

Flame Synthesized Nanostructured WO₃ Thin Films for Photoelectrochemical Water Splitting

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ABSTRACT

Tungsten oxide has been considered as a promising photoanode material for photoelectrochemical water-splitting technologies. In our study, we prepared nanostructured tungsten oxide thin films with different morphologies, such as granular, co-tube and flower-like structures, by aerosol flame deposition process. Thin film morphology were controlled by adjusting various process parameters, such as tungsten wire feed rate and various gas flow rates and so on. With higher tungsten wire feed rate, nucleation process of tungsten oxide vapor has higher tendency to take place in the flame before depositing on the substrate, which led to granular morphology of thin film formed. We first presented an approach to prepare double-layer nanostructured WO₃ thin film bloomed flower structure by a rapid single flame deposition process. This may provide a way to increase thin film total surface area, and facilitate charge transport of thin film photoelectrode in photoelectrochemical water splitting.

Keywords: Flame synthesis, Nanostructured WO₃ thin films, Photoelectrochemical water splitting, Aerosol flame deposition process, Double layers

1. INTRODUCTION

Photoelectrochemical (PEC) water splitting using semiconductor photoelectrodes is one of the most promising and environmentally friendly methods to produce hydrogen from water by utilizing renewable (solar) energy. Enormous efforts are being devoted to find adequate semiconductor photoelectrode materials and its preparation methods. Many semiconductor oxides, which show photocatalyst activity, have narrow band gap energies for capturing visible spectrum light. However, most of them are limited to use either simply due to high charge carrier recombination and unfavorable band edge position for H₂ evolution or unstable in aqueous solution. So far, there is no one oxide having a perfect material matching with all those requirement above and show high solar-to-hydrogen efficiency at the mean time. However, among all those semiconductor oxides, tungsten oxide (WO₃) is still one of most attractive and imperative photoanode material for PEC water splitting due to its good stability in aqueous solution and suitable band gap energy for considerable absorption within the solar spectrum, energetically

favorable valence band position for water oxidation and excellent electron transport property along with hole diffusion length [1].

There are various preparation methods to synthesize WO₃ thin film, such as thermal and chemical vapor deposition [2-5] and hydrothermal method [6]. However, these methods either involved multiple time-consuming steps or required expensive processing equipment or needed strict experimental condition. Flame vapor deposition (FVD) method [7-11] overcomes many of the above limitations and is an attractive and versatile method for growing 1-D nanomaterials. Flame synthesis has several distinct advantages, such as rapid formation rates, low-cost and scalability, simple fabrication process and flexibility in tuning the oxidation states and morphologies of as-grown nanostructures by varying various flame synthesis parameters [8-9].

Currently, there are only few research groups all over the world studying on fabrication of tungsten oxide thin films by Flame vapor deposition method for solar applications as far as we know. P.M. Rao et al group in Stanford University prepared WO₃ nanowires by flame reactor using tungsten wire as precursor [7-8]. However, it has to be mentioned that large amount of gas consuming due to the intrinsic burner dimension design and high substrate temperature on conductive glass which may damage the FTO conductive layer coated on glass are potential drawbacks needed to be overcome. In this study, we prepared presented a newly designed premixed burner for nanostructured WO₃ thin film fabrication, which could overcome the problems mentioned above.

2. EXPERIMENTAL

WO₃ thin films were prepared by aerosol flame deposition process. Its experimental schematic is showed in Figure 1. The premixed gas including CH₄, O₂ and N₂ are fed through the premixed burner, which consisted of 7 packed tubes with inner diameter of 2 mm. Tungsten wire (0.025 cm in diameter, \geq 99.9% purity, Sigma-Aldrich) was used as precursor. Tungsten wires were hold and placed in between burner tip and substrate at a given position. They were oxidized and generated WO_x vapors in methane combustion flame and subsequently deposited onto FTO-coated glass substrate to form tungsten oxide thin film. FTO-coated glass substrate with an area of 1.5 cm*1.5 cm was held by a substrate holder. Its temperature was

controlled through digital temperature controller. During deposition, a small amount of silver thermal paste (Arctic Silver, Visalia CA) was pasted onto the backside of the substrate to keep intimate thermal contact between the substrate and substrate holder which can only resist temperature below 200°C.

