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# Nano- and micro-structural control of WO<sub>3</sub> photoelectrode films through aqueous synthesis of WO<sub>3</sub>·H<sub>2</sub>O and (NH<sub>4</sub>)<sub>0.33</sub>WO<sub>3</sub> precursors†

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Nano- and micro-structured tungsten trioxide (WO<sub>3</sub>) photoelectrode films were prepared through an aqueous solution route. WO<sub>3</sub> precursor layers were deposited on glass substrates through heterogeneous nucleation from (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub> aqueous solutions at 50–60 °C. The crystal phase of the precursors changed from WO<sub>3</sub>·H<sub>2</sub>O to (NH<sub>4</sub>)<sub>0.33</sub>WO<sub>3</sub> with increasing (NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub> concentration (*x*), which involved a morphological change from micron-scale plates to nano-scale fine particles. The WO<sub>3</sub>·H<sub>2</sub>O and (NH<sub>4</sub>)<sub>0.33</sub>WO<sub>3</sub> layers were thermally converted to the monoclinic WO<sub>3</sub> phase. The fine-particle WO<sub>3</sub> films obtained from (NH<sub>4</sub>)<sub>0.33</sub>WO<sub>3</sub> layers showed a better photoanodic performance in the UV range below 350 nm, which was attributed to the larger surface area arising from the porous structure. On the other hand, platy-particle WO<sub>3</sub> films were obtained from WO<sub>3</sub>·H<sub>2</sub>O layers, which exhibited strong light scattering in the visible range, and resulted in an enhanced photoanodic response at wavelengths above 375 nm.

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## Introduction

Tungsten oxide (WO<sub>3</sub>) film materials have been receiving attention as visible-light-responsive photoanode materials owing to their relatively small band gap (2.5–2.8 eV) and photoelectrochemical stability in aqueous solutions.<sup>1–5</sup> In a photoelectrochemical system, the nano- and micro-structures of electrode materials significantly affect the device performance. Nanostructures (such as nanoparticles, nanowires, and nanorods) provide a larger surface area, that is, a larger number of active sites for photoelectrochemical reactions, which results in a more effective photo-energy conversion.<sup>2,6–8</sup> In addition, submicron- and micron-scale porous structures are reported to work as light-scattering layers, where the path length of the incident light in the film materials increases, which leads to more effective light absorption.<sup>9–13</sup> Thus, the fabrication techniques of nano- and micro-structures are widely investigated for the practical application of WO<sub>3</sub> materials.

The solution route is an effective synthetic method for nano- and micro-structured inorganic materials, where the size, morphology, crystal phase, and crystallinity of the products are influenced by processing parameters such as the concentration and temperatures of the precursor solutions. Many works have

attempted to prepare novel WO<sub>3</sub> materials using hydrothermal and solvothermal approaches.<sup>5,7,14–18</sup> Hong *et al.* reported that WO<sub>3</sub> nanocrystals could be synthesized by a hydrothermal reaction followed by additional calcination, and the products showed good photocatalytic and photoelectrochemical activities.<sup>14</sup> Zhang *et al.* prepared WO<sub>3</sub> nanotree films by hydrothermal oxidation of W substrates, which exhibited a high coloration efficiency as electrochromic materials.<sup>16</sup> Zheng *et al.* synthesized thin films consisting of WO<sub>3</sub> nanoplates with an exposed (002) plane, where orthorhombic WO<sub>3</sub>·H<sub>2</sub>O nanoplates were prepared as precursors by a hydrothermal method and then converted to monoclinic WO<sub>3</sub> by calcination.<sup>17</sup> Wang *et al.* suggested a 2-step hydrothermal method for making WO<sub>3</sub> nanoplate array films with (002) oriented facets on fluorine-doped tin oxide (FTO) glass substrates, where the WO<sub>3</sub> films exhibited a high electrochemical performance for water splitting.<sup>5</sup> Liu *et al.* prepared a WO<sub>3</sub>–CuS nanosheet heterojunction with enhanced photocatalytic performance by a simple on-step solvothermal method.<sup>18</sup> These studies suggest that solution routes are promising for the fabrication of nanostructured WO<sub>3</sub> materials with enhanced device properties.

