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One-step Rapid and Scalable Flame Synthesis of Efficient WO₃ Photoanodes for Water Splitting

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ABSTRACT: Photoelectrochemical water splitting is a promising approach for the carbon-free production of hydrogen from sun light. Here, robust and efficient WO₃ photoanodes for water oxidation were synthesized by scalable one-step flame synthesis of nanoparticle aerosols and direct gas-phase deposition. Nanostructured WO₃ films with **tunable** thickness, bandgap and controllable porosities were fabricated controlling the aerosol deposition time, concentration and temperature. Optimal WO₃ films demonstrate superior water oxidation performance reaching a current density of 0.91 mA at 1.24 V vs. reversible hydrogen electrode (RHE) and an IPCE of ~ 61% at 360 nm in 0.1 M H₂SO₄ solution. Notably, it is found that the excellent performance of these WO₃ nanostructures arises from the high in-situ restructuring temperature (~1000 °C), which increases oxygen vacancies and decreases charge recombination at the WO₃/electrolyte interface. These findings provide a scalable approach for the fabrication of efficient WO₃ and other metal oxides-based photoelectrodes for light-driven water splitting.

KEYWORDS: *one-step, scalable, robust, photoelectrochemical, water splitting, flame synthesis, WO₃,*

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Solar-driven photoelectrochemical (PEC) water splitting has been extensively studied as a means for production of solar hydrogen as a renewable and sustainable energy carrier.^[1] Low-cost earth-abundant semiconductors such as TiO₂, ZnO, hematite and WO₃^[2] are increasingly investigated as photoelectrodes. Nanostructured WO₃ is particularly attractive due to its suitable bandgap, high electron mobility, and low cost.^[3] The WO₃ bandgap of 2.6-2.8 eV can utilize ~12% solar light with a theoretical photocurrent density of ~ 4 mA cm⁻².^[4] In order to develop highly efficient WO₃ photoanodes, several techniques have been employed to fabricate tailored nanostructures such as sputtering, chemical vapour deposition, electrodeposition, anodic oxidization, sol-gel and hydrothermal methods.^[2c, 3b, 5] In addition to nanoparticles, various other WO₃ nanostructures like nanowires, nanoplates, nanosheets, and nanoflakes have also been developed through hydrothermal methods.^[2c, 5e-i] Often, a post-calcination treatment or multiple steps with limited scalability are required to further increase the crystallinity of the WO₃ nanostructures for enhancement of their PEC performance. The development of a one-step scalable method for the fabrication of efficient WO₃ photoanode is beneficial to facilitate its future implementation for PEC water splitting.

Flame synthesis is an established technology for the commercial production of nanoparticles like carbon black, fumed silica and other nanoparticle commodities.^[6] Recently, flame synthesis of nanoparticle aerosols and direct deposition has been applied to the fabrication of ultraporous networks of metal oxide semiconductors for optoelectronic devices.^[7] Such films consist of ultrafine nanoparticles and can be rapidly synthesized and directly deposited with more than 90%.^[8] However, a major limitation of such films is their poor mechanical stability due to their high porosity. Further optimization of the structural properties of these films is required for the fabrication of robust photoelectrodes for their application water splitting.

Here, a one-step rapid flame synthesis and deposition method for the fabrication of WO₃ photoelectrodes with **tunable** thickness, bandgap, and controllable porosities is introduced. It was observed that a short nanoparticle aerosol deposition time of 10 s is sufficient to fabricate robust WO₃ films on FTO substrate without the need of any post-calcination treatment. Optimal WO₃ nanostructured films show superior PEC performance reaching a current density of 0.91 mAcm⁻² at 1.24 V vs RHE with

a maximum IPCE of ca. 61% at 360 nm. This performance has been attributed to their higher donor densities and efficient charge transfer at the WO₃/electrolyte interface.

RESULTS AND DISCUSSION

The morphologies of WO₃ deposited at different height above the burner (HAB) are shown in Figure 1. As shown in Figure 1b, e and h, WO₃ nanocrystals are agglomerated into cauliflower structures and uniformly distributed on the substrates, which is quite similar to previously reported for flame-made ZnO films.^[9] With decreasing the HAB from 10 to 6 cm, the film becomes much denser and the intra-agglomerate pores decrease from ~1-2 μm at HAB of 10 cm to less than 100 nm at HAB of 6 cm. Meanwhile, at higher magnification (Figure 1a, d and g), the WO₃ nanocrystals within cauliflower structures increase in size. Therefore, the interspace among WO₃ nanocrystals within cauliflower structure is much denser at HAB of 6 cm than those formed at HAB of 8 and 10 cm. The cross-section SEM images of the films are presented in Figure 1c, f and i. The WO₃ films deposited at HAB of 8 and 10 cm demonstrate tree-like micro-sized structure that extended throughout the film cross-section terminating in cauliflower-like tips. The thickness of WO₃ films are ca. 1.5, 1.5, 2.5 μm for the HAB of 6, 8 and 10 cm, respectively. The WO₃ film deposited at HAB of 6 cm appears more robust than those deposited at HAB of 8 and 10 cm, and its morphology is different from those previously obtained by deposition of flame-made nanoparticle aerosols^[8a] at HAB of 20 cm.

