Morphology-Tailored Synthesis of Tungsten Trioxide (Hydrate) Thin Films and Their Photocatalytic Properties

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Supporting Information

ABSTRACT: Tungsten trioxide hydrate (3WO3·H2O) films with different morphologies were directly grown on fluorine doped tin oxide (FTO) substrate via a facile crystal-seed-assisted hydrothermal method. Scanning electron microscopy (SEM) analysis showed that 3WO3·H2O thin films composed of platelike, wedge-like, and sheetlike nanostructures could be selectively synthesized by adding Na2SO4, (NH4)2SO4, and CH3COONH4 as capping agents, respectively. X-ray diffraction (XRD) studies indicated that these films were of orthorhombic structure. The as-prepared thin films after dehydration showed obvious photocatalytic activities. The best film grown using CH3COONH4 as a capping agent generated anodic photocurrents of 1.16 mA/cm2 for oxidation of methanol and 0.5 mA/cm2 for water splitting with the highest photoconversion efficiency of about 0.3% under simulated solar illumination.

KEYWORDS: tungsten trioxide, hydrothermal, capping agent, photocatalyst, water splitting

1. INTRODUCTION

Assembly of functional nanoscale building blocks in thin film form for example with large surface area and desired morphologies is an important prerequisite for large scale electronic and optoelectronic applications with improved performance.1–3 Thin film tungsten trioxide (WO3) has attracted great interests due to its wide-ranging applications in a variety of technologies including electrochromic devices, gas sensors, photoelectrochemical devices, and dye-sensitized solar cells.4–9 As one of few n-type semiconductors, WO3 has also been considered to be an interesting photocatalytic material, due to its high resistance against photocorrosion, good stability in acidic solution (below ca. pH 4) and a suitable band gap for visible light absorption (∼2.6 eV).8,10

Thus far, thin films of WO3 have been grown by various techniques including physical vapor deposition (thermal evaporation and sputtering),11,12 and chemical methods (sol–gel and hydrothermal approach).13–17 Hydrothermal approach stands out to be a very promising route featuring low reaction temperature, flexible substrate selection and easiness for scaling-up. A number of hydrothermal methods have been used for the preparation of 1D WO3 nanostructures with various characteristic sizes and morphologies by adding different kinds of inorganic salts or surfactants.18–21

Some of the nanostructures with large surface area are assembled into thin film on conductive substrate, showing promising photocatalytic characteristics. For example, Hong investigated the size effect of hydrothermally grown WO3 nanoparticles for photooxidation of water and achieved a maximum photocurrent density of 0.6 mA/cm2 for the sample calcined at 600 °C.21 Although the photocatalytic characteristics of hydrothermally grown WO3 nanostructures have been reported, there have been few works focusing on photocatalytic behavior of hydrothermally grown WO3 films.22 Moreover, to directly grow WO3 thin film with controllable morphology and good adhesion on substrates using the hydrothermal methods is much harder to realize.

Herein, we report a simple hydrothermal approach to realize the morphology-controllable synthesis of tungsten oxide hydrate (3WO3·H2O) thin film on FTO glasses. Under the assistance of seed layers, 3WO3·H2O thin films composed of platelike, wedge-like, and sheetlike nanostructures could be selectively prepared by adding Na2SO4, (NH4)2SO4 and CH3COONH4 as capping agents.

Received: September 14, 2010
Accepted: December 8, 2010
Published: January 10, 2011
2. EXPERIMENTAL SECTION

2.1. Preparation of Crystal Seeds. One gram of Na2WO4·2H2O was dissolved into 15 mL of deionized water and then HCl was added until no more precipitate was formed. The precipitate was washed using deionized water in ice bath for 6 times to obtain 50 mL of precipitate-containing suspension. Then, 0.9 g of oxalic acid was added into the suspension under intense stir at ~50 °C. The precipitate was dissolved and the suspension was changed to transparent sol which was used as WO3 seed precursor. The pH of the above precursor was 1.7.

2.2. Preparation of Substrates. The as-prepared transparent WO3 seed precursor was spun coated onto FTO glasses which were ultrasonic cleaned beforehand by acetone, isopropanol, ethanol, and deionized water in sequence. The spin coating processes were performed at 3000 rpm for 30 s and repeated for 4 times, during each process the coated substrates were heated at 300 °C for ~10 min. All the substrates were then heated to 400 °C in atmosphere for 40 min.