Tungsten species are reported to exist as monomeric tungstate ions (WO<sub>4</sub><sup>2–</sup>) or paratungstate ions (HW<sub>6</sub>O<sub>21</sub><sup>5–</sup>, H<sub>2</sub>W<sub>12</sub>O<sub>42</sub><sup>10–</sup>, and so forth) in an aqueous media,<sup>19–23</sup> and such tungstate ions can deposit as various types of hydrous tungsten oxides (WO<sub>3</sub>·*x*H<sub>2</sub>O) and tungstates (H<sub>2</sub>WO<sub>4</sub>, H<sub>4</sub>WO<sub>5</sub> and so forth).<sup>6,8,24,25</sup> Previously, we have reported the preparation of nanostructured WO<sub>3</sub> particle materials, where WO<sub>3</sub>·H<sub>2</sub>O layered platy particles were first obtained as precursors through an aqueous solution process and then thermally converted to

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monoclinic  $\text{WO}_3$ .<sup>26</sup> In this case, the macroscopic layered structures of the precursors remained even after the thermal conversion to  $\text{WO}_3$ . Such synthetic routes through morphology-controlled precursors have also been reported by several groups.<sup>6,17,24</sup> A variation in the chemical composition and crystal phase of  $\text{WO}_3$  precursors would allow us to control the nano- and micro-structures of the resultant  $\text{WO}_3$  materials.

In this work, we address the nano- and micro-structural control of  $\text{WO}_3$  film materials through the control of the crystal phase of the precursor tungsten species by the aqueous solution route. Here, the reaction temperature for the nucleation and growth of tungsten species was set to 50–60 °C, which is milder than hydrothermal techniques, because such mild conditions are considered to be preferable for the phase control of  $\text{WO}_3$  precursors containing metastable phases. First,  $\text{WO}_3$  precursor layers were deposited on glass substrates through heterogeneous nucleation from  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$  aqueous solutions under mild conditions below 60 °C, and then thermally converted to monoclinic  $\text{WO}_3$  materials. Moreover, we evaluate the photoelectrochemical properties of the  $\text{WO}_3$  heat-treated films, and investigate the effect of the nano- and micro-structures on the photoanodic performances.

## Experimental

HCl aqueous solutions at pH 1.0 were prepared by diluting approximately 36.0 mass% hydrochloric acid (Wako Pure Chemical Industries, Osaka, Japan) with purified water.  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$  (0.010–0.50 g, Wako Pure Chemical Industries) was added and dissolved in 20 cm<sup>3</sup> of the HCl solutions under stirring at 80 °C for 3 min ( $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}] (x) = 0.17\text{--}8.5 \text{ mM}$ ). Soda-lime glass (20 mm × 40 mm × 1.0 mm), silica glass (20 mm × 40 mm × 1.0 mm), and fluorine-doped tin oxide (FTO) glass substrates (20 mm × 40 mm × 1.0 mm) were dipped in the  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$  solutions, and then the solutions were aged at 50 or 60 °C for 1–3 days. After the aging, precursor layers were deposited on glass substrates. The precursor layers were washed with purified water and dried at 60 °C for 1 day. The  $\text{WO}_3$  precursor films thus obtained were heated at 600 °C for 1 day in air for the thermal conversion to  $\text{WO}_3$ , where heat treatment was performed at a heating rate of 5 °C min<sup>-1</sup>.

The crystalline phases of the precursor and heat-treated films were identified by X-ray diffraction (XRD) measurements in the ordinary  $2\theta/\theta$  mode using an X-ray diffractometer (Model Rint 2550V, Rigaku, Tokyo, Japan) with  $\text{CuK}\alpha$  radiation operated at 40 kV and 300 mA. The morphologies of the film samples were observed using field emission scanning electron microscopy (FE-SEM) (Model JSM-6500F, JEOL, Tokyo, Japan). Optical transmission spectra were measured on the samples using an optical spectrometer (V-570, JASCO, Tokyo, Japan), where a FTO glass substrate was used as the reference.

