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Defect Engineering in Bismuth Vanadate Photoanodes via Swift Heavy Ion Irradiation for Optimized Photoelectrochemical Performance

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Swift heavy ion (SHI) irradiation, using Xe ions with 150 MeV energy and varying fluences (5 × 109 –5 × 1011 ions cm^{-1}) is explored as a method to introduce defects in the hydrothermally synthesized monoclinic BiVO4 (BVO) thin films, aiming to understand its impact on photoelectrochemical (PEC) performance for oxygen evolution reaction (OER). In the near surface region, the irradiation leads to the bismuth rich hillock formation and oxygen depleted ion tracks. 1-hour-long chronoamperometry measurements reveal photocurrent density increase of up to 58.6 % and 25.2 % for 5 × 109 and 1 × 1010 ions cm-1 irradiated samples while sample irradiated with the high fluences shows decrease in activity throughout the whole timeframe. This increase is accompanied by formation of ~150 nm deep and ~50 nm wide holes at the position of original ion tracks. Irradiation induces residual stresses while maintaining the monoclinic scheelite phase and [001] preferential orientation. Notably, high-fluence irradiation leads to amorphization, as confirmed by appearance of new Raman bands at 410 and 910 cm-1. Band gap reduction with increasing fluence, from 2.41 ± 0.06 eV for non-irradiated down to 2.32 ± 0.05 eV for 5×1011 ions cm-1 irradiated BVO, indicates changes in the electronic structure. Overall, the study contributes to the fundamental understanding of SHI-induced modifications in BVO films and lays the foundations for further research aimed at enhancing their efficiency and durability in practical PEC applications.

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