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The effect of swift heavy ion irradiation on physicochemical properties of monoclinic bismuth vanadate

Marko Jelić¹, Ekaterina Korneeva², Nikita Kirilkin², Tatiana Vershinina², Oleg Orelovich², Vladimir Skuratov², Zoran Jovanović¹, Sonja Jovanović¹

¹Vinča Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia, ²Joint Institute for Nuclear Research, Dubna, Russia

Monoclinic bismuth vanadate (BiVO₄) is considered to be one of the most promising photoanode materials for photoelectrochemical (PEC) water splitting due to its suitable band gap and band structure, good stability and low-cost synthesis. However, BiVO₄ 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, $10^{10} - 5 \times 10^{11}$ ions/cm²) on physicochemical properties of hydrothermally synthesized BiVO₄ thin films. X-ray diffraction study (XRD) showed that irradiated material preserved initial monoclinic scheelite crystal phase and preferential growth along [010] direction. As the fluence increased, a shift of the diffraction maxima towards lower 2θ values was observed indicating increased interplanar distances. Also, for the 5×10¹¹ ions/cm² irradiated sample, high degree of amorphization was noticed. 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. X-ray photoelectron spectroscopy (XPS) analysis of Bi 4f, V 2p and O 1s states showed that, after irradiation, increased amounts of V^{4+} and oxygen in the form of hydroxide occurred, especially at higher fluences. By using UV-Vis Diffuse Reflectance spectroscopy we showed that band gap decreased with the increase of fluence. Photocurrent densities obtained from linear sweep voltammetry indicated that irradiation with fluences higher than 10^{10} ions/cm² have a notable negative effect on PEC oxygen evolution reaction. However, 1-hour-long chronoamperometry measurements of 10¹⁰ ions/cm² irradiated sample revealed an increase of photocurrent densities. In order to get a better insight into preceding phenomena, we performed XRD, SEM and XPS analysis after PEC process.