The photoanodic properties of the  $\text{WO}_3$  films were evaluated in a three-electrode cell using a potentiostat (HZ-7000, Hokuto Denko, Osaka, Japan) consisting of the film electrode sample, a platinumized Pt electrode, and a saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively, and of a buffer solution of pH 7, which was an

aqueous solution of 0.2 M  $\text{Na}_2\text{B}_4\text{O}_7$ , 0.14 M  $\text{H}_2\text{SO}_4$ , and 0.3 M  $\text{Na}_2\text{SO}_4$ , as the supporting electrolyte.

Action spectra of the films were measured at 1.0 V versus SCE, where a xenon lamp light was monochromatized using a monochromator (SPG-100s, Shimadzu, Kyoto, Japan). The intensity of the monochromatized light was measured using a power meter (NOVA, PD300-UV, Ophir Japan, Saitama, Japan), and was approximately 23 μW at a wavelength of 500 nm. For this measurement, the film was first illuminated for 10 s, and then the light was turned off. The difference in current before and after turning off the light was taken as the photocurrent. Quantum efficiency, that is, the incident photon-to-current efficiency (IPCE), was calculated from the photocurrent and incident light intensity.

## Results and discussion

### Preparation of $\text{WO}_3$ precursor films

$\text{WO}_3$  precursor layers were deposited on soda-lime glass substrates from the  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$  solutions of  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}] (x) = 0.17\text{--}8.5 \text{ mM}$  by aging at 60 °C for 1 day. Fig. 1 shows the appearance of the  $\text{WO}_3$  precursor layers on the soda-lime glass substrates. Yellowish layers formed on the substrates at  $x = 0.17\text{--}1.7 \text{ mM}$ , where the amount of the precursors increased with increasing  $x$  (Fig. 1a and b). The color of the precursor layers changed to white at a higher  $x$  above 4.3 mM (Fig. 1c), where partial cracking was often observed on the surface.

Fig. 2 shows the XRD patterns of the  $\text{WO}_3$  precursor layers prepared at  $x = 0.17\text{--}8.5 \text{ mM}$ . The yellowish precursors obtained below  $x = 1.7 \text{ mM}$  were identified as the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  phase. On the other hand, the increase in the  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$  concentration (*i.e.*, the increase in the amount of  $\text{NH}_4^+$  ions in the solutions) resulted in the formation of the ammonium tungstate phase. The diffraction peaks of the



Fig. 1 Optical micrographs of the  $\text{WO}_3$  precursor layers on soda-lime glass substrates prepared at  $x = 0.17$  (a), 1.7 (b), and 8.5 (c) mM.



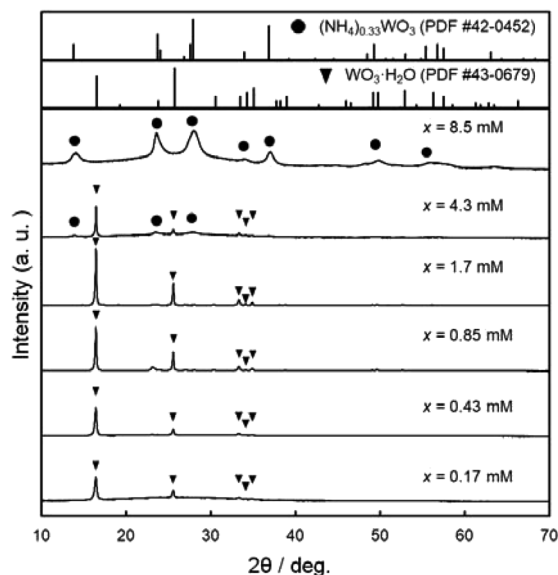


Fig. 2 XRD patterns of the  $\text{WO}_3$  precursor layers on soda-lime glass substrates prepared at  $x = 0.17$ – $8.5$  mM.

