2 June 2005; accepted for publication 24 February 2006
Available online 20 March 2006

Abstract

The interface of the rutile (1 0 0) surface with NaCl solutions has been simulated by classical molecular dynamics. In contrast to earlier simulations the protonation and hydroxylation equilibriums have been adjusted for different pH values (4, 7.4, and 9). The short range order close to the surface is described by two water layers with some orientational order and intermediate layers of positive or negative ions depending on the surface charge. A Stern model is confirmed with a dense layer of counterions on the charged TiO_2 surface and a diffuse layer, which only consists of few ions in our system. The increase of orientational order of the water molecules close to the surface is described by an exponential function with a decay parameter of 1.9 Å, superposed by a damped oscillation which is independent of the pH value. The diffusion is significantly slower than in the bulk within a range of 13 Å from the surface. We propose a common approach for describing the different *z*-dependences of orientational order and of the diffusion coefficients.

Keywords: Molecular dynamics; Electrochemical phenomena; Titanium dioxide

1. Introduction

Favourable mechanic properties make titanium a widely used material for medical implants [1]. In biological systems the metal is passivated by a thin oxide layer with a thickness of 5–100 Å, which is in contact with an aqueous solution or with water vapour in air. The biocompatibility of titanium is determined by the properties of this oxide layer. Studies mainly focus on the stable (1 1 0) and (1 0 0) rutile surfaces [1,2]. Any exposure to H_2O leads to at least partial hydroxylation [3]. We found earlier that (1 0 0) is more reactive with respect to H_2O than the more common (1 1 0) structure [4]. This finding is consistent with a recent investigation of several TiO_2 systems at different levels of hydration, which revealed a higher surface energy and smaller stability of (1 0 0) than of (1 1 0) [5].

Data on the point of zero charge (PZC) are reported in the range of pH = 5–7 for rutile, respectively [6]. A general description of the surface hydroxylation equilibriums is provided by the MUlti SIte Complexation Model (MUSIC) [7–9]. It assigns hydroxylation equilibriums to discrete reactions such as the adsorption of hydroxyl groups at surface Ti atoms (pK_{12}) and the protonation of bridging oxygen atoms (pK_{21}).

Recently detailed experimental and theoretical studies of rutile have shown that on the perfect surface no dissociation of water is observed [10–12]. Spontaneous dissociation affords oxygen vacancies and does not yield singly coordinated hydroxyl groups. This indicates that these groups are very unstable and that the interaction between titanium in the surface and free OH^- groups in the solution is weak. Thus, water is mainly physisorbed in the physiological pH range and few adsorbed OH^- groups and protons will coexist, implying that pK_{12} is greater than pK_{21}. Giacomelli et al. solve the Poisson–Boltzmann equation for a (1 1 0) rutile surface with two independent hydroxylation equilibriums and use $pK_{12} = 6.5 > pK_{21} = 5.5$ corresponding to a point of zero charge (PZC) at the average of the two p*K*-values, i.e. pH = 6.0 [13]. The model describes their

---

* Corresponding author. Tel./fax: +49 3834 86 4423.
E-mail address: langel@uni-greifswald.de (W. Langel).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.02.042

measurements of surface charge at highly disperse titanium oxide. On bulk materials such as anatase on anodically oxidized bulk titanium lower PZC values of 4.8–5.3 [14] are observed. The shift may be due to incomplete oxidation of the Ti surfaces, which provide more Ti sites for the adsorption of hydroxyl groups, but less bridging oxygens for protonation.

The occupation of the chemisorption sites cannot be calculated directly from the p*K*-values, since the effective equilibrium constants on the surface are shifted by the electrostatic surface potential. Without accounting for this effect distribution curves with very pronounced pH dependences are obtained [15, Fig. 1] which do not reflect the situation.

Simulations of adsorption phenomena in aqueous solutions of larger protein molecules afford an atomistic description of electrochemical double layers, since it will be perturbed by the adsorption in a way which cannot be straightforward predicted by a continuum model. The results of the unperturbed interface should be first compared with established electrochemical models.