The composition and crystallinity of these WO₃ films were investigated by energy-dispersive spectrum (EDS) and X-ray diffraction (XRD). As shown in Figure 2a, the elements of W and O can be clearly seen in the EDS spectra, while other elements like Sn and trace amount of C comes from FTO substrate and probably atmospheric CO₂ adsorption, respectively. Figure 2b shows XRD patterns which reveal that the crystal structures of WO₃ films with different HAB are monoclinic WO₃ (JCPDS No. 72-0677) with typical peaks located at 23.2°, 23.8° and 24.5° corresponding to the (002), (020) and (200) facets.^[2c, 10] In addition to XRD peaks of FTO substrate, no other peaks can be observed, indicating that all films are pure monoclinic WO₃. From XRD analysis, the average crystal sizes of WO₃ are computed to ca. 19.6, 34.7 and 44.3 nm for the HAB of 10, 8 and 6 cm, respectively. Notably, the relative intensity of the (020) diffraction peak in the WO₃ film at HAB of 6 cm is much higher than that of the other peaks, suggests

that WO₃ nanocrystals are partially aligned along the [020] direction,^[2c, 10] which is different from the other two WO₃ films deposited at HAB of 8 and 10 cm. The preferential orientation of WO₃ nanocrystals in [020] direction is attributed to the increasing deposition temperature at lower HAB, due to the heating from the hot flame aerosol. This is in line with reports indicating that high calcination temperature promotes WO₃ growth in the [020] direction.^[11]

The optical properties of flame-made WO₃ films were investigated by UV-vis absorption. Figure 2c shows the UV-vis spectra of WO₃ films obtained at different HAB and a wide absorbance between ca. 450 to 200 nm can be clearly seen in these spectra. Meanwhile, the onset absorbance is gradually red-shifted with HAB decreased from 10 to 8 then to 6 cm, suggesting the bandgap gradually reduced with the decrease of HAB.^[2c, 2e] In order to deduce the bandgap of these WO₃ films, Tauc plot (shown in Figure 2d) was applied. The bandgap of these three different WO₃ films are 2.68, 2.69 and 2.77 eV for WO₃ at HAB of 6, 8 and 10 cm, respectively. From the comparison, it can be seen that the bandgap of WO₃ at HAB of 6 cm is comparable with that of WO₃ at HAB of 8 cm after post-calcination treatment, but still narrower than that of WO₃ at HAB of 10 cm. The variable bandgap of WO₃ at different HAB is connected with their flame deposition condition and further post-calcination treatment applied to the HAB 8 and 10 cm only (Figure S1).^[2e] From the above **characterizations**, therefore, it can be concluded that different deposition HAB, and thus temperature and oxygen partial pressure, influences the morphology, the crystal structure, and the optical properties of the WO₃ films.

In order to optimize the films' optical density, WO₃ films with different flame aerosol deposition time were deposited on FTO at HAB of 6 cm. As shown in Figure 3a, the photocurrent density during water oxidation increased when the flame deposition time increased from 5 to 10 s, and then gradually decreased if extending the deposition time to 20 and 30s, which indicates that 10 s is the optimal deposition time at HAB of 6 cm reaching a current density of 0.91 mA cm⁻² at 1.24 V vs. RHE in 0.1 M H₂SO₄. The change of current density for WO₃ films with different deposition time might be closely connected with the light penetration depth in WO₃ film (the transmittance spectra and optical density is shown in Figure S2) and the resistance change of the FTO substrate during flame deposition. Notably, the

flame temperature is ca. 1000 °C at HAB of 6 cm and the longer deposition time will eventually damage the FTO decreasing its conductivity.

The performance of WO₃ film synthesized at different HAB is also investigated. The curves of current density vs. potential (J-V) for 15 s of WO₃ film at HAB of 8 cm and 20 s of WO₃ film at HAB of 10 cm are plotted in Figure 3b. Due to the weak mechanical stability on FTO substrate, the 20 s of WO₃ deposited at a HAB of 10 cm displays poor performance with very weak current density even after post-calcination treatment (Figure S3b). It was found that WO₃ film peeled off from FTO substrate after potential scan. The limited mechanical stability is not improved even after the post-calcination treatment, which impedes its further PEC investigation. When the deposition HAB was reduced to 8 cm, the current density reached 0.75 mA cm⁻² at 1.24 V vs. RHE. This was much higher than the same WO₃ film without post-calcination treatment (0.36 mA cm⁻² at 1.24 V, Figure S3b), suggesting that the calcination treatment can reduce the defect density, further increase the crystal size from 13.1 to 19.6 and 19.4 to 34.7 nm for the films deposited at HABs of 10 and 8 cm, respectively (Figure S4), and interparticle contacts and/or improve the contact between the interface of WO₃ and the FTO substrate, which further facilitate the excited charge transfer.^[2e] Because the deposition rate is higher at low HAB,^[12] here, different aerosol deposition times were chosen in order to guarantee that the thicknesses of WO₃ films at different HAB are comparable with each other. From the comparison, it can be observed that the as-prepared 10s of WO₃ films deposited at an HAB of 6 cm demonstrate significant higher current density than that of the WO₃ films at HAB of 8 and 10 cm even after post-calcination. This is tentatively attributed to the better grain-boundary interconnectivity of the HAB of 6 cm films, which may improve the photo-excited charges transfer efficiency across the film structure. A control experiment was carried out to investigate the impact of the calcination treatment on the current density of the WO₃ films deposited at a HAB of 6 cm. As shown in Figure S3a, there is a slight decrease of the current density after the calcination treatment, indicating that the 10s WO₃ film deposited at a HAB of 6 cm has already been sufficiently sintered during the deposition.^[13] On the other side, the impact of the necking treatment, previously widely investigated for -Ta₃N₅, has been further explored, here, for the WO₃ film deposited at a HAB of 8 cm. As shown in Figure S5, the current density increases significantly from 0.75 to 0.9 mA cm⁻² at 1.23 V vs. RHE after