$(\text{NH}_4)_{0.33}\text{WO}_3$  phase appeared over  $x = 4.3$  mM, and single-phase  $(\text{NH}_4)_{0.33}\text{WO}_3$  products were obtained at  $x = 8.5$  mM. The paratungstate ion,  $\text{W}_{12}\text{O}_{42}^{10-}$ , changes to monomeric tungstate ions (e.g.,  $\text{WO}_4^{2-}$  and  $\text{HWO}_4^-$ ) or other paratungstate species (e.g.,  $\text{HW}_6\text{O}_{21}^{5-}$  and  $\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$ ) in aqueous solutions depending on the pH value, concentrations, and coexisting ions in the solutions.<sup>19–23</sup> Here,  $\text{W}_{12}\text{O}_{42}^{10-}$  ions were thought to change to  $\text{WO}_4^{2-}$  ions under acidic conditions, and then deposit as the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  phase at lower  $\text{NH}_4^+$  contents and as the  $(\text{NH}_4)_{0.33}\text{WO}_3$  phase at higher  $\text{NH}_4^+$  contents.

Fig. 3 shows the SEM images of the  $\text{WO}_3$  precursor layers prepared at  $x = 0.17$ – $8.5$  mM by aging at  $60^\circ\text{C}$  for 1 day. The morphologies of the precursors drastically varied with the changing crystal phase. Aggregates of platy particles were observed for the yellowish  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers obtained at  $x = 0.17$ – $1.7$  mM (Fig. 3a–f), where the number of platy particles on the substrates increased with increasing  $x$  (Fig. 3a, c and e). Moreover, the size of platy units became larger from approximately  $1\ \mu\text{m}$  to  $7$ – $10\ \mu\text{m}$  with increasing  $x$  from  $0.17$  to  $1.7$  mM (Fig. 3b, d and f). The white  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers prepared at  $x = 8.5$  mM were found to consist of fine particles below  $50$  nm in size (Fig. 3g and h).

### Preparation $\text{WO}_3$ heat-treated films and their photoanodic properties

We attempted to make  $\text{WO}_3$  photoelectrode films from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers consisting of platy particles ( $x = 1.7$  mM) and  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers consisting of fine particles ( $x = 8.5$  mM). In the previous section, the precursor layers were obtained by aging at  $60^\circ\text{C}$  for 1 day, where the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_{0.33}\text{WO}_3$  products each had problems concerning the exposure of the glass substrates, which was undesirable for the electrochemical evaluations. In the case of the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers of  $x = 1.7$  mM, the amount of precursor was not sufficient to cover the glass

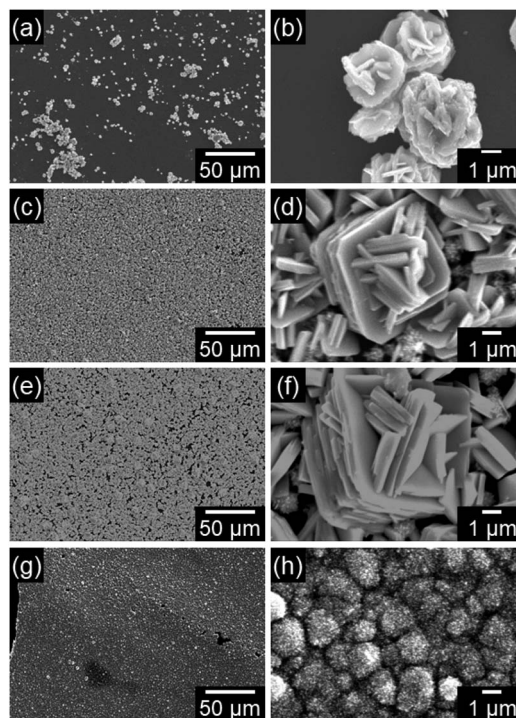


Fig. 3 SEM images of the  $\text{WO}_3$  precursor layers on soda-lime glass substrates prepared at  $x = 0.17$  (a and b),  $0.85$  (c and d),  $1.7$  (e and f), and  $8.5$  (g and h) mM.