2.3. Preparation of Precursors and Hydrothermal Syntheses. Na2WO4·2H2O (0.0655 g) was dissolved into 20 mL of deionized water and then ~4 mL of HCl was added into the solution until no more precipitate was formed. The above suspension was kept in an ice bath for 10 min and then the upper liquid was removed. Deionized water was added into it to obtain a final 20 mL suspension. Then 0.14 g of oxalic acid was added into the above suspension under intensely stir at ~50 °C. After the solution was stirred for 5 min, 0.04 g of capping agent Na2SO4 was added. For the cases using other capping agents, 0.04 g of (NH4)2SO4 or 0.1 g of CH3COONH4 was used as WO3 seed precursor. The pH of the above precursor was 1.7.

2.4. Characterizations. The crystal structure of the products was identified by X-ray powder diffraction (XRD, Siemens) using Cu Kα1 radiation (λ = 0.15406 nm) at 30°/min. X-ray diffraction intensity, indicating selective orientation of (222) planes parallel to the substrate. The various selective orientations can be attributed to the different capping effect of salts in the condensation and polymerization of WO6 octahedral clusters.

Figure 1. Schematic illustration of the film fabrication process.

Figure 2. XRD patterns of the as-synthesized thin films prepared (a) without any salt added, (b) with Na2SO4, (c) with (NH4)2SO4, and (d) with CH3COONH4 added.

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where D is the average crystalline size, β is the corrected broadening (full width at half-maximum), K is a constant taken as 0.89 here, λ is the wavelength of the X-ray radiation (Cu Kα1 = 0.15406 nm), and θ is the diffraction angle. The average crystalline size for nanostructures of 3WO3·H2O films synthesized without capping salt is estimated at 24.0 nm. The sizes of nanostructures for adding Na2SO4, (NH4)2SO4, and CH3COONH4 are 21.4, 27.3, and 24.5 nm, respectively. However, the diffraction patterns of these films show some differences in the intensities. The films grown with Na2SO4 or CH3COONH4 show a highest peak intensity of (220), suggesting that most of the (220) planes are parallel to the substrate. In the patterns of the films grown without salt or with (NH4)2SO4 a peak attributable to the (222) diffraction exhibits high intensity, indicating selective orientation of (222) planes parallel to the substrate. The various selective orientations can be attributed to the different capping effect of salts in the condensation and polymerization of WO6 octahedral clusters.
According to previous reports,19 1D WO3 nanostructures could be controllably synthesized by addition of sulfate as the capping agent by a hydrothermal approach. Inspired by these results, morphology-controllable synthesis of WO3 film may be realized by adding sulfate or other capping agents into the precursor to direct the nanostructures’ growth. Hence Na2SO4 was introduced in our synthesis. Morphologies of the as-synthesized film are shown in Figure 3. It can be seen that a film consisting of platelike nanostructure is assembled on the surface of FTO (Figure 3a and b). These nanoplates with clear crystal facets gathered together and a lot of pores were formed among these accumulated nanoplates, leading to a coarse surface. Cross-sectional image of the film (Figure 3c) shows its thickness is about 2 μm, and the as-synthesized film has a good adhesion to the substrate. Figure 3d shows the HRTEM image of a single nanoplate. Clear lattice fringes corresponding to the (220) plane of the substrate. Figure 3d shows the HRTEM image of a single nanoplate.

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To investigate the influence of the seed layer on the morphology of as-synthesized film, bare FTO substrate without any seed layer was compared. It can be seen that flower-like particles spreading on the surface of FTO with diameter of ~8–10 μm and height of ~2–4 μm were synthesized (Figure 4a,b). Some particles are not completely developed which may due to the randomness of self-assembly process. The higher-magnification image of a single particle (Figure 4b) shows that the center of particle is made up of lamina layers and many small nanoplates grow along the center. From this result, we can get a conclusion that the seed layer does play a key role in assembling the 3WO3·H2O thin film and offers the nucleation and growing sites for the film. These flower-like particles can be easily removed from the substrate. However, the film grown with seed layers shows good adhesion to the substrate, which further verifies the crucial impact of seed layer on assembling of the 3WO3·H2O film.