the necking treatment is applied to the 15s of WO₃ films deposited at a HAB of 8 cm. This is comparable to that of WO₃ film at HAB of 6 cm and further confirms the importance of the grain boundary interconnectivity for the efficient separation and collection of the photo-generated electrons/holes. Decreasing the HAB below 6 cm broke the FTO and thus was not investigated. Two other different fabrication methods were also adopted for the fabrication of WO₃ films to provide a comparison with the flame-deposited films. The morphologies and XRD patterns of the WO₃ films fabricated by drop-casting and sputtering are presented in Figure S6 and S7. As shown in Figure 3b, WO₃ film fabricated by drop-casting had higher photocurrent density than the WO₃ films fabricated by sputtering, but still much lower than that of the 10s flame-made WO₃ films deposited at HAB of 6 cm. Considering the very short deposition time of only 10 s and the no-need for other calcination treatments, this flame synthesis method is a one-step ultra-rapid approach that can be easily scaled up for the production of WO₃ films with high PEC performance.

The stability of 10s of WO₃ film at HAB of 6 cm was investigated by monitoring the current density vs. time. As shown in Figure 3c, the current density of WO₃ film at HAB of 6 decreases from initial 0.77 to 0.62 mA cm⁻² after 1 h of measurement at 1.24 V. In contrast, WO₃ films at HAB of 8 cm decreased by 56.5% from initial 0.64 to 0.36 mA cm⁻² within 1 hours of measurement, which indicates that the WO₃ film obtained at HAB of 6 cm has improved stability.

In order to analyze the underlying reasons of the higher performance of the WO₃ films obtained at HAB of 6 cm, the electrochemical active surface areas of all the WO₃ photoanodes were firstly measured via cyclic voltammograms with various scan rates (Figure S8a). After fitting the linear curve for the capacitive currents at different scan rates, the slope values can be computed with the larger slope value indicating larger electrochemical active surface area.^[10] After normalization of the slope values, it can be clearly seen that 15s of WO₃ film at HAB of 8 cm has the largest electrochemical active surface areas amongst all the WO₃ films fabricated by flame or by the other two methods. However, the current density of the films obtained at HAB of 8 cm is lower than that obtained at 6 cm HAB (Figure S8b). This indicates that the electrochemical active surface area is not the main contributor to the higher current density of the best performing WO₃ films (10 s at HAB of 6 cm).

To further explore the main factors contributing to the PEC performance of these photoanodes, the porosities of various WO₃ films were calculated (Figure S9). The porosity of flame-made WO₃ film could be tuned from ca. 59% to 77% by varying the deposition HAB. The relationship between the porosity and current density is shown in Figure 3d. It can be seen that the current density gradually increased with the porosity increasing from 28% to 59% and decreased with the porosity increasing from 67.8% to 77.5%. This suggests that nor porosity or surface area are the key contributors to the performance of the 10s WO₃ films at HAB of 6 cm, which have the highest current density. This is also in line with the analysis of aforementioned electrochemical active surface areas (Figure S8b). Mott-Schottky (MS) and electrochemical impedance spectroscopy (EIS) measurements were also conducted with the flame-made WO₃ films fabricated at different HAB. The MS curves of the WO₃ films deposited for 10 s and 15 s at HAB of 6 and 8 cm, respectively, are shown in Figure 4a. Both samples show positive slopes in the MS plots indicating a n-type semiconductor behaviour.^[2a] Meanwhile, the WO₃ film at HAB of 6 cm show substantially smaller slope compared to that of WO₃ film at HAB of 8 cm, indicating significantly increased donor densities.^[5e] Based on the MS equation, the donor densities of the WO₃ film at HAB of 6 cm is calculated to be $9.44 \times 10^{20} \text{ cm}^{-3}$, around 1.7 time higher than that of the WO₃ film at HAB of 8 cm. From the comparison, it is suggested that WO₃ film fabricated at HAB of 6 cm might have higher oxygen vacancies than that of post-calcinated WO₃ film fabricated at HAB of 8 cm, and thus benefit of improved charge transport in WO₃ and at the interface between FTO and WO₃.^[2a, 5e] In order to prove the oxygen vacancies, Raman analysis of the flame-made films was performed for the different HABs (Figure S10). Two strong Raman peaks located at 804 and 715 cm⁻¹ are assigned to the $\nu(\text{O}-\text{W}^{6+}-\text{O})$ vibrational stretching mode of the W-O-W bridging oxygen and a medium strong peak at $\sim 272 \text{ cm}^{-1}$ is associated with $\delta(\text{O}-\text{W}^{6+}-\text{O})$ bending mode, while the weak peaks at $\sim 326 \text{ cm}^{-1}$ and $\sim 449 \text{ cm}^{-1}$ correspond to the vibrations of the $\text{O}-\text{W}^{5+}-\text{O}$ and $\text{W}^{5+}=\text{O}$ bonds,^[14] respectively, indicating the presence of oxygen vacancies.^[15] Notably, the WO₃ film deposited at a HAB of 6 cm shows the highest Raman spectra intensity ratio for the two peaks related to the oxygen vacancies related, indicating that the WO₃ film at HAB of 6 cm has higher oxygen vacancies than those obtained at the other HABs. It is also possible that

the preferential [020] direction of the WO_3 at HAB of 6 cm increases the electron mobility and hence, the electron transport properties.^[10]

