Electronic Supplementary Information for

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

Experimental

Preparation of nanocrystalline WO_3 film[1]

Nanocrystalline WO_3 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 SnO_2-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 WO_3 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 (Na_2SO_4) 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:

$$\mathrm{IPCE} = 1240j/\lambda I,$$

where j is the photocurrent density at +1.2 V vs Ag/AgCl (mA cm^{-2}), λ 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

1 C. Santato, M. Odziemkowski, M. Ulmann and J. Augustynski, *J. Am. Chem. Soc.*, 2001, **123**, 10639-10649: C. Santato, M. Ulmann and J. Augustynski, *J. Phys. Chem. B*, 2001, **105**, 936-940.

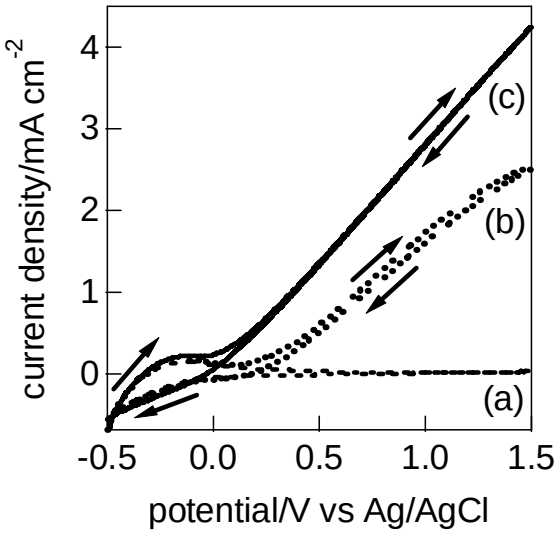

Fig. S1 Cyclic voltammograms for WO_3 flake-wall film (film-B) in an aqueous solution of 0.1 mol L^{-1} Na_2SO_4 under (a) dark and (b) visible light irradiation, and (c) in an aqueous solution of 0.1 mol L^{-1} Na_2SO_4 with 10vol% methanol under visible light irradiation**.**

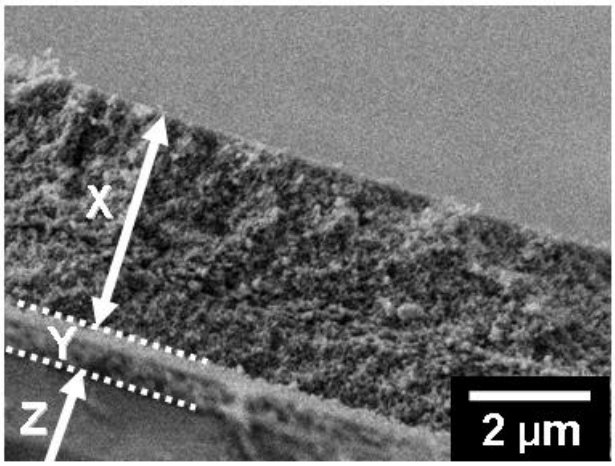

Fig. S2 SEM cross-sectional image of nanocrystalline WO_3 thick film (film-C) (X: nanocrystalline WO_3, Y; SnO_2, and Z: glass)

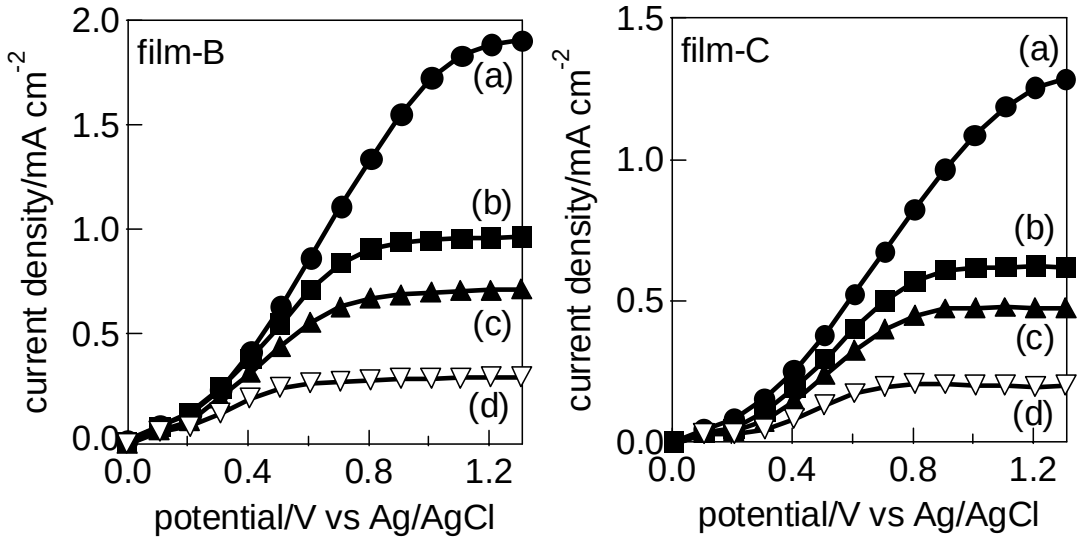

Fig. S3 Current-potential plots for film-B and film-C in an aqueous solution of 0.1 mol L^{-1} Na_2SO_4 under visible light irradiation (a) without neutral density (ND) filter, with (b) ND-70%, (c) ND-50%, and (d) ND-20%.

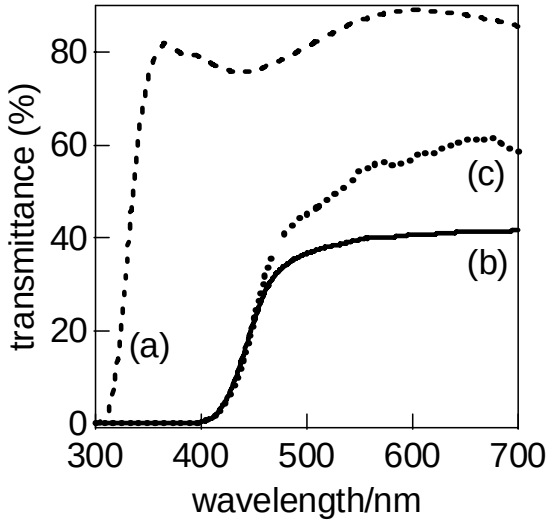

Fig. S4 Diffuse transmittance spectra of (a) SnO_2 glass, (b) film-B, and (c) film-C.