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Highly stable and efficient photoelectrochemical water oxidation at an anisotropically crystallized monoclinic WO_3 film with predominant growth of (202) plane

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An anisotropically crystallized monoclinic WO_3 films were synthesized on fluorine-doped tin oxide (FTO) electrode by a one-step hydrothermal method using oxalic acid (Oxa) as a structure directing agent. The WO_3 film (denoted as WO_3(*w*-Oxa)) prepared with Oxa was composed of relatively large layered-sheets with 2 ~ 5 μm length with predominant growth of the (202) plane (parallel to the substrate), in contrast to small layered-sheets with 1 ~ 2 μm length with predominant growths (020) or (200) planes for the WO_3(*w/o*-Oxa) film prepared without Oxa. Although the photocurrents were generated above 0.6 V vs. RHE for WO_3(*w*-Oxa) and WO_3(*w/o*-Oxa) electrodes, the incident photon to electron conversion efficiency ($IPCE_{420}$ = 38%) at 420 nm and 1.23 V vs RHE for the former was 2.7 times higher than that (14%) of the latter. The higher $IPCE_{420}$ for the WO_3(*w*-Oxa) is ascribed to higher charge separation (η_{sep} = 50 %) and catalytic (η_{cat} = 95 %) efficiencies compared to those (η_{sep} = 19 % and η_{cat} = 82 %) for the WO_3(*w/o*-Oxa) electrode. The photoelectrochemical impedance spectroscopic (PEIS) measurement suggested effective bulk charge transport in the WO_3(*w*-Oxa) electrode compared to the WO_3(*w/o*-Oxa) electrode, which works to the advantage of suppressed recombination of photogenerated charges (electrons and holes), being responsible for the higher η_{sep}, eventually causing the higher IPCE for the WO_3(*w*-Oxa) electrode. The WO_3(*w*-Oxa) electrode showed the high photocurrent stability (95% remain for 7 h) and Faraday efficiency (FE_{O2}) of 95% for water oxidation. The high stability and FE_{O2} of the WO_3(*w*-Oxa) electrode result from the suppression of the competed photo-oxidation of the surface by the attenuated hole accumulation due to efficient water oxidation at the (202) facet surface.