The EIS measurements were conducted to evaluate the kinetics of charge transfer for the WO_3 films. The Nyquist diagrams in the frequency range of 100 kHz-10 mHz for WO_3 films at HAB of 6 cm and WO_3 films at HAB of 8 cm are shown in Figure 4b. The equivalent circuit of Randle circuit is also displayed in the inset, in which R_s is the solution resistance, R_{ct} is the charge transfer resistance across the interface of electrode/electrolyte, and CPE is the constant phase element for the electrolyte/electrode interface.^[16] The arcs in the Nyquist plot are related to charge transfer at interface of WO_3 /electrolyte. The fitted values of R_{ct} were 899 and 958.7 Ω for WO_3 films at HAB of 6 cm and WO_3 films at HAB of 8 cm, respectively. The WO_3 films at HAB of 6 cm has a high charge transfer efficiency showing a lower R_{ct} value than that of WO_3 films at HAB of 8 cm. Efficient charge transfer at the WO_3 /electrolyte interface can also hinder charges recombination.^[16]

To evaluate the impact of the flame exposure on the conductivity of FTO substrates, a series of EIS measurements were also carried out and the R_s values were compared. R_s is deduced as solution resistance, but it can also be used to indirectly evaluate the conductivity of FTO substrates if the experimental condition keeps the same except of the working electrodes. As shown in Figure below, R_s are analysed as 23.8, 26.8, 33.8, 36.5 ohms for the bare FTO, FTO exposed to a nanoparticle-free flame at a HAB of 10 cm, at a HAB of 8 cm, and at a HAB of 6 cm, respectively. This indicates that exposure of the substrate to the flame increases the resistance of FTO substrates. However, as the deposition time is very short, the resistance of the FTO even at low HAB is still sufficiently low. In order to further investigate whether the deposition of the WO_3 films influenced the resistance of FTO substrates, the R_s values are also deduced after the deposition of WO_3 films at different HAB. It was found that the R_s values are 23.9 and 25.8 ohms for the WO_3 films deposited at a HAB of 8 and 6 cm, respectively, which are comparable to that of the bare FTO substrates. This suggests that the deposition of WO_3 films can act as a protective layer inhibiting the direct flame contact to the FTO substrate and its damage. Overall, there is no obvious impact on the conductivity of FTO substrates for the deposition of WO_3 films at different HAB within the deposition time utilized here.

The incident photon-to-current conversion efficiency (IPCE) spectrum of the WO₃ film made at a HAB of 6 and 8 cm were further investigated. As shown in Figure 4c, the WO₃ film at HAB of 6 cm shows a rising IPCE from 460 nm, in line with its bandgap, and reaches a maximum IPCE of ca. 61% at 360 nm. This is significantly higher than that obtained with WO₃ films deposited at a HAB of 8 cm (~ 45% at 360 nm).

The PEC performance of the WO₃ films deposited at a HAB of 6 cm was compared to state-of-the-art WO₃ photoanodes in Table 1. The current density of the flame-made WO₃ photoanodes can reach 0.91 mA cm⁻² at 1.24 V vs. RHE, which is comparable to some of the best pure WO₃ photoanodes reported.^[2c, 5e-h, 10, 17] Notably, most of the synthesis methods require several hours for fabrication and also needs a post-calcination treatment to further increase the film crystallinity.^[2c, 5e-h, 10, 17] In contrast, the flame deposition method presented here requires 10 s for the fabrication of efficient WO₃ photoanodes without the need of any post-calcination treatments. The superior PEC performance of the WO₃ deposited at a HAB of 6 cm is closely connected with its high deposition temperature (~1000 °C). This results in both a robust film morphology and more oxygen vacancies which improve the charge-transfer efficiency across the WO₃/electrolyte interface, and results in higher current density and high IPCE. Furthermore, the ultra-rapid fabrication process (10 s) at HAB of 6 cm enables to avoid damage to the FTO substrate. In contrast, the WO₃ films fabricated at HAB of 8 and 10 cm are more porous and thus have higher surface areas than that at HAB of 6 cm. However, the low donor densities, and high charge recombination at the interface and the poorer mechanical stability greatly diminish their PEC performance. Notably, flame synthesis is a flexible method that can be easily scaled up and extended to fabricate other metal oxide based photoelectrodes without any post-calcination treatment.