Two groups treated metallic surfaces by molecular dynamics simulations, where in contrast to oxides no chemisorption and dissociation of H_2O had to be taken into account [16–19]. The simulations showed that the double layer and the reorientation of the water dipoles can be described this way, but extremely high ionic concentrations were employed. Recently, the interface of rutile and ionic solutions was studied by molecular dynamics and by X-ray diffraction [20,21], but the introduction of surface hydroxylation into these calculations is not directly correlated to the pH-value of the solution. We want to study the adsorption of biomolecules and thus have to build up a model with realistic pH-values and ionic concentrations. Moreover, the mobility of both the water molecules and the ions near the surface has a major impact on the properties of the dissolved molecules and should be understood.

So far we have studied the adsorption of H_2O [12] and of single amino acid molecules on TiO_2 in vacuum and aqueous solution [4], and in later stages of the project adhesion proteins such as collagen [14,22] shall be included. The aim of the present paper is to compare molecular dynamics simulations of double layers of Na^+ and Cl^- ions in water on titanium oxide without perturbation by molecular solutes with established continuum approaches. A very common one is the Stern model, which predicts a rigid Helmholtz layer of adsorbed counterions and a diffuse Gouy–Chapman layer. In this layer the concentration of ions with the same sign as the surface charge smoothly decreases when approaching the surface, whereas the excess concentration of the ions with opposite sign increases [23].

2. Methods of calculation

We choose the (1 0 0) surface since the cited data may suggest that it may also be more reactive than (1 1 0) with respect to biomolecules. TiO_2 is modelled here as a slab with five layers and a height of approximately 11 Å being oriented in parallel to the *xy* boundary plane of the orthorombic cell with a total height of $z = 83$ Å (Fig. 1a). The *z*-axis in the figures starts at the centre of the slab, the bridging oxygen atoms on the surface being found at $z = 5.5$ Å on this scale.

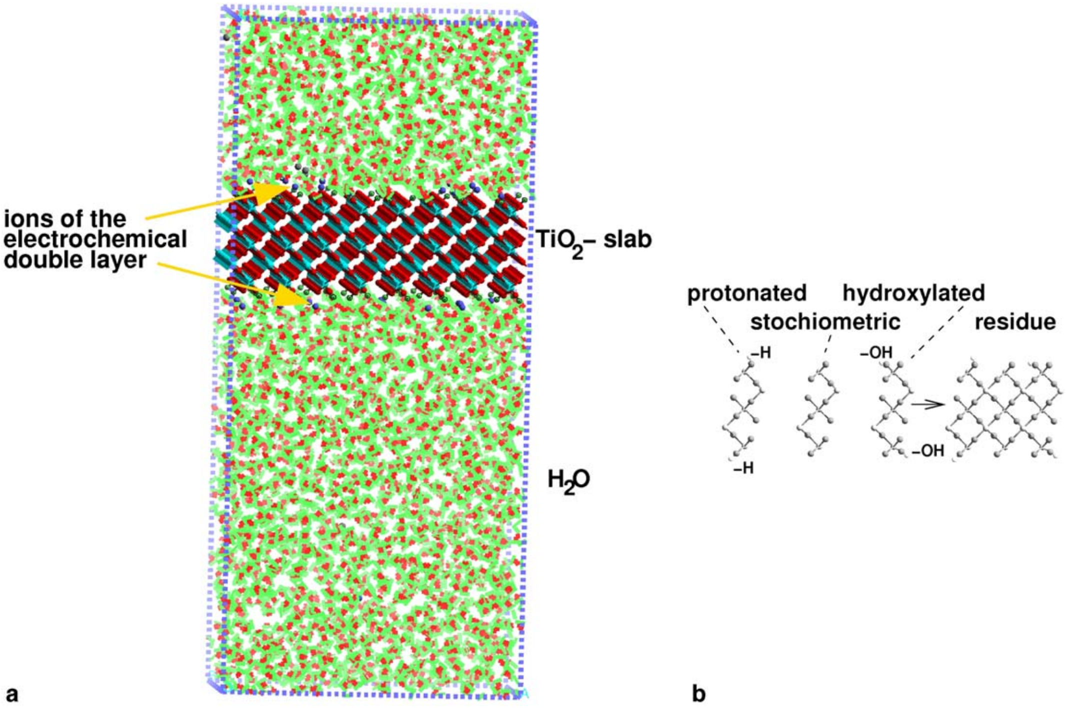

Fig. 1. (a) Slab model of the TiO_2 (1 0 0) surface in the simulation cell. (b) Residues for the generation of protonated, stochiometric and hydroxylated surface.