



Phosphonic acid adsorption at the TiO₂ anatase (101) surface investigated by periodic hybrid HF-DFT computations

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Abstract

Phosphonic acid (H₃PO₃) is a candidate as an anchor group that can be used to bind a wide range of molecules to TiO₂ surfaces, with practical applications for example in dye-sensitized solar cells. Adsorption geometries and energies of H₃PO₃ on the TiO₂ anatase (101) surface have therefore been investigated using quantum-chemical periodic hybrid ab initio Hartree Fock density functional theory calculations employing the B3LYP functional and a split-valence basis set. According to the calculations, the most stable adsorption arrangement is a molecular monodentate configuration with a calculated adsorption energy of 47.1 kcal/mol. There are several additional molecular monodentate and dissociative bidentate adsorption modes with calculated adsorption energies exceeding 40 kcal/mol. For comparison, we have also calculated the adsorption strength of formic acid (HCOOH), which is the currently most widely used anchor group in the solar cell applications, at the same level of theory, to be weaker than 30 kcal/mol. The greater adsorption strength of phosphonic acid compared to formic acid is in good agreement with experimental observations regarding differences in the long-term stability between the two different anchor groups. Implications of the current findings for the design of better dye-sensitized solar cells are discussed.

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1. Introduction

Molecular adsorption at metal-oxide surfaces is of general interest in many applications, including the rapidly growing field of photoelectrochemistry. Especially dye-sensitized solar cell systems [1–3]

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have received much attention during the last decade. These donor-acceptor systems are composed of dye molecules bound to nanocrystalline semiconductors through one or more anchor groups [4]. Even if most parts of the systems are well understood separately, the interactions between the parts are still largely unknown.

The structural and electronic interactions between metal oxide substrates and aromatic and organometallic adsorbates are of particular interest, as they are crucial to ensure efficient charge separation following photo-excitation of the dyes in the solar cells. At the same time, the anchoring of the dye must be sufficiently robust to ensure the desired long-term stability of the solar cells. The adsorption of dye molecules via designated anchor groups to titanium dioxide has therefore recently been studied both experimentally [4–6] and theoretically [7–13]. The currently most efficient dye-sensitized solar cells are based on nanocrystalline TiO₂ electrodes sensitized by ruthenium dyes that have carboxylic acid anchor groups [1,2]. The carboxylic acid anchor groups appear to give exceptionally good electronic coupling across the dye-semiconductor interface [14]. The interaction of carboxylic acid with different metal oxides surfaces has therefore been the subject of several experimental and theoretical studies [15,16]. Although the carboxylic acids are highly efficient in terms of good electronic coupling, they frequently have problems with the long-term stability due to slow desorption from the semiconductor surface in presence of water. Phosphonic acid offers a serious alternative as an anchor group [17–23], as experimental studies have indicated that it tends to bind more strongly to metal oxide surfaces, thus displaying better long-term stability compared to formic acid anchors [24–28]. It can also be noted that phosphonic acid anchored on titanium has applications in implant systems [29,30].

The objective of this paper is to study the adsorption of phosphonic acid on anatase (101) surface, which is one of the most prominent titanium dioxide surfaces in the typical TiO₂ nanocrystalline electrodes used in the solar cells. The investigation is carried out using periodic hybrid ab initio Hartree Fock density functional theory calculations. In particular, adsorption energies

are calculated for different adsorption geometries in search of the most likely adsorption modes. The results for phosphonic acid are also compared to calculations on formic acid using comparable methodology.

2. Methods and computational details

The computations were carried out using hybrid ab initio Hartree Fock density functional theory and periodic boundary conditions, as implemented in the CRYSTAL03 program [31]. The B3LYP functional [32,33] was used. This functional has proven successful both for studying molecular systems, and more recently also for condensed-phase studies [34], making it an attractive choice for studies of molecular adsorbates on solid surfaces.

An atom-centered Gaussian basis set of double-zeta split-valence quality where the core electrons for non-hydrogen atoms were replaced by effective core potentials was used [35]. This basis set has also been used in similar earlier studies [7,15,36].

In order to study the chemistry at the anatase surface within a periodic framework, the anatase crystal cell dimensions and coordinates were first varied to find the minimum B3LYP energy of the crystal. The obtained energy-minimum crystal structure was then cleaved parallel to the (101) surface plane twice to form a two-dimensional periodic slab with the thickness of about 6 Å, see Fig. 1. This corresponds to 12 layers of different atomic-coordinate values along the direction perpendicular to the surface (the *z*-axis). An orthogonal 2 × 1 surface cell was constructed, and the coordinates were geometry-optimized using analytical gradients [37] to find the relaxed surface structure.

In the molecular adsorption studies, the geometry of the H₃PO₃ molecule was first relaxed when placed on different sites at the TiO₂ surface. Initially a thinner 6-layer slab with the TiO₂ atoms fixed in their surface relaxed positions was used. When a minimum was found, the larger 12-layer slab (16 Ti and 32 O in the surface cell) was used and the molecule was relaxed again. Then the relaxation was extended to comprise also the sur-

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