

Supporting Information

Enabling Solar Water Oxidation by BiVO₄ in Strongly Acidic Solutions

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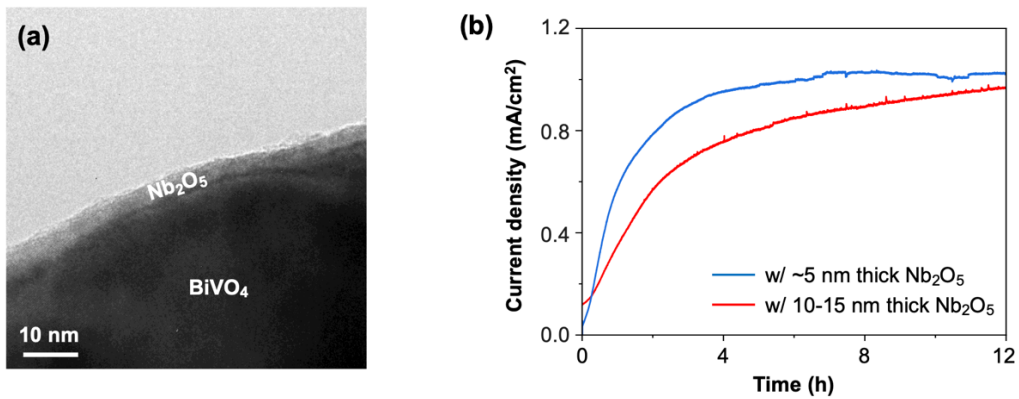


Figure S1. (a) TEM image of BiVO₄ coated with a ~5 nm thick Nb₂O₅ layer. (b) The $J-t$ plots of BiVO₄/Nb₂O₅ samples, one with a ~5 nm thick Nb₂O₅ layer (blue) and the other with 10-15 nm thick Nb₂O₅ layer (red), in 0.1 M HNO₃ containing 20 mM Co²⁺ under AM 1.5G illumination (100 mW/cm²). The applied potential was 0.7 V vs RHE. The thin Nb₂O₅ layer needed less activation time, but the photocurrent densities of the two samples became comparable over time.

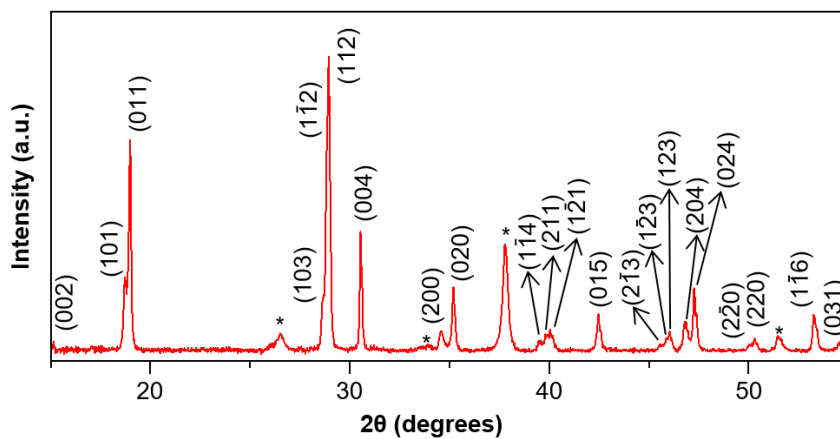


Figure S2. XRD pattern of BiVO₄/Nb₂O₅ showing the purity and crystallinity of BiVO₄ (ICSD100602). No peaks related to crystalline Nb₂O₅ were observed. Peaks from the FTO substrate are marked with asterisks (*).