For comparison, precursor solution without any salt (with seed layer and other conditions remain the same as in Figure 3) was compared as well. It can be seen from images c and d in Figure 4 that dense thin film made up of irregular particles with different sizes was prepared, which is quite different from those films grew using capping salts. Hence, the morphologies of nanostructures are determined by the capping agents, similar to the hydrothermally grown 1D WO3 nanostructures grown with capping agent.15,18,19

To further investigate the influence of cations on the morphology of the as-synthesized thin film, we added (NH4)2SO4 into the precursor instead of Na2SO4. Figure 5a shows the top-view images of the resultant film. It can be seen that a film composed of uniform wedge-like nanostructures was synthesized. These wedge-like nanostructures with size of ~2 μm gathered together and a lot of pores can be obviously observed among them. These pores are formed due to the accumulation of the nanowedges. It is obvious that the obtained nanostructures grown with (NH4)2SO4 have sharp edges and smaller characteristic size compared with the nanostructures grown with Na2SO4. The cross-sectional image (inset of Figure 5a) shows that the thickness of the as-prepared film is ~2 μm. The HRTEM image of the edge of a single "wedge" in Figure 5b shows its crystal lattices of 0.38 nm corresponding to the d-spacing of (002) planes. Clear lattice fringes indicate its single-crystal quality. The inset of Figure 5b depicts the SAED image of the single "wedge". Regular diffraction spots also prove the wedge is single-crystalline.

The above result indicates that besides sodium ions, ammonium ions also has some effect in directing the crystal growth of 3WO3·H2O nanostructures and determining the final morphologies of the as-synthesized films. Up to now, controllable synthesis of WO3 nanostructures has been achieved by adding...
various salts as capping agents, such as RbSO$_4$, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$ and NaCl.$^{15,18}$ However, to the best of our knowledge, acetate is rarely reported. As acetate has been widely used for ZnO nanostructure synthesis,$^{23}$ we studied the influence of CH$_3$COONH$_4$ as a capping agent on the as-synthesized film. SEM images of the as-obtained film are shown in images a and b in Figure 6. It can be seen that the thin film consists of sheet-like nanostructures. The "nanosheet" with a thickness of ∼50 nm grew disorderly on the substrate, forming a quite rough surface. It can be further seen from the higher magnification (Figure 6b) that some edges of the nanosheets are not smooth, showing a zigzag shape. Numerous pores are existed among these nanosheets. These nanostructures should be more beneficial for accelerating the interface electron kinetics between the sheet and electrolyte for its larger active surface area. Figure 6c shows the TEM image of a nanosheet and its ragged edge can be clearly discerned. The inset of Figure 6c shows the SAED pattern of the nanosheet and its single-crystal quality could be proved by the regular diffraction spots. Clear lattice fringes correspond to the d-spacing of (002) planes with lattice spacing of 0.38 nm, which was taken from the corner area of the nanosheet (the inset of Figure 6d) are shown in Figure 6d, further indicating its single-crystal quality, which is in good agreement with Figure 6c. The above results indicate that acetate do have a capping effect on the crystal growth of 3WO$_3$·3H$_2$O nanostructures. Moreover, it can be seen that the HRTEM image and SAED pattern of the selected area from the film grown with CH$_3$COONH$_4$ is quite similar to that grown with (NH$_4$)$_2$SO$_4$ due to their same crystalline structure (orthorhombic phase of 3WO$_3$·H$_2$O). And the similar HRTEM images and SAED patterns imply that the as-synthesized nanostructures with (NH$_4$)$_2$SO$_4$ and CH$_3$COONH$_4$ may have the same growth direction. However, it can be seen that the morphologies, sizes, and thickness of the nanostructures synthesized using different salts are different (Figure 5 and 6); moreover, the arrangement of these different nanostructures in the grown films are also different. These factors significantly affect the intensities of diffraction peaks of the films.
With the increase in $H^+$ concentration, the intermediate $H_2WO_4$ shows high condensation polymerization tendency where two hydroxyl ligands combine to eliminate water and form a shared oxygen bond between the two tungsten centers. Further addition of acid will result in the formation of dihydroxy ligands $W^-$ ($\text{OH}_2^-$) by progressively hydrated tungsten oxo ligands ($W=O$). After further condensation and increase in the cross-linking degree of these ligands, a final three-dimensional octahedral $WO_6$ structure in which tungsten centers are cross-linked to adjacent tungsten centers via four or six shared oxygen bonds, forming structures similar to those found in polyoxo-tungstates.\textsuperscript{17,24} Then the oxalic acid is added into the complex coordination system and a transparent colloidal is obtained. It is believed that the oxalic acid will tailor the long coordination complex through hydroxyl groups, since the colloidal particle size is largely dependent on the concentration of oxalic acid.\textsuperscript{27} Finally, induced by various salts, these short coordinated clusters undergo further condensation and polymerization by hydrothermal reactions under elevated temperature and high pressure, forming platelike, wedgelike, and sheetlike nanostructures on the surface of seed-layer-coated substrate. The seeds coated on substrate act as nucleation and growth sites. The whole process in detail is schematically illustrated in the Supporting Information, Figure S4.