The morphology of tungsten oxide thin film is strongly affected by experimental conditions. There are several process parameters, which could be adjusted, such as the ratio of CH₄: O₂: N₂, various gas flow rate, the number of tungsten wire and its position, substrate temperature, and the distance between tungsten wire and substrate.

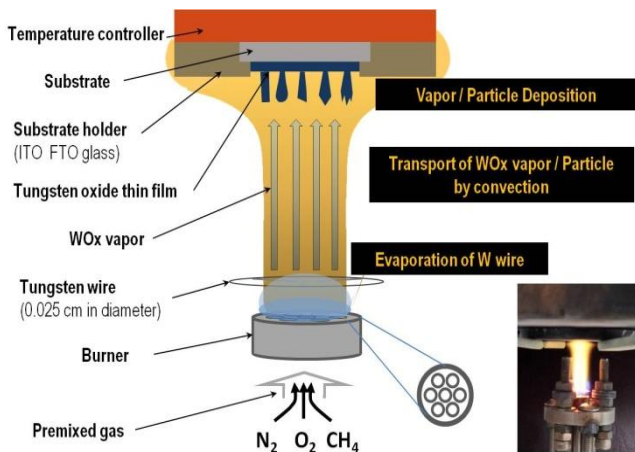


Figure 1: Schematic and photograph of the experimental setup for aerosol flame deposition synthesis of W₁₈O₄₉ nanostructured thin films.

The morphologies, compositions and crystal structures of resultant WO₃ thin films were characterized by scanning electron microscopy (UHR-SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM-2010), X-ray diffraction (HRXRD, X'Pert PRO MPD).

3. RESULTS AND DISCUSSIONS

Tungsten wire consuming rate is one of most important process parameters in our experimental process, it can be adjusted by changing tungsten wire design and position. Figure 2 shows SEM images of tungsten oxide thin films prepared for different tungsten wire feed rate. Thin films with granular structures were formed. As tungsten wire feed rate decreases from 18.3 μg/s (6 minutes deposition) to 4.5 μg/s (10 minutes), thin film thickness decreases from 11 μm to 0.6 μm. And meanwhile, granular structures became denser and more compact with each other. Its diameter of decreases from approximately 3 μm to 300 nm as presented in inset top view images. It can be noticed that primary particles on each granulates also became smaller. With tungsten feed rate decreasing, initial tungsten oxide vapor concentration generated in the flame decreases. Lower vapor concentration led to smaller primary particles which

is more easier to get sintered with existed nanogranulates and eventually resulted in denser nanostructures. It proves that when tungsten wire feed rate is higher than 4.5 μg/s while keeping other process conditions as follows: CH₄:O₂:N₂=1:1.5:4, Total gas velocity $v=1.41$ m/s, H_{S-B}=3cm, H_{W-B}=4 mm, T_{sub}=100 °C, tungsten oxide vapor condensed and nucleated in the flame stream and particles grew and formed before depositing on the substrate.