CONCLUSION

We have reported a one-step ultra-rapid flame-based method for the fabrication of efficient WO₃ photoanodes for water oxidation. A short deposition time of 10 s is sufficient for the fabrication of robust WO₃ films that do not require post-calcination treatment and achieve a photocurrent density for water oxidation of 0.91 mAcm⁻² at 1.24 V vs RHE in 0.1M H₂SO₄ and an IPCE of ~ 61% at 360 nm. Optimization of the structural properties of these flame-made WO₃ films reveal that the high deposition

temperature achieved for short time at a height above the nozzle of 6 cm improves the film donor concentration and charge-transfer efficiency without damaging the FTO substrates. This results in a significantly better performance than that of flame-made films deposited at higher height above the burner or fabricated by other methods such as sputtering or drop-casting of the same flame-made WO_3 particles. These findings provide a flexible and scalable one-step approach for the rapid fabrication of robust photoanodes made of earth-abundant low cost metal oxides such as WO_3 and Fe_3O_2 .

METHODS

Synthesis of WO_3 photoelectrodes. A flame spray pyrolysis (FSP) system was used for the direct deposition of WO_3 film onto FTO substrates or collection of WO_3 powder on a filter paper for the fabrication of drop-casting photoelectrode. The detailed procedures were prepared as follows: The FTO glass (PV-TECH, $7 \Omega \text{ cm}^{-1}$) was cleaned with soap water, acetone and 2-propanol sequentially. A total W-metal atom concentration of 0.2 mol L^{-1} was prepared by dissolving ammonium (meta) tungstate hydrate (Aldrich, purity > 97%) in a 1:1 (volume ratio) mixture of diethylene glycol monobutyl ether (Aldrich, purity > 98.5%) and ethanol (Aldrich, purity > 99.5%). This solution was supplied through a syringe pump at a rate of 5 mL min^{-1} , and dispersed into a fine spray with 7 L min^{-1} oxygen at a constant pressure drop of 2 bars. The spray was ignited by supporting premixed methane/oxygen flames ($\text{CH}_4 = 1.2 \text{ L min}^{-1}$, $\text{O}_2 = 2 \text{ L min}^{-1}$). A substrate holder placed at different height above the burner (HAB) was utilized for the deposition of WO_3 films on FTO substrates with different controlled time. With the exception of the WO_3 deposited at an HAB of 6 cm, the rest WO_3 photoelectrodes were sintered at $500 \text{ }^\circ\text{C}$ for 2 h with 5°C ramming rate under air environment. The drop-casting WO_3 film was fabricated by dispersing 50 mg of WO_3 powder in 1 mL of ethanol, then take $100 \mu\text{L}$ of mixed solution and drop-cast on FTO substrates until it is totally dry for further post-calcination treatment.

WO_3 was deposited on FTO films by a DC magnetron sputtering system (AJA ATC 2400) using 99.99% pure W metal as a target, Ar as a sputtering gas, and O_2 as a reactive gas with the gas flow Ar/ O_2 18/2 sccm. The chamber was evacuated to a base pressure of 9×10^{-7} Torr before deposition. Sputtering deposition was performed at a gas pressure of 4×10^{-3} Torr for 120 minutes at room temperature with a power of 200 W. The as-prepared films were annealed in a furnace at $500 \text{ }^\circ\text{C}$ for 2 h at ambient pressure prior to run PEC test.

PEC measurement and Characterizations. The PEC measurements were performed in a home-made one-compartment reactor with a quartz window. A three-electrode configuration was used with Pt wire, Ag/AgCl electrode, and FTO/WO₃ as the counter, reference, and working electrodes, respectively. A 0.1 M of H₂SO₄ solution (pH = 0.69) was used as the electrolyte and all the potential values have been reported vs. RHE based on $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}$. Amperometric J-T curves were measured at 1 V vs. Ag/AgCl on an Electrochemical Workstation (CHI 660E, USA). A xenon lamp (NewSpec, LCS-100) with an AM 1.5G filter was used as the light source for the measuring the photocurrent. The illumination area was set by an aperture to 0.785 cm². The Mott–Schottky analysis was performed in a three-electrode configuration in 0.1 M of H₂SO₄ solution with 1 kHz frequency in the dark. EIS was conducted using a 5 mV amplitude perturbation of between 100K and 0.01 Hz with an applied voltage of 0.4 V vs. Ag/AgCl under light illumination in a three-electrode configuration.

The morphology and EDS was investigated by using Zeiss Ultraplus (FESEM) at 3 kV. The crystallinity was characterized by X-ray diffraction using Bruker system (XRD, D 2 Phaser, USA) equipped with Cu K α radiation of average wavelength 1.54059 Å. The absorbance spectra were measured with a Perkin–Elmer (Lambda 1050 UV/vis/NIR) Spectrophotometer and a 150 mm integrating sphere. Raman spectra of WO₃ films were collected using IM-52 Raman microscope (Snowy Range) with 785 nm laser excitation under 40X objective. The laser power of 70 mW and integration time of 0.5 second were applied for all the samples. The capacitive current was measured by using cyclic voltammograms within potential range between 0.4 to 0.6 V vs. Ag/AgCl with various scan rates in a 0.1 M H₂SO₄. The porosities of WO₃ films were calculated based on their average mass divided by the bulk mass of WO₃ (density, 7.16 g/cm³) with the same of volume.

