## Temperature control of nanowire/hexagonal prismatic WO<sub>3</sub> structure with a high performance for photoelectrochemical water oxidation

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A photoanode capable of efficiently promoting water oxidation is a key essence for realizing a photoelectrochemical (PEC) water splitting cell for hydrogen production. WO<sub>3</sub> is a promising photoanode for PEC water oxidation due to its high oxidation potential. WO<sub>3</sub> photoanodes with specific nanostructures have been actively studied to improve PEC performance for water oxidation, and there are various ways to control the nanostructure. Recently, we reported efficient visible-light-driven water oxidation on an in situ N<sub>2</sub>-intercalated WO<sub>3</sub> nanorod photoanode using hydrazine (N<sub>2</sub>H<sub>4</sub>).<sup>1</sup> In this report, we demonstrate that nanowire (NW) and hexagonal prismatic (HP) WO<sub>3</sub> photoanodes can be easily produced by controlling the synthesis temperature during the synthesis of WO<sub>3</sub> powder using N<sub>2</sub>H<sub>4</sub>.

 $N_2H_4$  derived WO<sub>3</sub> ((N<sub>2</sub>H<sub>4</sub>)WO<sub>3</sub>) precursor was synthesized by adding tungstic acid to water at controlled temperatures of 20~45°C and adding N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O dropwise with stirring.

The (N<sub>2</sub>H<sub>4</sub>)WO<sub>3</sub> precursor synthesized at 20°C had a nanowire structure, which transitioned to a hexagonal prismatic structure (45°C) as the synthesis temperature was increased (Fig. 1A). The NW-WO<sub>3</sub> and HP-WO<sub>3</sub> photoanodes were prepared by adding the NW- or HP- (N<sub>2</sub>H<sub>4</sub>)WO<sub>3</sub> precursor to a methanol solution dissolved in polyethylene glycol, coating it on an ITO substrate, and sintering it at 550°C under an oxygen atmosphere. Interestingly, the WO<sub>3</sub> morphology was maintained after calcination. IPCE at 420 nm (47%) was 3.1 times higher than that of the NW-WO<sub>3</sub> photoanode (15%) (Fig. 1B). Electrochemical impedance spectra and X-ray revealed diffraction that the high PEC performance of the HP-WO<sub>3</sub> electrode was attributed to the crystal structure of the HP-WO<sub>3</sub> particle surface.



Fig. 1 A) SEM images of precursor (left; 20°C, right; 45°C), B) IPCE curves of NW-WO<sub>3</sub> (blue) and HP-WO<sub>3</sub> (red) in HClO<sub>4</sub> (pH 0) at 1.23 V vs. RHE under light irradiation.

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