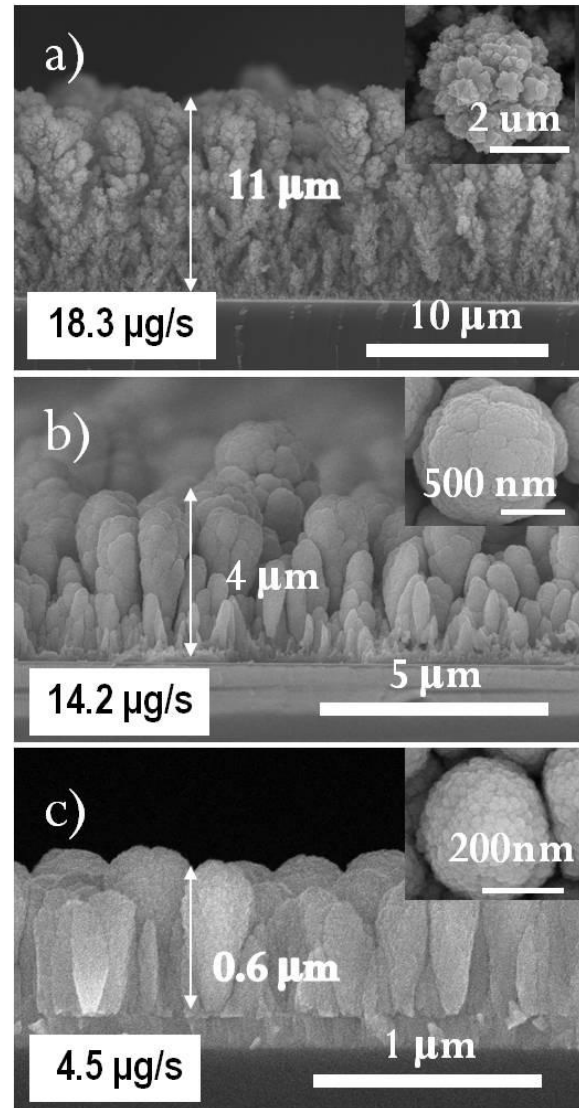


Figure 2: Cross-section SEM images of tungsten oxide nanostructures grown on ITO-coated glass at different tungsten wire consuming rate V , a) 18.3 μg/s; b) 14.2 μg/s; c) 4.5 μg/s. (CH₄:O₂:N₂=1:1.5:4, Total gas velocity $v=1.41$ m/s, H_{S-B}=3cm, H_{W-B}=4 mm, T_{sub}=100 °C, $t_D=6$ mins for a $t_D=10$ mins for b,c)

When the process condition was adjusted as follows, CH₄:O₂:N₂=1:1.5:5, Total gas velocity $v=1.25$ m/s, H_{S-B}=2.5cm, H_{W-B}=2.5mm, $V_w=3.9$ μg/s, T_{sub}=100 °C, $t_D=8$ mins, Tungsten oxide thin film with co-tube like nanostructured morphology were obtained as presented in

SEM images of Figure 3(A). Fuel-rich flame led to the formation of sub-stoichiometric tungsten oxide. Its thin film is blue and it could be converted to tungsten trioxide by air annealing which is yellow as showed in photographs in Figure 3. Typical XRD patterns indicated that the as-grown and annealed nanostructures are crystalline $W_{18}O_{49}$ and monoclinic WO_3 respectively. In addition, annealing has no large impact on the morphology by comparing SEM images of top view, however, the little difference maybe be due to the energetically unstability of sub-stoichiometric structure had tendency to become energetically stable at annealing temperature.