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Author Contributions

R.B., T.T. and H.C. performed materials synthesis, characterization and PEC measurements. H.C., G.L and A.T. contributed to the writing of the manuscript. All authors contributed to the data analysis.

Notes

The authors declare no competing financial interest.

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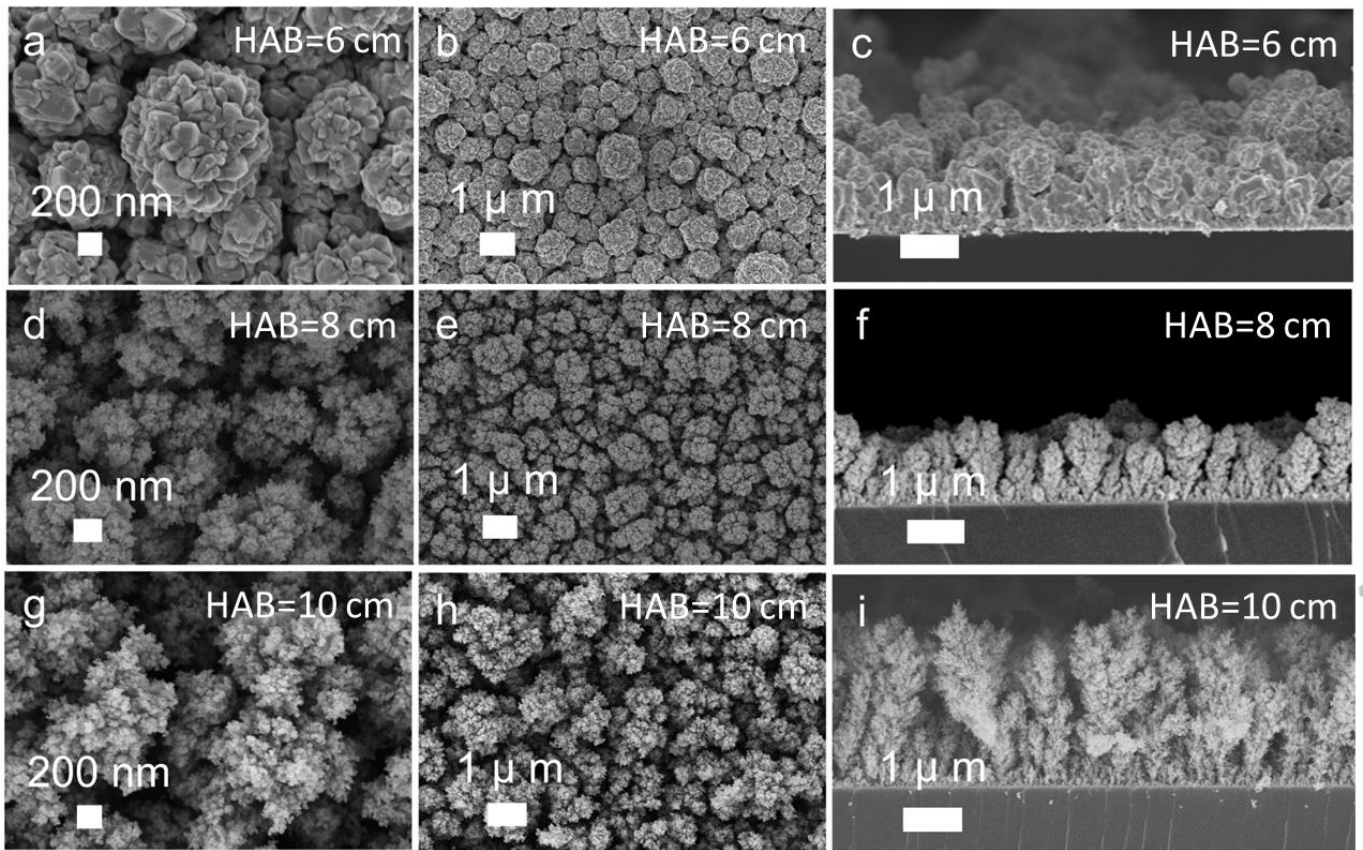


Figure 1. Morphological characterization of WO_3 films. typical top-view SEM images of WO_3 films deposited at HAB of 6 cm (a-b), 8 cm (d-e) and 10 cm (g-h) with different magnifications and their corresponding cross-sectional SEM images (c, f, i).

