Electronic Supplementary Information for

**Fabrication and Photoelectrochemical Property of Tungsten(VI) Oxide Films with a Flake-Wall Structure**

**Experimental**

**Preparation of nanocrystalline WO₃ film**

Nanocrystalline WO₃ films were prepared by a sol-gel technique using colloidal solution of tungstic acid. The colloidal solution was obtained by passing an aqueous solution of sodium tungstate through a column filled with a proton exchange resin (DOWEX 50WX2, 100-200 mesh), followed by collecting in ethanol under magnetic stirring. The solution was partially evaporated to reach a concentration of ca. 1.0 mol L⁻¹ and added by Poly(ethylene glycol) 300. After sonication of SnO₂-coated glass in acetone and in 2-propanol solution, the viscous solution was deposited on the glass by a paste-squeegee method and annealed at 773 K for 30 min. This film was used as a base layer for preparation of flake-wall films (film-A and film-B). In order to prepare nanocrystalline WO₃ thick film (film-C), this procedure was repeated to reach the desired film thickness.

**Photoelectrochemical reaction**

The photoelectrochemical property of the prepared films was investigated using a three-electrode system in a cylindrical glass vessel: a platinum wire as a counter electrode and a silver/silver chloride (Ag/AgCl) electrode in 3 mol L⁻¹ sodium chloride as a reference (+0.209 V vs. SHE) were used. An aqueous solution of 0.1 mol L⁻¹ sodium sulfate (Na₂SO₄) was used as a supporting electrolyte. The electrode potential was swept in the anodic direction at a rate of 20 mV s⁻¹ using a potentiostat (Princeton Applied Research PARSTAT 2263). Visible light irradiation (> 400 nm) was performed using a 300-W xenon arc lamp equipped with a cut-off filter (Asahi Techno Glass L42) under magnetic stirring of the electrolyte.

**Calculation of IPCE value**

Monochromatic light irradiation was performed using 300-W xenon arc lamp (ILC Technology CERMAX-LX300F) equipped with a band-pass filter (Asahi Spectra Co.). The electrode potential was shifted from 0.0 to +1.5 V relative to the Ag/AgCl reference electrode. IPCE value was calculated by a following equation:

\[ \text{IPCE} = \frac{1240j}{\lambda I}, \]
where \( j \) is the photocurrent density at +1.2 V vs Ag/AgCl (mA cm\(^{-2}\)), \( \lambda \) is the wavelength of the band-pass filter (nm), \( I \) is the incident photon flux (mW cm\(^{-2}\)). \( I \) was measured using an optical power meter 3664 (Hioki).

**References**

**Fig. S1**  Cyclic voltammograms for WO$_3$ flake-wall film (film-B) in an aqueous solution of 0.1 mol L$^{-1}$ Na$_2$SO$_4$ under (a) dark and (b) visible light irradiation, and (c) in an aqueous solution of 0.1 mol L$^{-1}$ Na$_2$SO$_4$ with 10vol% methanol under visible light irradiation.

**Fig. S2**  SEM cross-sectional image of nanocrystalline WO$_3$ thick film (film-C) (X: nanocrystalline WO$_3$, Y; SnO$_2$, and Z: glass)
Fig. S3  Current-potential plots for film-B and film-C in an aqueous solution of 0.1 mol L\textsuperscript{-1} Na\textsubscript{2}SO\textsubscript{4} under visible light irradiation (a) without neutral density (ND) filter, with (b) ND-70\%, (c) ND-50\%, and (d) ND-20\%.

Fig. S4  Diffuse transmittance spectra of (a) SnO\textsubscript{2} glass, (b) film-B, and (c) film-C.