$WO_3$ is an n-type semiconductor with a band gap $\sim 2.6$ eV, which can utilize $\sim 12\%$ of solar spectrum.\textsuperscript{28} Moreover, it shows a high stability in acid bath. These advantages make it a promising candidate in photocatalytic degradation of organic compounds and water splitting to produce hydrogen.\textsuperscript{7,8,29} To investigate their photocatalytic performances, all the films were calcined in atmosphere at 500 °C for 30 min. As previously reported,\textsuperscript{15} WO$_3$ film prepared by a sol–gel method shows the highest photocatalytic activity after being calcined at 500 °C. The crystal structure evolution as a function of temperature is also investigated on the film synthesized with $\text{Na}_2\text{SO}_4$ as capping agent. It can be seen from Figure 7 that there is no obvious differences in the diffraction pattern of as-prepared film for a calcination temperature up to 300 °C. Because of the dehydration, some peaks’ relative intensities get changed. After calcination at 400 °C, the XRD pattern gets obviously changed, showing some characteristic diffraction peaks of monoclinic $WO_3$ (PDF 24–0747). It is believed that this is a mixture of both orthorhombic and monoclinic structure. For calcination temperature of 500 °C, the structure changes to monoclinic $WO_3$ (JCPDF 24–0747) with lattice constants of $a = 7.297$ Å, $b = 7.539$ Å, and $c = 7.688$ Å (see the Supporting Information, Figure S3). Our experiment results show that the other two films prepared using $(\text{NH}_4)_2\text{SO}_4$ and $\text{CH}_3\text{COONH}_4$ as capping agents follow the same crystal structure change after calcination.

Figure 8 shows the UV–vis absorption spectra of the films after calcination. It can be seen that all the films show high UV light absorption. Moreover, the absorption band edge for films prepared with $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4$ as capping agents show obviously red shifts. The broadened light absorption is much desired for photocatalytic applications, because more photo excited electrons will be generated contributing a higher photocatalytic efficiency.

To investigate the photocatalytic properties of as-prepared films, the photocurrent densities were measured in a 1 M $H_2SO_4$ solution containing $0.1$ M methanol under illumination ($100$ mW/cm$^2$)
(Figure 9). It can be seen that the current densities in dark are small (typically <100 μA/cm²) for all calcined films in the effective range of applied potentials. Compared to the film synthesized without capping agent (0.40 mA/cm²), the photocurrent densities of the films with Na₂SO₄, (NH₄)₂SO₄, and CH₃COONH₄ capping agents show an obviously increase of 112, 140, and 180% to 0.85, 0.96, and 1.12 mA/cm² at 1.4 V vs Ag/AgCl, respectively. The photocatalytic performances of the films are in good agreement with the optical absorption. Moreover, the open-circuit voltages (Vₜₕₜₜ) are negatively shifted from 0.42 V of the one without salt to 0.31, 0.29, and 0.32 V for WO₃ films obtained with Na₂SO₄, (NH₄)₂SO₄, and CH₃COONH₄ capping agents, respectively, which are attributed to the numerous pores existing among the nanostructures assembled in films that could increase the interface between the photoanode and electrolyte, facilitating the hole transfer to methanol more efficiently.

The WO₃ nanostructures absorb effective photons that caused the generation of valence band holes (h₀⁺) and conduction band electrons (e₀⁻). These photon-generated holes serve as oxidation sites for the absorbed methanol molecules, i.e.

\[
\text{WO}_3 + h_0^+ \rightarrow \text{WO}_3^+(h_0^+, e_0^-)
\]

\[
\text{CH}_3\text{OH} + 2h_0^+ \rightarrow \text{CO} + 2H^+ + H_2
\]

\[
2H^+ + 2e^- \rightarrow H_2
\]

The best film prepared with CH₃COONH₄ renders the highest photocurrent density of about 1.16 mA/cm² (at 1.45 V). However, this value is smaller compared to the reported porous sol–gel WO₃ films (4.1 mA/cm², AM 1.5, film thickness 2.8 μm). The inferior catalytic performance for photodegradation of methanol may be due to the less optimum film thicknesses and slow carrier transporting kinetics. Further study is required to optimize the parameters.