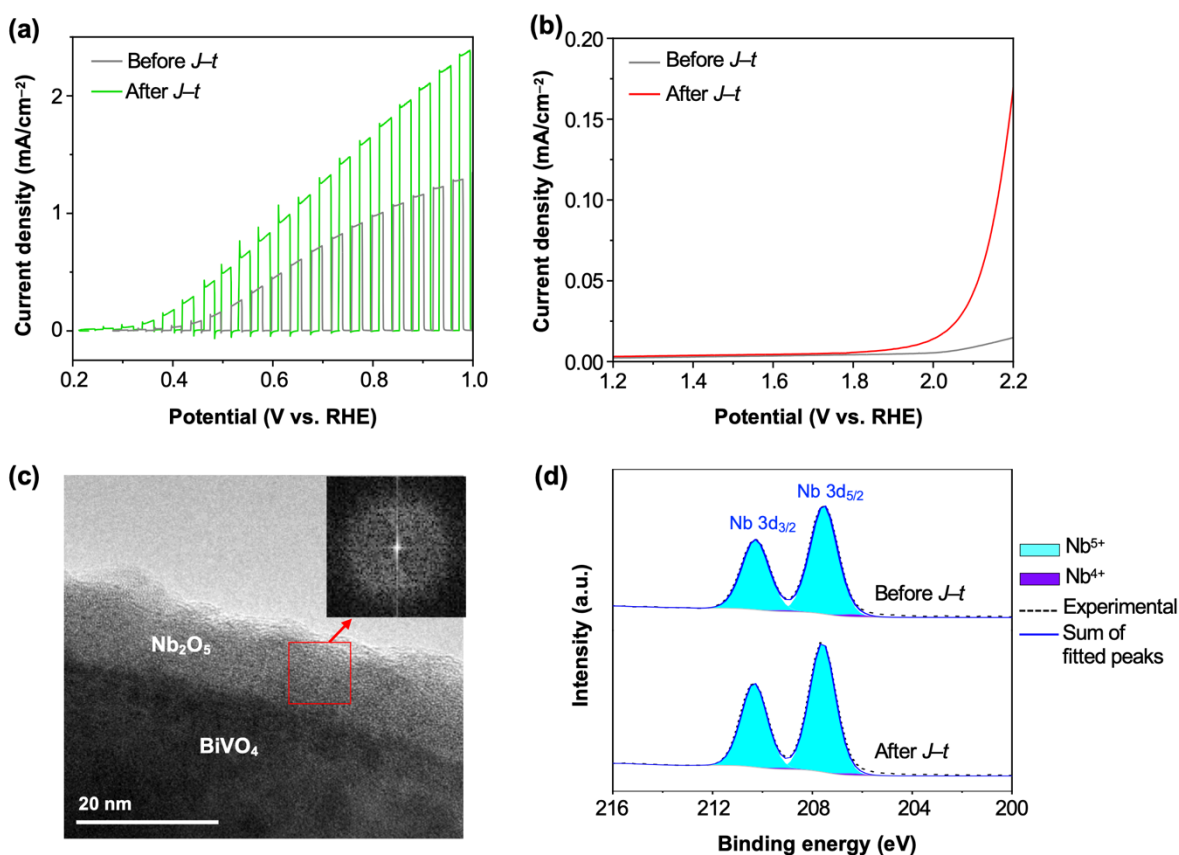


Figure S3. (a) J - V plots of BiVO₄/Nb₂O₅ for sulfite oxidation measured in 0.5 M borate buffer containing 0.4 M sulfite under AM 1.5G illumination (100 mW/cm²) before (grey) and after (green) the activation process. (b) J - V plots of BiVO₄/Nb₂O₅ measured in 0.1 M HNO₃ comparing OER performances in the dark before (grey) and after (red) the activation process. (c) TEM image measured after the activation process showing no differences from that taken before the activation process shown in **Figure 1d**. (d) Comparison of the Nb 5d XPS spectra before and after the activation process. The activation process refers to the constant potential POER performed at 0.7 V vs RHE in 0.1 M HNO₃ under AM 1.5G illumination (100 mW/cm²) for 12 h shown in **Figure 3b**.

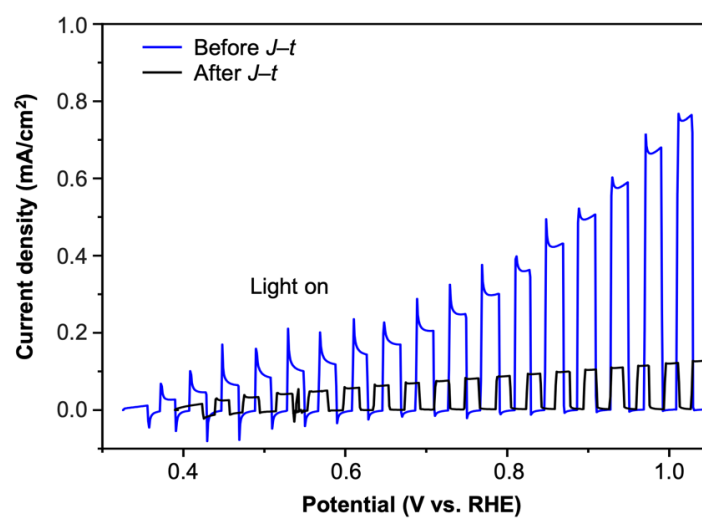


Figure S4. J - V plots of unprotected BiVO_4 measured in pH 1 HNO_3 solution under AM 1.5G illumination (100 mW/cm^2) before (blue) and after (black) the J - t measurement shown in **Figure 3b**.

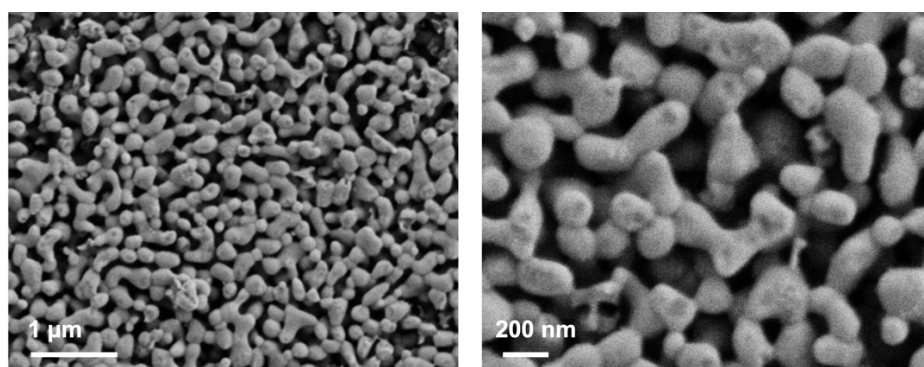


Figure S5. SEM images of unprotected BiVO_4 after the J - t measurement with Co^{2+} shown in **Figure 6b**.