

## Surface Reduction in Monoclinic $\text{BiVO}_4$ for Photocatalytic Applications

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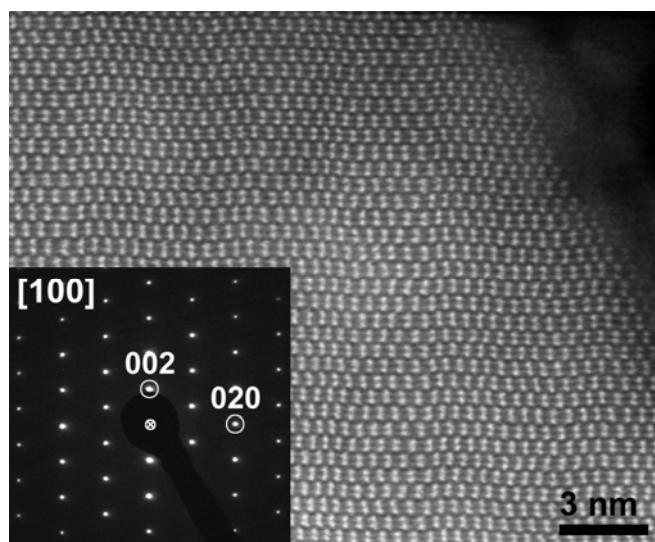
Bismuth vanadate ( $\text{BiVO}_4$ , short BVO) is a promising photoelectrochemically active candidate for water splitting used for hydrogen generation. Compared to  $\text{TiO}_2$ , i.e. the most widely used and investigated photocatalyst, BVO uses visible instead of ultraviolet light for its photoelectrochemical activity. Amongst the three polymorphs of BVO, the monoclinic clinobisvanite BVO (m-BVO) phase exhibits the highest photocatalytical activity. This is due to both, the favorable band gap energy of  $\sim 2.4$  eV and the valence band position, which is suitable for driving water oxidation under irradiation. Despite the fact that the conduction band is reported to be too low relative to the proton reduction potential for hydrogen evolution [1], the water splitting reaction can be promoted by simultaneously using a hydrogen evolution catalyst, such as a noble- or transition-metal catalyst [2]. Apart from the low charge carrier mobility of m-BVO [3], which can be improved by using various dopants [2,4], another crucial point, which affects m-BVO's photocatalytic activity, concerns oxygen vacancies. These vacancies, which have been recognized to play a key role in the photocatalytic performance of m-BVO, are the dominant intrinsic defects in m-BVO [5] and might act as harmful photogenerated carrier traps [6]. However, little is known about the concentration and the distribution of oxygen vacancies in m-BVO.

In this contribution we present a study based on atomic-resolution scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) which aims at investigating the distribution and concentration of oxygen vacancies in pristine m-BVO. High-resolution imaging of grains of BVO rules out the presence of relevant structural defects or structural modifications that could account for oxygen vacancies. However, spatially resolved EELS measurements reveal a distinct shift of the vanadium  $L_{3,2}$  edge towards lower energies when the electron probe is positioned near the surface of the particles. Indeed, in a surface shell of about 5 nm the vanadium  $L_{3,2}$  edge is shifted by about 1 eV towards lower energy compared with the corresponding bulk measurement. Comparing this shift with the location of the vanadium L-edge measured in three vanadates of different oxidation state, namely  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ , allows for explaining this shift in terms of a surface reduction in m-BVO. Within a surface area of about 5 nm thickness, the oxidation state of vanadium is reduced from +5 to about +4. The reduction of the vanadium oxidation state demands for a concentration of oxygen vacancies above 10%. The rather high amount of oxygen vacancies might question the stability of m-BVO phase. However, m-BVO has the scheelite structure, which is known to easily accommodate cations with various oxidation states, and to tolerate cation and oxygen vacancies [7]. In order to confirm the STEM/EELS results, X-ray photoelectron spectroscopy (XPS) was carried out on pellets of powder samples. The XPS measurements unambiguously confirmed the surface reduction in m-BVO ruling out effects to the electron irradiation in STEM for this electron-sensitive material.

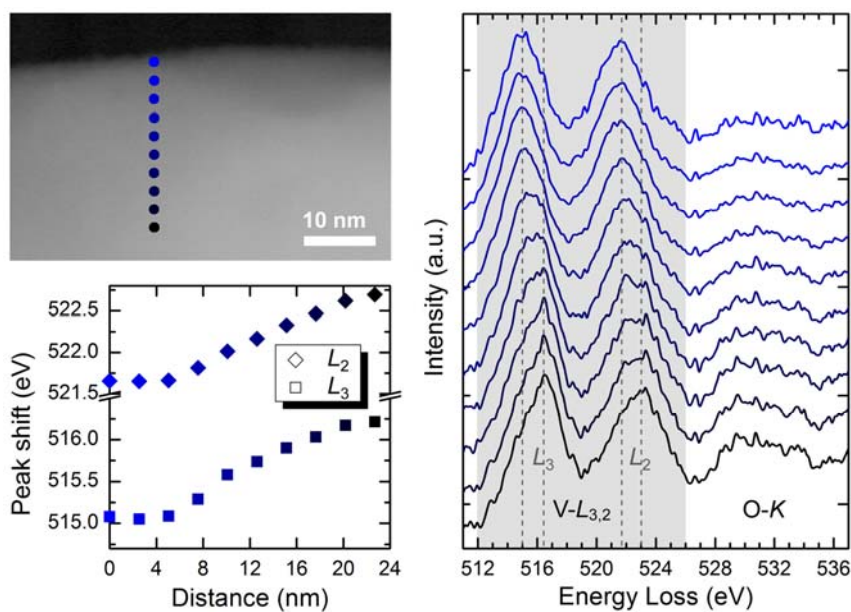
We thus conclude that oxygen vacancies in m-BVO are accumulated in a distinct surface layer of about 5 nm thickness. The occurrence of this surface reduction shell must be considered in the optimization of the photochemical activity of m-BVO and in possible dopant strategies.

## References:

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**Figure 1.** High-angle annular dark-field STEM micrograph revealing the structural intactness at the surface of m-BVO, despite of an oxygen concentration that is roughly 10% lower than in the bulk.



**Figure 2.** Line scan of EEL spectra of the vanadium  $L_{3,2}$  edge, the location of the measurements and the plot of the peak shifts of the  $L_3$  and  $L_2$  line.