substrates, and thus the substrate was partially exposed (Fig. 3a, c and e). The substrate exposure was solved by increasing the aging time to 3 days ( $x = 1.7$  mM, aged at  $60^\circ\text{C}$ ) (ESI, Fig. S1a and b†). On the other hand, the  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers of  $x = 8.5$  mM were often cracked and delaminated owing to the larger amounts of precursors. Low-temperature aging at  $50^\circ\text{C}$  ( $x = 8.5$  mM, aged for 1 day) reduced the deposition amount of the  $(\text{NH}_4)_{0.33}\text{WO}_3$  precursor, which resulted in the suppression of cracking (ESI, Fig. S1c and d†). These  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers with no substrate exposure were used to make the  $\text{WO}_3$  heat-treated films.

$\text{WO}_3$  heat-treated films were prepared from the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers consisting of platy particles ( $x = 1.7$  mM, aged at  $60^\circ\text{C}$  for 3 days) and the  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers consisting of fine particles ( $x = 8.5$  mM, aged at  $50^\circ\text{C}$  for 1 day). The precursors were deposited on silica glass substrates, and then thermally converted to  $\text{WO}_3$  films by heating at  $600^\circ\text{C}$  for 1 day. Fig. 4 shows the XRD patterns of the  $\text{WO}_3$  precursors and heat-treated films on silica glass substrates. The diffraction patterns attributed to the monoclinic  $\text{WO}_3$  phase were detected for the heat-treated products.

Fig. 5 shows the micrographs and SEM images of the  $\text{WO}_3$  heat-treated films on silica glass substrates. The heat-treated films were cloudy and the film color became light yellow after the heat treatment (Fig. 5a and c). Crack-free films were obtained from the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers (Fig. 5a), while cracking and delamination were occasionally observed for the  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers after heating (Fig. 5c). The nano- and micro-structures of the precursors remained even after the thermal conversion to



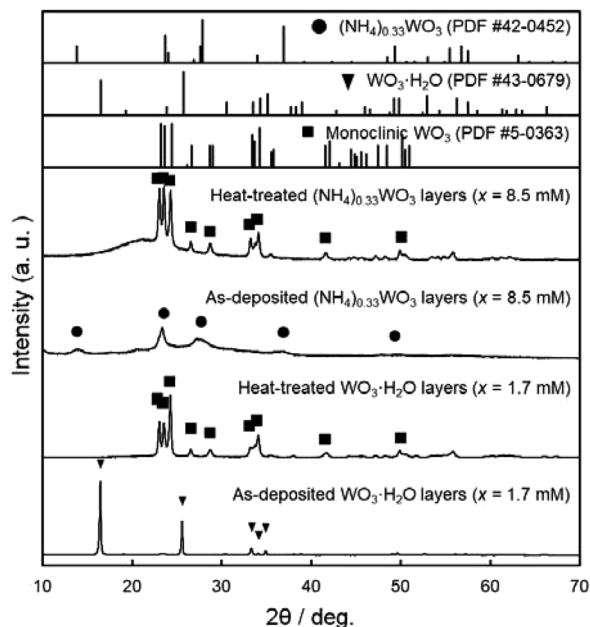


Fig. 4 XRD patterns of the  $\text{WO}_3$  precursor layers and heat-treated films prepared on silica glass substrates at  $x = 0.17$  mM (aged at  $60^\circ\text{C}$  for 3 days) and  $8.5$  mM (aged at  $50^\circ\text{C}$  for 1 day).