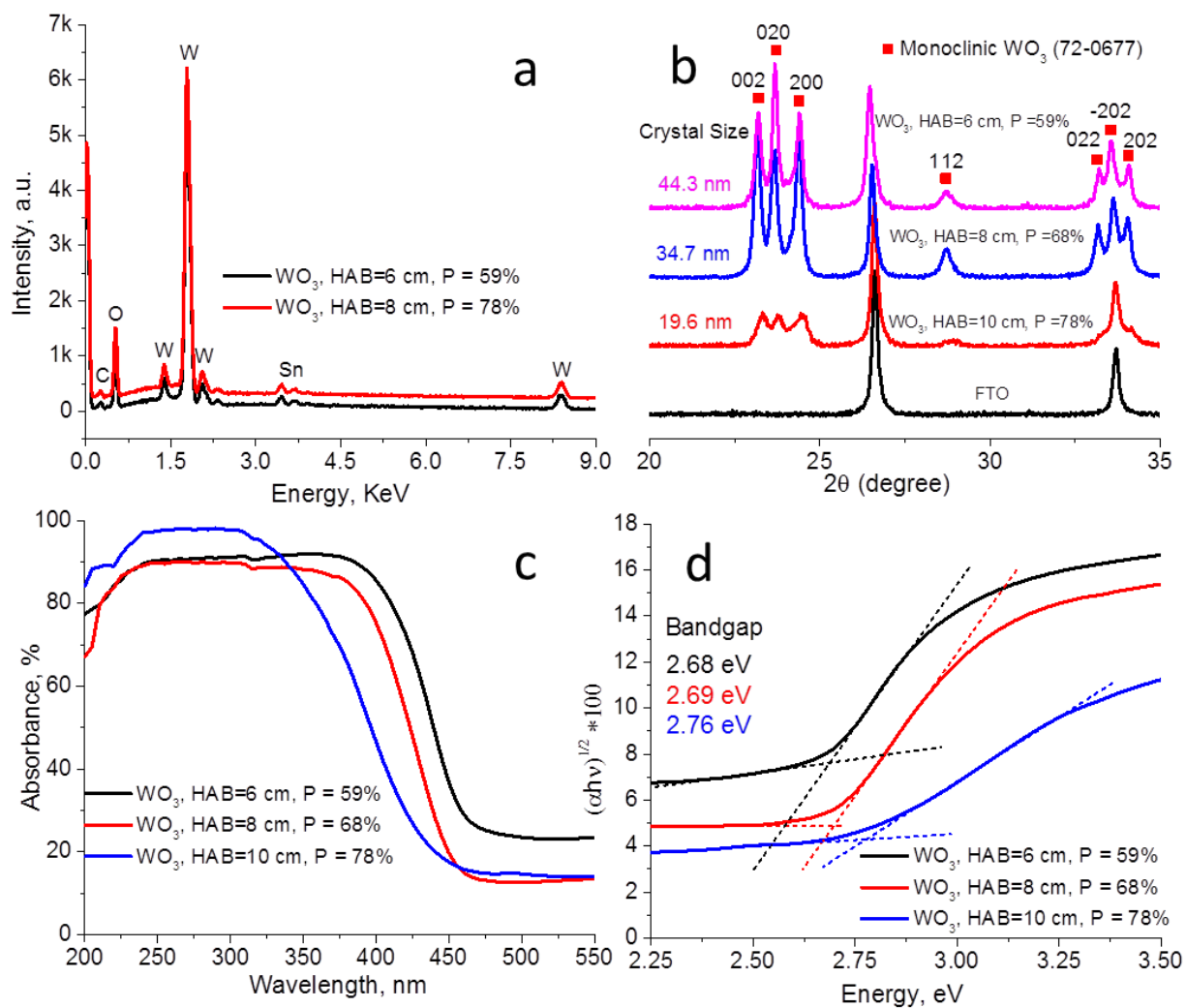


Figure 2. Structural and optical characterizations of WO_3 films. a, EDS, b, XRD, c, UV-vis spectra, d, Tauc plots of various WO_3 films deposited at different HAB and their corresponding porosity (P).