The photoelectrochemical performance of film synthesized with CH₃COONH₄ capping agent for hydrogen production through water splitting was also investigated in 1 M H₂SO₄ and shown in Figure 10a. The highest photocurrent density of about 0.5 mA/cm² can be obtained under illumination, which is comparable to other reported values. The photoconversion efficiency (PCE) of light to hydrogen energy is calculated according to the following eq.

\[
PCE(\%) = \left[ \frac{J_p (E_{WS} - E_{app})}{I_o} \right] \times 100
\]

where \(J_p\) is the photocurrent density (mA/cm²), \(I_o\) is the incident light intensity (100 mW/cm²), \(E_{WS}\) is the standard reversible
potential for water splitting reaction (1.23 V for the water-splitting reaction at pH 0), and $E_{\text{app}}$ refers to the absolute value of the applied potential $E_{\text{app}}$, which is obtained as

$$E_{\text{app}} = |E_{\text{meas}} - E_{\text{ocp}}|$$

where $E_{\text{meas}}$ is the electrode potential at which the photocurrent density $j_p$ is measured, and $E_{\text{ocp}}$ is the electrode potential at open circuit condition under the same illumination intensity. It can be seen from Figure 10b that a highest PCE value of about 0.3% is obtained at 0.65 V bias for our experiment. More work is underway to improve the photoconversion efficiency by optimizing the electrolyte, film thickness and annealing conditions.

The band diagram of the WO$_3$ photoanode and operation of the photoelectrochemical cell were schematically shown in Figure 11. When the WO$_3$ photoanode is placed in contact with the electrolyte, a depletion layer at the interface will be formed resulting from the move of electrons from WO$_3$ to electrolyte, producing an upward bending of the band.

Upon illumination, photogenerated electrons will be excited and injected into the conduction band, leaving the holes in the valence band. An external bias is required to pump the electrons to the cathode and elevate the cathode (Pt) Fermi level $E_F$ above the H$_2$ energy level, thus making the process of water decomposition possible.

The hydrogen ions will be reduced by electrons, and hydrogen will be formed at the side of Pt. At the same time, the holes in the valence band will transfer to the electrolyte to oxidize water and oxygen will be generated on the surface of WO$_3$. The efficiency of the cell could be further improved by precisely tailoring the WO$_3$ nanostructures and increasing its surface area.

4. CONCLUSIONS

We report a hydrothermal approach to directly grow porous tungsten trioxide hydrate (3WO$_3$·H$_2$O) thin films with different morphologies on transparent conductive glasses in a large scale. Systematic investigations of the influence of seed layer and different capping agents on the morphologies and structures of the as-synthesized films have been carried out. It was found that flower-like particles with sizes of $\sim$8–10 $\mu$m were synthesized and spread on the substrate without seed layers. Under the assistance of seed layer, dense thin film was formed without capping agent. After adding suitable amount of CH$_3$COONH$_4$, (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_4$ into the precusor, thin films consisted of sheetlike, wedgelike, and platelike nanostructures could be synthesized, respectively. The dehydrated porous films showed high photocatalytic activities for photodegradation of methanol. The film grown using CH$_3$COONH$_4$ as the capping agent could generate anodic photocurrents of 1.15 mA/cm$^2$ for oxidation of methanol and 0.5 mA/cm$^2$ for water splitting, the highest photoconversion efficiency of about 0.3% can be obtained for water splitting under simulated solar illumination.

■ ASSOCIATED CONTENT

Supporting Information. Additional figures, XRD patterns, and schematic (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

■ ACKNOWLEDGMENT

We thank the Science and Engineering Research Council (A*STAR) of Singapore (Grant No. 092 101 0057), the National Research Foundation Research Fellowship program (NRF-2009-RF-09) of Singapore for support. The work is also supported by National Natural Science Foundation of China (NSFC) (Projects 61006037 and 61076015).

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