

Computational study of electrochemical reduction on anatase-type TiO₂ nanoparticles

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[Abstract]

Electrochemical reduction of organic acids was investigated on 101 surface of anatase-type TiO₂ using slab models. These findings were compared to nanoparticles with 101 faces. The electrochemical differences between the slab and nanocrystal can be explained with the reduced bandgap of the later, and this bandgap is determined by the shape and size of the nanoparticle. We studied the orbitals around the band gap as well as their role in electrochemical reactions.

[Introduction] The electrochemical reduction of organic acids on anatase TiO₂ electrode has been recently reported by Yamauchi [1]. Such an electrochemical reaction has a potential to produce alcohol products with high selectivity and efficiency, and these products can be used as alternative fuel in carbon neutral cycles. However so far the reaction is reported only for oxalic acid, and other acids like acetic acid cannot be reduced. The preparation history of the electrode and the morphology of the oxide nanoparticles can largely determine the efficiency of such an electrode. Therefore we performed theoretical analysis on the surface bind organic acid molecules to understand better the limiting factors of this electrochemical reaction.

[Methods] The calculations were performed with Density-Functional Based Tight-Binding method (DFTB) as implemented in DFTB+ software [2]. Slater-Koster parameter sets of mio and tio were used. Surface models of 101 anatase slab were created with 3 layer thickness, and 4x4 widths. During optimization reactions, the unit cell size and the lowest anatase layer were fixed, while the other two layers with the substrate were freely relaxed.

Model of anatase nanoparticles was created from bulk anatase cut along 101 surfaces. To reach charge equilibrium, -OH were attached to apexes of the nanoparticle, resulting in a stoichiometry of Ti₉₈O₁₉₄(OH)₄. The position on this capping both assures the termination of the low coordinating Ti ions as well as compensating the extra positive charge in the most positive part of the nanoparticle.

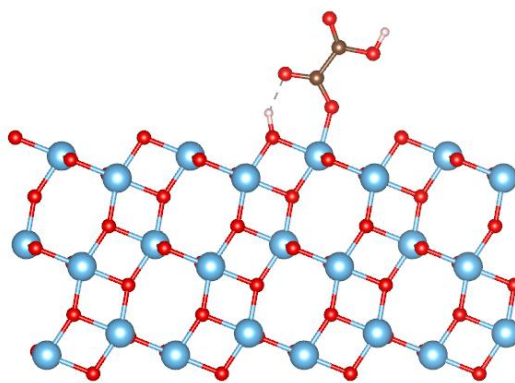


Fig. 1. Dissociative absorption of oxalic acid on anatase 101.

[Results and Discussion] Carboxylic acids can absorb in several different geometries to the 101 anatase surface. The energetically the most stable geometry is a dissociative geometry absorption (see in Fig. 1), where the anchoring carboxylic group is deprotonated and bind to a surface. Such an absorption is very strong (in order of 150 kJ/mol), and very similar to all the acids we studied including oxalic and acetic acid, too. The reduced aldehyde forms of the

molecules has a much weaker absorption, (in order of 15 kJ / mol), which suggest that the reduction of the anchoring groups is energetically unfavorable. This absorption is actually weaker than that of for alcohols (30-35 kJ/mol) or water (38-40 kJ/mol). This leads to the conclusion that we can only expect the reduction of the distant carboxylic group in the case of oxalic acid, and for the same reason simple acids like acetic acid cannot be reduced. Such a strong absorption of the carboxyl group actually protects it from the reduction.

We also studied the differences between slab models and nanoparticles. TiO₂ nanoparticles, unlike surface slab models, always have a strong dipole moment, which interfere with absorption of organic acids as well as the solvent water molecules. Moreover, the HOMO-LUMO gap in the nanoparticle is much smaller (2.54 eV) than the bandgap associated with the slab model (3.07 eV) or the experimental bandgap of bulk anatase (3.02 eV). This reduced bandgap is much dependent on the actual geometry of the nanoparticle, and mainly due to lower energy LUMO levels associated with the Ti ions on the nanoparticle apex and edges. The most important energy levels and orbitals are shown in Figure 2. In electrochemical reactions, the coupling between the orbitals of the organic substrate and the LUMO levels / low edge of conduction band has an important role, and the electron promotion through the latter is the main mechanism of reduction. By lowering these LUMO levels, the electrochemical reduction can be promoted via much lower energy orbitals. Morphology of the electrode therefore has direct connection with energetics of electrochemical reduction on these nanoparticles.

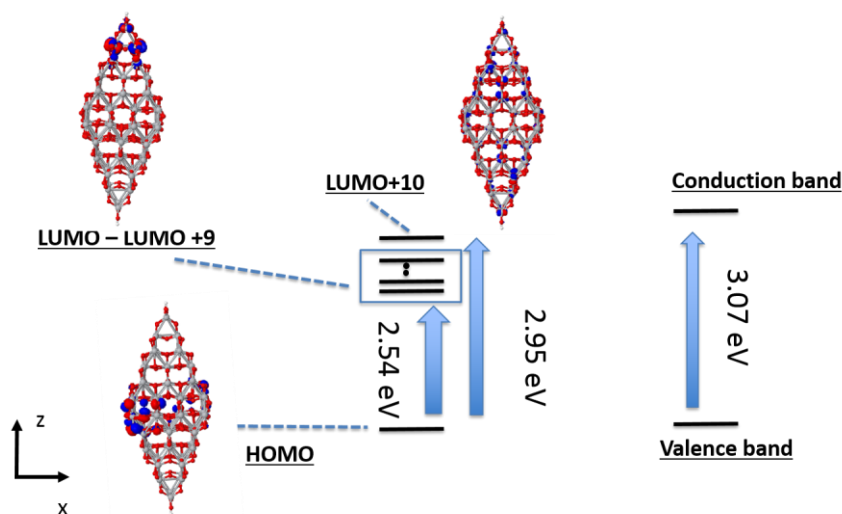


Fig. 2. Orbitals around the HOMO-LUMO gap in the anatase nanoparticle.

[References]

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