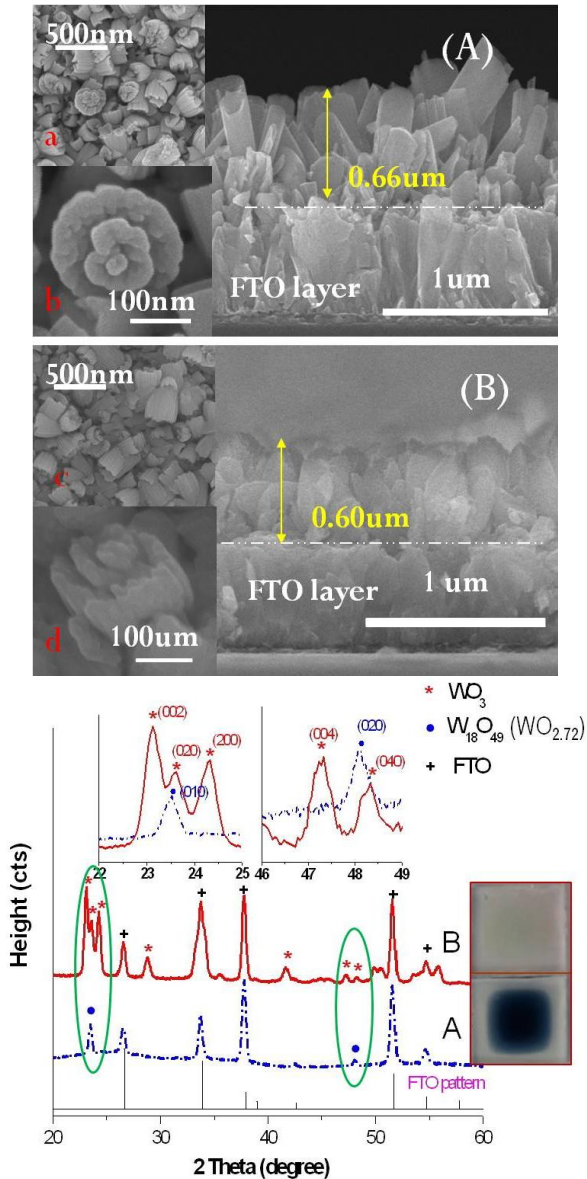


Figure 3: Cross-section, top view (a-d) SEM images and XRD patterns of tungsten oxide nanostructured thin films grown on FTO-coated glass in fuel-rich flame (A) as-grown, (B) after annealing (400°C for 1 h). ($CH_4:O_2:N_2=1:1.5:5$, Total gas velocity $v=1.25$ m/s, $H_{S-B}=2.5$ cm, $H_{W-B}=2.5$ mm, $V_w=3.9$ μ g/s, $T_{sub}=100$ °C, $t_D=8$ mins)

$W_{18}O_{49}$ has intrinsically anisotropic 1-D growth property. It could be obtained in fuel-rich flame, However, This co-tube like nanostructures are actually composed of thin 1-D growth nanowires which grew shoulder by shoulder with each other as we take a look closely at top view. It provided a way to prepare WO_3 thin film with co-tube morphology by forming co-tube nanostructured $W_{18}O_{49}$ in fuel-rich flame with after annealing.

