X-ray Raman scattering of photocharged $BiVO_4$ reveals beneficial effect on the space charge region

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Photoelectrochemical (PEC) water splitting is a promising method to directly convert sunlight and water into hydrogen, a promising material that could become very important in the oncoming energy transition. Bismuth vanadate ($BiVO_4$) is an extensively investigated ternary metal oxide semiconductor that has shown interesting properties for PEC water splitting. It is the best performing metal oxide photoanode to date and the band gap of 2.4 eV is suitable to make $BiVO_4$ a good top absorber in tandem with a low band gap bottom absorber to perform highly efficient solar water splitting.

One of the main drawbacks of $BiVO_4$ is charge recombination at the surface. Recently, it was found that a technique called photocharging creates a thin layer on the surface of $BiVO_4$, improving its performance as a photoanode drastically. [1,2] To understand the electronic implications of this surface layer on the bulk of the $BiVO_4$, X-ray Raman scattering (XRS) spectroscopy was performed to study the V L_3 and L_2, and the O K-edge of the material. Through grazing incidence XRS spectroscopy measurements, it was found that the oxidation state of vanadium is altered in the first 60 nm of the material. The O K-edge spectrum was simulated using FDMNES, which revealed a change in electron confinement and occupancy in the oxygen pre-edge. These insights, combined with ultraviolet-visible spectroscopy (UV-vis) and X-ray photoelectron spectroscopy (XPS) data, revealed that the surface layer forms a heterojunction with $BiVO_4$, leading to favourable band bending and strongly reduced surface recombination.

During the talk I will also discuss possibilities for performing operando (photo)-electrochemical XRS experiments that could become feasible after the current ESRF upgrade. Both cell design and limitations of these operando experiments will be discussed.

References

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