Supplementary Information

Fabrication of (001)-oriented monoclinic WO_3 films on FTO substrates

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1. Experimental details

1.1 Materials

$Na_2WO_4•2H_2O$ (SamChun Chemical, ≥ 98%), citric acid (Sigma-Aldrich, 99.5+%), oxalic acid dehydrate (Junsei, ≥ 95.5%), tungstic acid (Aldrich, ≥ 99.0%), poly(vinyl alcohol) (PVA) (Aldrich, 99+%), H_2O_2 (Junsei, 35%), PEI (polyethylenimine) (Aldrich, M_w 25000), HCl (DaeJung Chemical, ≥ 35%), Ethanol (Aldrich, 99.9%) were used without further purification. The commercial fluorine-doped tin oxide (FTO) coated glasses (Pilkington FTO glass (TEC 8), 6~9 ohm/sq) (2 cm × 2 cm) were cleaned with ethanol, acetone and deionized water in sonication bath (Hwashin, Powersonic 410) each for 20 min and dried for using.

1.2 Preparation of the spin-coating seed layer (SSL)

The spin-coating WO_3 seed layer on FTO coated glass was made by spin coating (1500 rpm for 20 sec) a solution which was made by dissolving 1.25 g H_2WO_4 and 0.5 g poly(vinyl alcohol) (PVA) in 10 mL 35 wt% H_2O_2 on FTO glass, followed by annealing at 500 ^oC for 2 h in air for the subsequent hydrothermal reaction.[1]

1.3 Preparation of the rubbing seed layer (RSL)

1.3.1 Synthesis of $WO_3•H_2O$ nanoplates powder for rubbing

The experimental process was carried out as following: 1 g of $Na_2WO_4•2H_2O$ was dissolved in 50 ml of water, then 0.9 ml of 50% L-lactic acid solution was added and continuely stirred until completely dissolved. The pH of the solution was adjusted to 1.0 by using 6 mol/L HCl aqueous solution. The white gel type precursor was formed and transferred into a teflon-lined stainless steel autoclave (inner volume is about 66 ml). The autoclave was tightly sealed and put in oven for reaction at 120 ^oC for 24 h. Yellow powder type product was obtained after three times washing with deionized water and ethanol by centrifuge and drying at 60 ^oC for longer than 6 h.

1.3.2 Prepararion of RSL

A 2% PEI ethanol solution was first spin coated (2000 rpm for 20 seconds) on clean FTO surface to produce a sticky ultra thin film. Then, the as-synthesized $WO_3•H_2O$ nanoplate powder was carefully grinding into very thin powder and rubbed on PEI layer by finger.[2] Finally, the requisite calcination process was done at 500 ^oC for 2 h in air to remove the organic layer and make the WO_3 tightly connected on to FTO surface. The rubbing process is a high human operability required work. It should

also be mentioned that, the spin coating speed and time should be carefully adjusted to produce the uniform and suitable thickness PEI layer. If the layer is too thick, the amount of powder attached on the surface will be too much, then some of them maybe vertically aligned thus destroy the one axis oriented property. Otherwise, if the layer is too thin, some parts of the film maybe fail to attach the powder which will also decrease the electrochemical property of the film.

1.4 (001) highly oriented monoclinic WO_3 nanorods fabricated on RSL

0.125 g of tungstic acid and 0.96 g of citric acid were added into 50 ml deionized water and stirred more than two days until the solution became homogeneous. Transferred the homogeneous solution into autoclave and adjusted the pH of the solution into 1.5 by using 6 mol/L HCl. The RSL-coated FTO substrate was put into autoclave vertically on a teflon holder. Sealed the autoclave and started the hydrothermal reaction at 180 ^{o}C for 24 h. After finished the reaction, took the film sample out and washed three times with deionized water, ethanol and acetone and dried in air at 60 ^{o}C.

1.5 monoclinic WO_3 nanorods fabricated on SSL with different pHs of the reaction solution

0.125 g of tungstic acid and 0.96 g of citric acid were added into 50 ml deionized water and continues stirs more than two days until the solution became homogeneous. Transferred the homogeneous solution (initial pH 1.9) into autoclave and adjusted the pH of the solution into 2.3 and 2.5 by using 0.5 mol/L NaOH. The SSL-coated FTO substrate was put into autoclave vertically on a teflon holder. Sealed the autoclave and started the hydrothermal reaction at 180 ^{o}C for 12 h. After finished the reaction, took the film sample out and washed three times with deionized water, ethanol and acetone and dried in air at 60 ^{o}C.