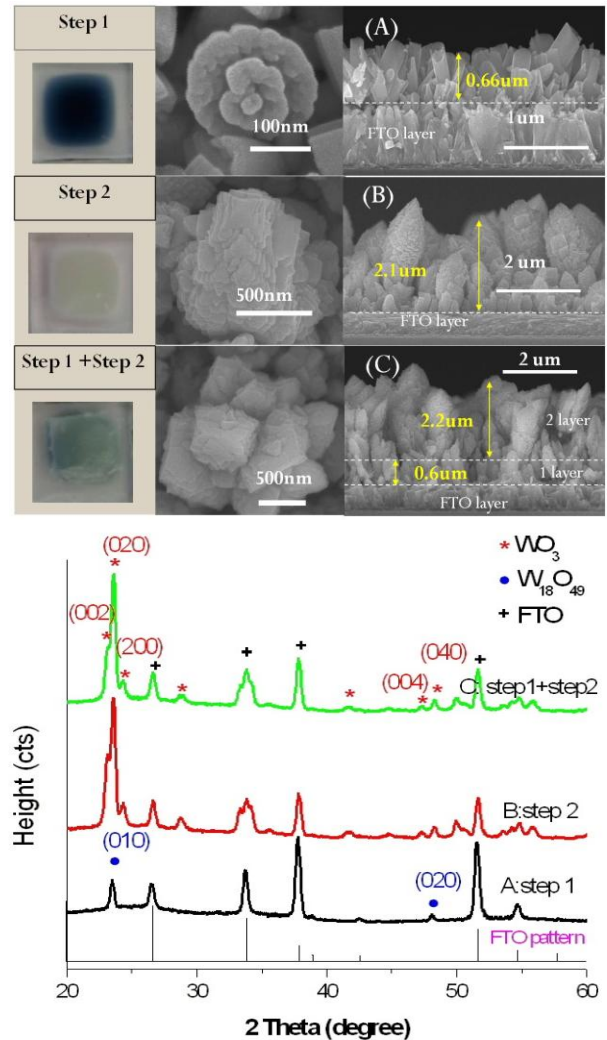


Figure 4: SEM images and XRD pattern of tungsten oxide nanostructures of tungsten oxide nanostructures grown on FTO-coated glass with (A) Step 1, in fuel-rich flame, total gas velocity $v=1.25$ m/s, $V_w=3.9$ μ g/s; (B) Step 2, in fuel-lean flame, total gas velocity $v=1.33$ m/s, $V_w=8.3$ μ g/s. (C) Step 1 plus Step 2. ($T_{sub}=100$ °C, $t_D=8$ min, $H_{S-B}=2.5$ cm, $H_{W-B}=2.5$ mm same for each step)

When O_2 is enough for complete reaction in the case of fuel-lean flame, WO_3 could be formed and nearly cubic WO_3 crystal tends to grow as an isotropic 3-D structure. SEM images of B in Figure 4 presented WO_3 thin film prepared in fuel-lean flame ($CH_4:O_2:N_2=1:3:5$). It illustrated that flower bud like columnar structure with

diameter around 900 nm were grown on the substrate. It is quite larger than about 200 nm of co-tube structure. Nanostructures with as large as 900 nm diameter are less favorable for charge transport in photo-electrochemical water splitting when it compares with nanostructures with small diameter. However, by utilizing fuel-lean flame, WO₃ thin films could be obtained in a single deposition process without post-annealing.

We first presented an approach to prepare double-layer nanostructured WO₃ thin film by a rapid single flame deposition process. This process includes two steps: step 1, preparing sub-stoichiometric tungsten oxide in fuel-rich flame as first layer as showed in . Step2, depositing WO₃ thin film in fuel-rich flame as 2 layer. If thin film prepared in step 1 used as the substrate in step 2, double layers of WO₃ thin films could be obtained as showed in SEM images in Figure 4. By doing so, higher flame temperature combining O₂- rich atmosphere of fuel-lean flame led W₁₈O₄₉ thin film prepared in first step converting to WO₃. It is confirmed by XRD as illustrated XRD pattern in Figure 4. The interesting thing is that when we look at this top view, as if the flower bud grown in step 2 bloomed with the help of step 1, from which co-tube like structure were obtained. This may provide a way to increase thin film total surface area, and facilitate charge transport of thin film photoelectrode in photoelectrochemical water splitting.

4. CONCLUSIONS

Nanostructured tungsten oxide thin films could be obtained by aerosol flame deposition process. With higher tungsten wire feed rate, nucleation process of tungsten oxide vapor has higher tendency to take place in the flame before depositing on the substrate, which led to granular morphology of thin film formed. At a certain condition, co-tube structured sub-stoichiometric tungsten oxide could be obtained in fuel- rich flame. By post-annealing, this sub-stoichiometric tungsten oxide could be converted to monoclinic tungsten trioxide, which is known of higher photocatalyst property, with nearly no change on morphology. WO₃ thin film could be obtained directly in fuel- lean flame with no need of post-treatment, which offers higher flame temperature and sufficient O₂ for complete oxidation. However, WO₃ thin films grown in this condition tended to have large diameter of nanostructures due to the intrinsic isotropic growth property of WO₃. In this study, we first presented an approach to prepare double-layer nanostructured WO₃ thin film bloomed flower structure by a rapid single flame deposition process. This may provide a way to increase thin film total surface area, and facilitate charge transport of thin film photoelectrode in photoelectrochemical water splitting. The AFD method

offers a new approach to synthesize monoclinic WO₃ thin films with different nanostructures and multiple layers.

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