

# Electrochemical Properties of TiO<sub>2</sub> (Anatase, Rutile) Surfaces: Effects of Flatband Potential

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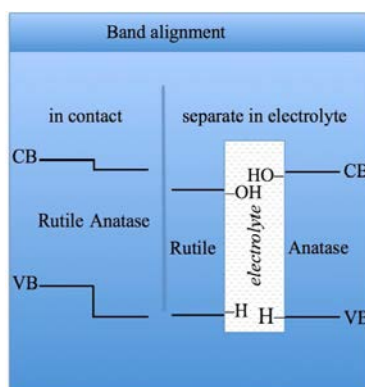
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The electronic band alignment of titania surfaces is of fundamental implication for photocatalysis, solar cells and solar fuel generation (e.g. water splitting). The position of conduction band (CB) edge controls the reductive photocatalytic reactions, (e.g. hydrogen evolution from water or CO<sub>2</sub> reduction), potential of dye-sensitized solar cell (DSC), recombination blocking in perovskite solar cells, etc. However, there is a considerable controversy about the position of CB in TiO<sub>2</sub> (anatase, rutile, including the crystals with distinguished facets). [1] Long-time debate concerns the fact that the CB edge of rutile (in contrast to anatase) is not sufficiently upshifted compared to the energy equivalent to the H<sup>+</sup>/H<sub>2</sub> reduction potential. [2] A standard electrochemical tool monitoring the CB edge is the flatband potential. It is measured by Mott-Schottky plots from electrochemical impedance spectroscopy, onset of anodic photocurrent of water oxidation or dark H<sup>+</sup> reduction, cyclic voltammetric mapping of DOS including the electron trap states, spectroelectrochemical determination of optical absorbance of CB electrons, etc. The staggered alignment in mixed phases, such as in anatase/rutile, is assumed to enhance photocatalytic activity of titania, but it is widely disputed whether the conduction band edge of rutile or that of anatase is higher. Photoelectron spectroscopy (PES) and most DFT simulations support the former, but the flatband potential measurements provide just opposite results. The controversy can be explained by taking into account the adsorption of OH<sup>-</sup> and H<sup>+</sup> ions from the electrolyte solution on the electrode surface. [3,4] Furthermore, PES indicates that the CB edge of (001)-anatase is upshifted by 0.1 eV referenced to (101)-anatase in agreement with the DFT calculation [5] and with the electrochemical flatband potentials [6] (upshift of CB by 60 meV) but there are again some conflicting works claiming the opposite (see Ref. [7] for discussion).

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