1.6 (001)-oriented monoclinic WO_3 microplate fabricated on SSL

0.1 g of tungstic acid and 0.7 g of oxalic acid was added into 50 ml deionized water and followed a continuously stirring for more than two days to make a homogeneous and transparent solution. Then the precursor with pH 1.5 (adjusted by 6 M HCl) and a piece of SSL-coated FTO glass were both transferred into autoclave. The SSL-coated FTO glass was kept vertically on a teflon holder. The hydrothermal process was done at 180 ^{o}C for 24 h. Finally the film sample was washed three times with deionized water, ethanol and acetone and dried in air at 60 ^{o}C.

2. Characterization

X-ray diffraction (XRD, Rigaku miniFlex-II desktop, Cu-Kα radiation with λ = 0.154056 nm) patterns, high resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED, JEOL JEM-2100 F) pattern were used to check crystallinity and crystal structure of the nanoplate powder sample. Surface and cross-sectional morphologies of the films were obtained using a Hitachi Horiba S-4300 scanning electron microscope (SEM) operated at 20 kV. Photo electrochemical measurements were conducted with potentiostat PL-9 in a conventional three-electrode cell in a V-style with quartz window cell at room temperature under chopped (1 Hz: light on and off) 1 sun (Asahi HAL-320 sun simulator) illumination, employing a coiled Pt wire and an Ag/AgCl electrode as counter and reference electrode, respectively. Photocurrent-potential was measured using linear sweep voltammogram from -0.2 V to 1.0 V at a scan rate of 10 mV/s. Cyclic voltammetry (CV) was also measured in the same system, potential area was chose from 0.4 V to -0.8 V at a scan rate of 50 mV/s. 0.5 M Na_2SO_4 (pH ≈ 6.3) was used as electrolyte solution in all photoelectrochemical and electrochemical properties checking.

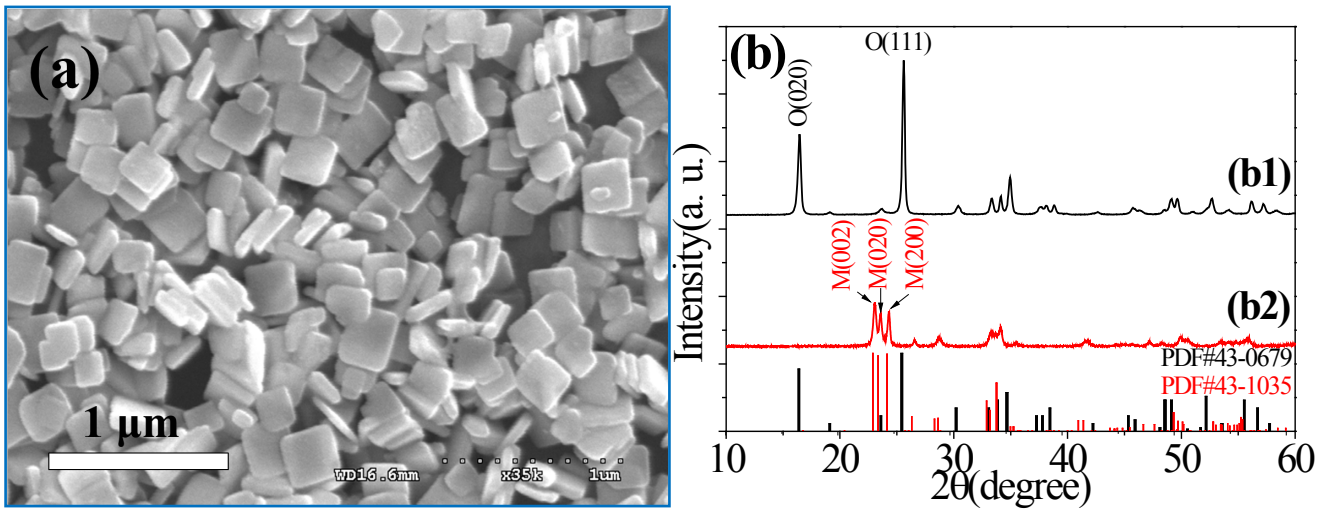

Fig. S1 (a) SEM pictures of $WO_3 \cdot H_2O$ nanoplate powder sample. (b) XRD patterns of as-synthesized $WO_3 \cdot H_2O$ nanoplate powder (b1) brfore and (b2) after calcination at 500 ^oC for 2 h in air. O: orthorhombic phase $WO_3 \cdot H_2O$ (JCPDS no. 43-0679); M: monoclinic phase WO_3 (JCPDS no. 43-1035).

