

The influence of electronic states on the photocatalytic activity of titanium dioxide in reduction processes

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In recent years a number of publications on heterogeneous photocatalysis is increasing along with the growing number of semiconductor applications as photocatalysts. More and more sophisticated materials designed to facilitate various photocatalytic processes are engineered. Activity of a semiconductor photocatalyst are determined by its electronic structure. Photocatalytic processes which may occur at the surface of wide bandgap semiconductors depend not only on the potentials of the valence and conduction band edges, but also on the electronic states within the bandgap. The electronic states (*ES*), which are localized close to the conduction band edge, may act as an electron-trapping sites or electron donors, depending on their origin and the electrostatic potential distribution in their vicinity. Thus, they can mediate various electron transfer mechanisms either within the semiconductor or between molecules adsorbed at the surface, which are crucial for the photocatalytic processes.^[1-3] Moreover, *ES* can significantly affect photoinduced processes which are related to the charge carriers diffusion in nanostructured material.^[4] They can become an efficient recombination centers^[5] or participate in electron transfer between the semiconducting support and redox-active species.^[3]

One of the most often used photocatalyst is titanium dioxide. Electronics states, as well as other parameters (crystallinity, specific surface area, phase composition *etc.*), may influence the photocatalytic activity of titanium dioxide. Although this material has been intensively studied for many years, its electronic structure is usually oversimplified using concepts of the band edges or the flatband.

Recently, we proposed a modified spectroelectrochemical method as a new technique to characterize the electronic states.^[6-7] Distribution of additional electronic states localized within the bandgap can be qualitatively and quantitatively characterized using this approach. The proposed method has been applied to determine the influence of the surface states localized within the bandgap on the photocatalytic processes such as carbon dioxide, oxygen and water reduction. Correlations between efficiencies of those reactions and electronic structures will be presented and discussed.

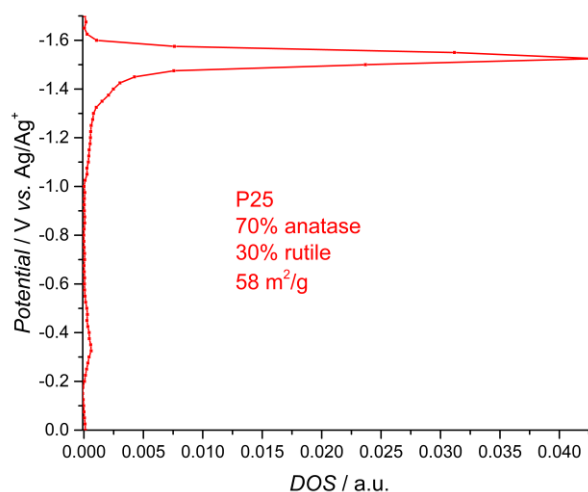


Figure 1. Density of vacant states (DOS) patterns for titanium dioxide (P25) measured in $0.1 \text{ mol/dm}^3 \text{ LiClO}_4$ acetonitrile electrolyte.

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