

# The impact of swift heavy ion irradiation on bismuth vanadate photoanode for photoelectrochemical water oxidation

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Photoelectrochemical (PEC) water splitting is a promising method for environmentally benign production of energy in the form of chemical fuels. Monoclinic bismuth vanadate ( $\text{BiVO}_4$ ) stands out as an excellent candidate for photoanode material due to its suitable band structure, good stability and low-cost synthesis. However,  $\text{BiVO}_4$  has poor charge transfer properties due to the high rate of electron-hole recombination and understanding the effects contributing to it is important for further improvements. Herein, we report the effect of swift heavy ion irradiation (Xe, 150 MeV,  $1 \times 10^{10}$ – $5 \times 10^{11}$  ions/cm<sup>2</sup>) on physicochemical properties of hydrothermally synthesized  $\text{BiVO}_4$  thin films. X-ray diffraction study (XRD) showed that irradiated material preserved initial monoclinic scheelite phase and preferential growth along [010] direction together with the presence of notable amorphization for  $5 \times 10^{11}$  ions/cm<sup>2</sup> irradiated sample. Scanning electron microscopy (SEM) of all samples showed prismatic grains with an average size of 600 nm. In irradiated samples formation of ion tracks, ~ 10 nm in diameter, was observed. Raman spectroscopy analysis confirmed presence of bands that correspond to the monoclinic scheelite phase along with the appearance of new bands for  $5 \times 10^{11}$   $\text{BiVO}_4$  at 420 and 915 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) analysis of Bi 4f, V 2p and O 1s states showed that, after irradiation, increased amounts of V<sup>4+</sup> and oxygen vacancies occurred, especially at higher fluences. By using UV-Vis Diffuse Reflectance spectroscopy we showed that band gap decreased with the increase in fluence. Photocurrent densities, obtained from 1-hour-long chronoamperometry measurements, indicated that irradiation with  $1 \times 10^{10}$  ions/cm<sup>2</sup> fluence leads to the enhanced PEC oxygen evolution with time. In order to get a better insight into preceding phenomena, we performed XRD, SEM and XPS analysis after PEC process.

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