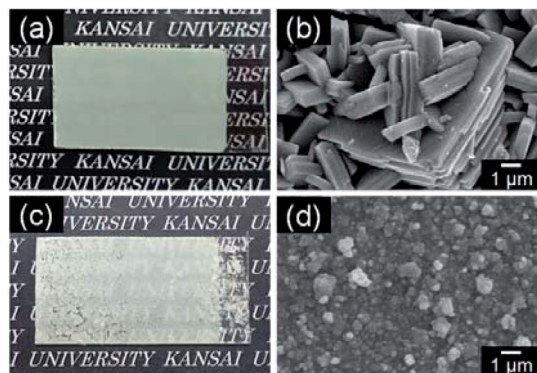


Fig. 5 Optical micrographs (a and c) and SEM images (b and d) of the  $\text{WO}_3$  heat-treated films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  (a and b) and  $(\text{NH}_4)_{0.33}\text{WO}_3$  (c and d) precursor layers on silica glass substrates.

the monoclinic  $\text{WO}_3$  phase (Fig. 5b and d). Platy particles of approximately  $10\ \mu\text{m}$  were observed for the  $\text{WO}_3$  heat-treated films prepared from the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers (Fig. 5b). Previously, we have reported the topotactic transformation of  $\text{WO}_3 \cdot \text{H}_2\text{O}$  plates to  $\text{WO}_3$  platy particles by heating, where the flat face of  $\text{WO}_3$  plates was the (001) plane of monoclinic  $\text{WO}_3$ .<sup>26</sup> Thus, in the present work, the flat face of the platy particles observed on the substrates was deduced to be the (001) plane of monoclinic  $\text{WO}_3$ , as well as the previous one. On the other hand, porous films consisting of fine particles were obtained from the  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers (Fig. 5d). The cross-section SEM images of the  $\text{WO}_3$  heat-treated films are shown in Fig. 6. The thickness of the heat-treated films obtained from the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and

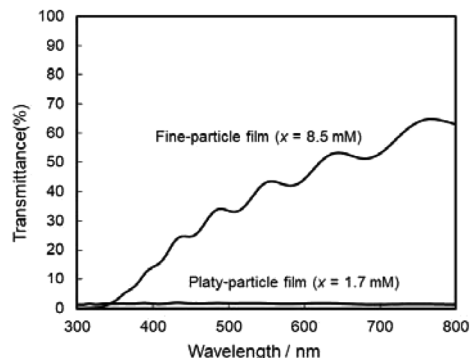


Fig. 6 Cross-section SEM images of the  $\text{WO}_3$  heat-treated films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  (a) and  $(\text{NH}_4)_{0.33}\text{WO}_3$  (b) precursor layers on silica glass substrates.

$(\text{NH}_4)_{0.33}\text{WO}_3$  layers was approximately  $4.3$  (Fig. 6a) and approximately  $2.6\ \mu\text{m}$  (Fig. 6b), respectively.

The photoanodic properties were evaluated for the  $\text{WO}_3$  heat-treated films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  (platy particles) and  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers (fine particles), where the heat-treated films were prepared on FTO glass substrates. We checked that the change of substrates from silica glass to FTO glass didn't affect the crystal phases and morphologies of the products. Fig. 7 shows the optical transmission spectra of the  $\text{WO}_3$  heat-treated films on FTO glass substrates. As shown in Fig. 5, the  $\text{WO}_3$  heat-treated films were cloudy (Fig. 5a and c), which was attributed to the light scattering by the submicron- and micron-scale particles and aggregates in the film layers. From the optical transmittance analysis, the heat-treated films actually exhibited a low transparency in the visible range of  $300\text{--}800\ \text{nm}$ , even though  $\text{WO}_3$  materials absorb UV and visible light at wavelengths below  $470\ \text{nm}$ . Especially, a very low transmittance (almost 0%) was detected in the entire visible range for the platy-particle  $\text{WO}_3$  films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers. On the other hand, in the case of the fine-particle  $\text{WO}_3$  films obtained from  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers, the transmittance slightly increased with increasing wavelength from  $350\ \text{nm}$ . The low transparency of the platy-particle films was thought to result from the enhanced light