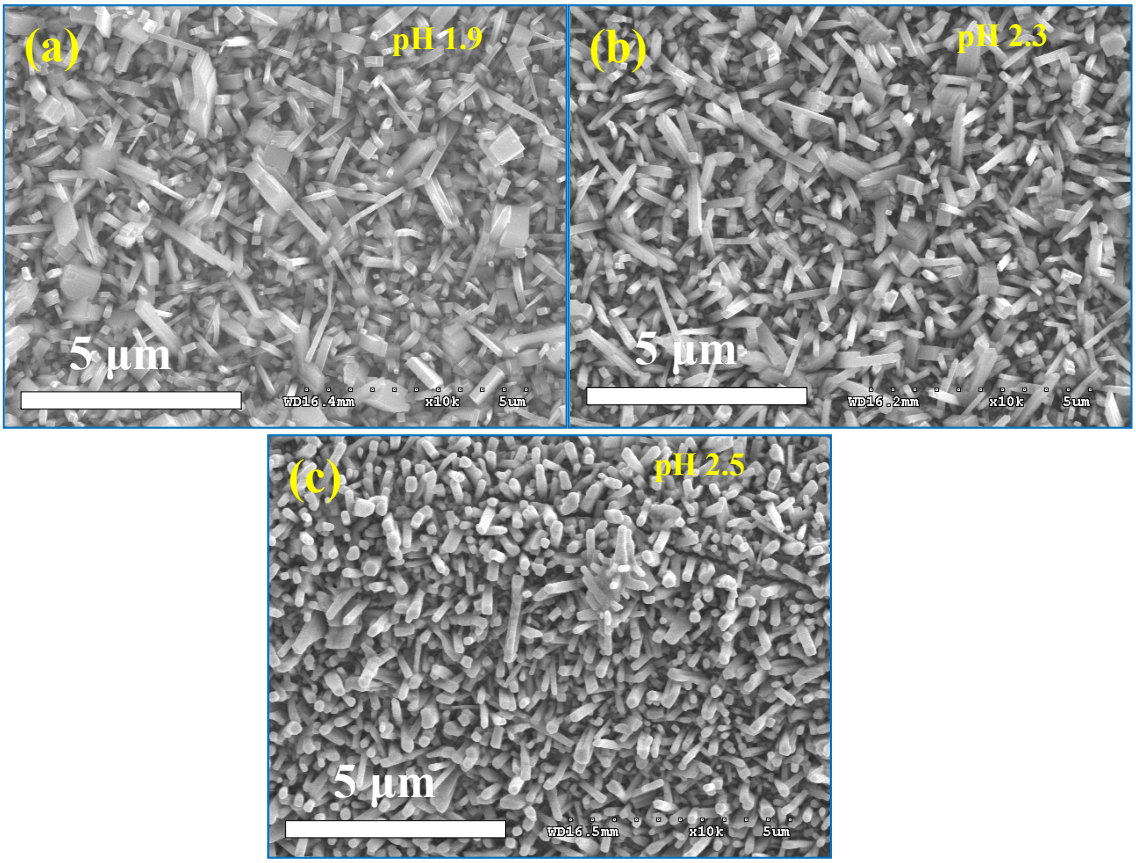

Fig. S2 Low magnification SEM images of WO_3 films synthesized by the spin-coated seed layer assisted by a hydrothermal method at 180 ^{o}C for 12 h using 0.1 mol citric acid as a capping agent at different pH values. (a) pH 1.9, (b) pH 2.3, (c) pH 2.5.