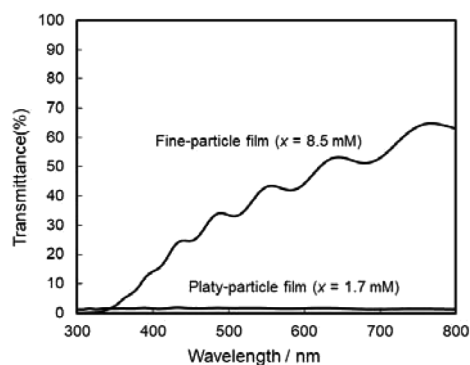


Fig. 7 Optical transmission spectra of the  $\text{WO}_3$  heat-treated films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_{0.33}\text{WO}_3$  precursor layers on FTO glass substrates.



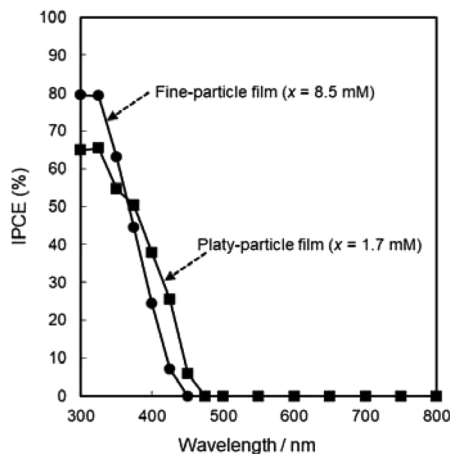


Fig. 8 Action spectra of the  $\text{WO}_3$  heat-treated films obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_{0.33}\text{WO}_3$  precursor layers on FTO glass substrates.

scattering owing to the larger micron-scale platy particles. Fig. 8 shows the action spectra of the  $\text{WO}_3$  heat-treated films, which were measured at a working electrode potential of 1.0 V *versus* SCE. The photocurrent under monochromatized light was detected at wavelengths below 450 nm, which agreed with the photoabsorption of  $\text{WO}_3$  materials (band gap energy of  $\text{WO}_3$  is 2.5–2.8 eV). In the UV range below 350 nm, the IPCE value of the fine-particle films was higher than that of the platy-particle films. Because the photoelectrochemical reactions occur on the surface of the electrode materials, the larger surface area, arising from the porous structure consisting of fine particles, would result in a more efficient energy conversion. On the other hand, at wavelengths over 375 nm, the platy-particle films exhibited higher IPCE than the fine-particle films. As shown in Fig. 7, the platy-particle films showed strong light scattering in the visible range. Such light scattering has been reported to elongate the light path length in film layers, which enhances the light utilization efficiency.<sup>9–13</sup> Here, the micron-scale platy particles obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers could act as a light-scattering layer, which results in the more effective photo-energy conversion in the visible range.

## Conclusions

We achieved the morphological control of  $\text{WO}_3$  film materials by an aqueous solution process.  $\text{WO}_3 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers were prepared on glass substrates through heterogeneous nucleation from  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$  aqueous solutions, and then thermally converted to monoclinic  $\text{WO}_3$  films. The variation in the crystal phase of the precursors led to the morphological change of the resultant  $\text{WO}_3$  films. Micron-scale platy-particle films were obtained from  $\text{WO}_3 \cdot \text{H}_2\text{O}$  layers, while  $(\text{NH}_4)_{0.33}\text{WO}_3$  layers provided nano-scale fine-particle films. The larger surface area of the fine-particle films resulted in a better photoanodic response in the UV range below 350 nm. On the other hand, the micron-scale platy particles exhibited strong light scattering in the visible range, which elongated the light path length in the film layers, leading to the improvement of the

light utilization efficiency at wavelengths over 375 nm. We propose that the morphological control techniques of  $\text{WO}_3$  film materials through the aqueous solution route and the photo-electrochemical properties depending on the nano- and micro-structures are useful for the development of high-efficiency solar cell devices.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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