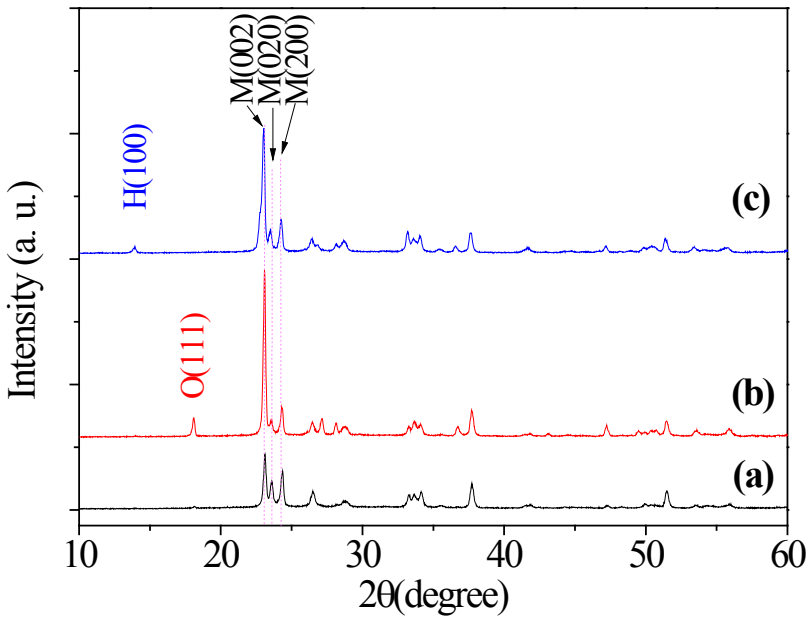

Fig. S3 XRD patterns of WO_3 films synthesized by the spin-coating seed layer assisted by a hydrothermal method at 180 ^oC for 24 h using 0.1 mol oxalic acid as a capping agent at (a) pH 1.0 and (b) pH 1.5 (Figure 4(c)); (c) XRD pattern of the WO_3 film obtained at pH 1.5 after annealing at 500 ^oC for 2 h in air. (M: monoclinic WO_3; O: orthorhombic WO_3•$0.33H_2O$; H: hexagonal WO_3)

At pH 1.0, the obtained WO_3 film was monoclinic crystal phase (JCPDS no.43-1035); no clear orthorhombic WO_3•$0.33H_2O$ peak at 18.09^o (in (b) pattern) can be observed in the XRD pattern as shown in (a). At pH 1.5, the orthorhombic WO_3•$0.33H_2O$ crystal phase (JCPDS no. 72-0199) appeared; after annealing at 500 ^oC for 2 h in air, the orthorhombic phase was transferred to hexagonal WO_3 crystal phase (JCPDS no. 33-1387) as Su *et al*.[3] reported. However, in our work, the intensity of the typical peak at 13.9^o was very low; in addition, considering the three main peaks of monoclinic at 23.1^o, 23.6^o and 24.3^o, corresponding to (002) , (020) and (200) crystal facets respectively, were almost not changed. Therefore, we can get a conclusion that the orthorhombic WO_3•$0.33H_2O$ crystal phase in the film obtained at pH 1.5 is very less and main phase is monoclinic. The HR-TEM image in Fig S4 (a) also give an additional evidence. The film obtained at pH 1.5 can be regarded as monoclinic WO_3.

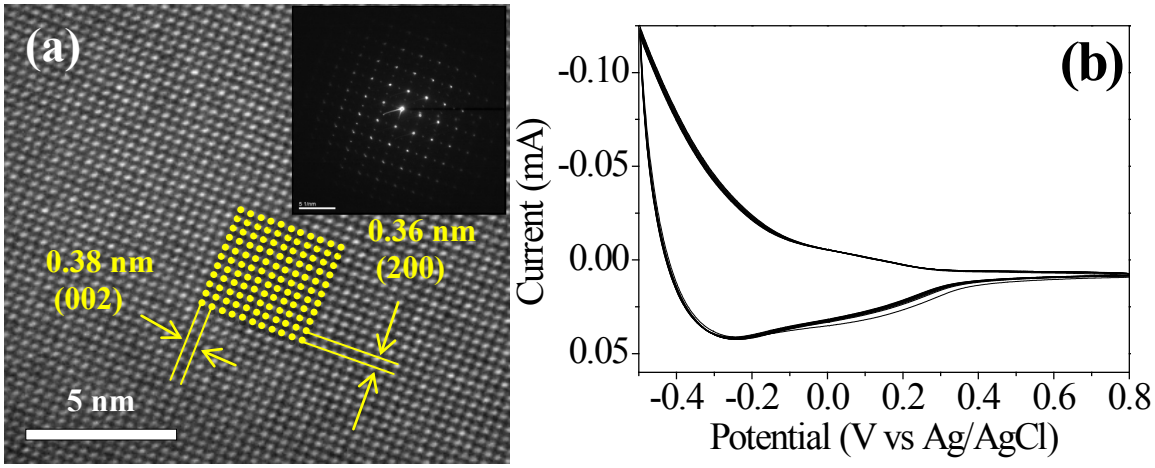

Fig S4 (a) HR-TEM with SEAD pattern and (b) 10 CV curves of WO_3 films synthesized by the spin-coated seed layer assisted by a hydrothermal method at 180 ^{o}C for 24 h using 0.1 mol oxalic acid as a capping agent at pH 1.5.

References

[1] J. Su, X. Feng, J. D. Sloppy, L. Guo and C. A. Grimes, *Nano Lett*., 2011, **11**, 203.

[2] J. S. Lee, J. H. Kim, Y. J. Lee, N. C. Jeong and K. B. Yoon, *Angew. Chem. Int. Ed*., 2007, **46**, 3087.

[3] J. Su, L. Guo, N. Bao and C. A. Grimes, *Nano Lett*., 2011, **11**, 1928.