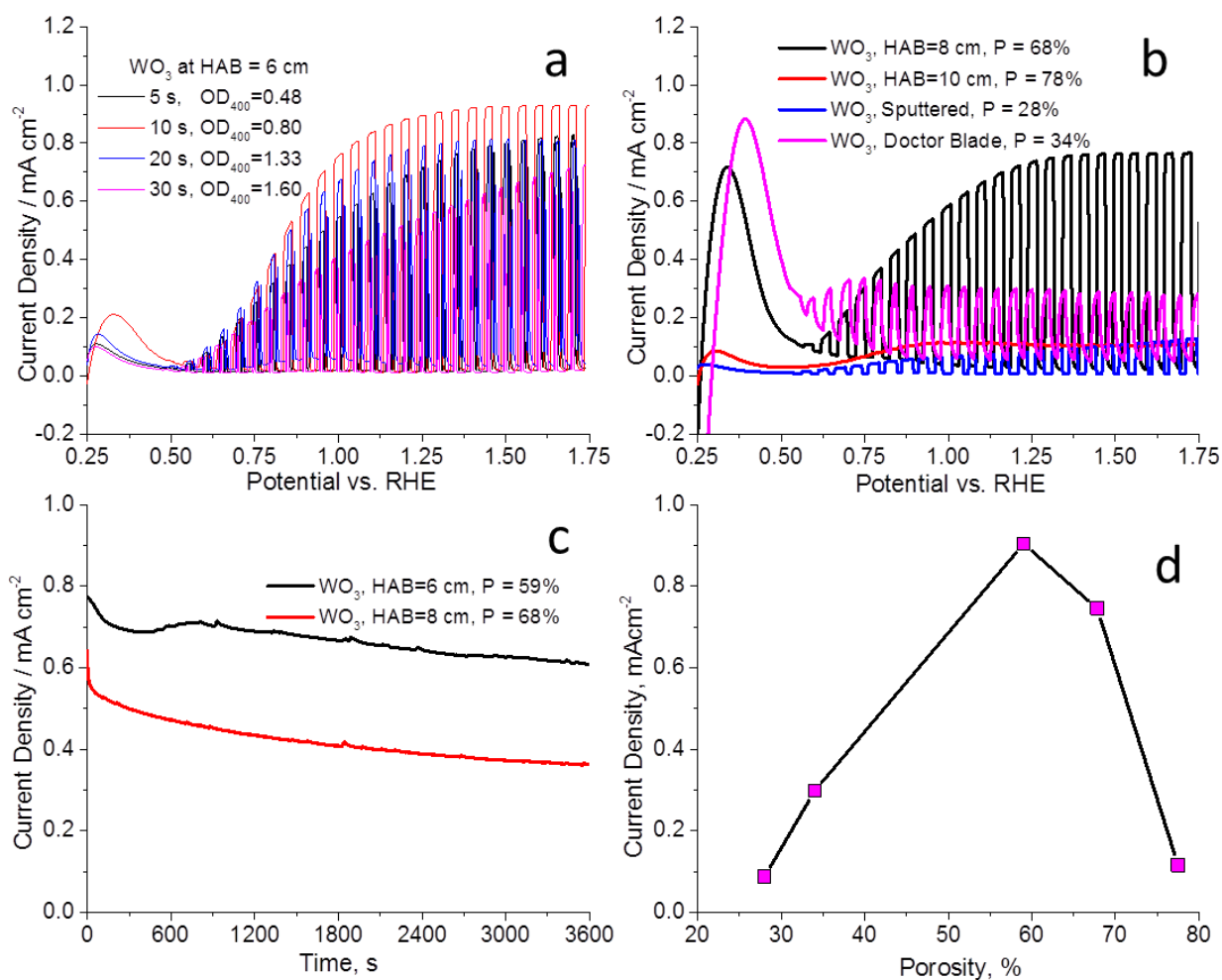


Figure 3. PEC performance of the WO₃ films. (a) J-V curves of WO₃ film fabricated at HAB of 6 cm with different deposition time; (b) J-V curves of WO₃ film fabricated at different HAB and different methods; (c) Chronoamperometry of WO₃ films at HAB of 6 cm and 8 cm at an applied potential of 1.24 V vs. RHE; (d) the relationship between the current density of WO₃ films fabricated by different methods with their porosities (d).

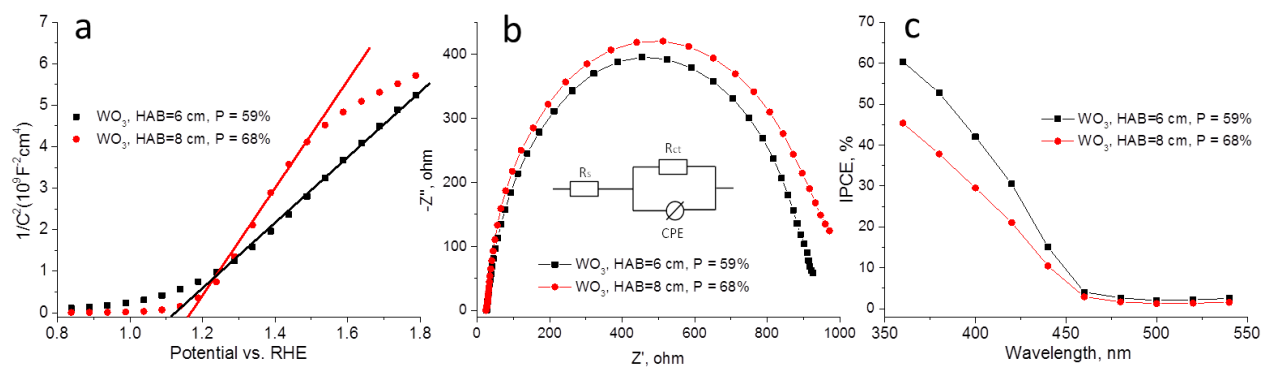


Figure 4. Electrochemical characterizations of WO₃ films. (a) Mott–Schottky plots measured at 1 kHz in the dark; (b) Nyquist plots collected at 0.64 V vs. RHE under illumination; The inset provides the equivalent circuit used to fit the impedance data. (c) Wavelength dependence of IPCE measurement at 1.24 V vs. RHE.

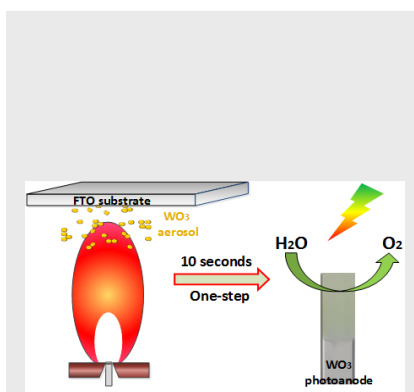
Table 1. Comparison of the state-of-art WO₃ photoanode for PEC water splitting.

Material	Method/total fabrication time including post-treatment	Electrolyte (Light source)	Current density	Reference
WO ₃ film	Flame Nanoparticle Aerosol Deposition/10 s	0.1M H ₂ SO ₄ (AM 1.5 G)	0.91 mA cm ⁻² at 1.23V vs. RHE	This work
WO ₃ nanoflake arrays	Hydrothermal / > 6 h	0.1 M Na ₂ SO ₄ AM 1.5 G	1.43 mA cm ⁻² vs ~1.2 V vs. Pt	5f
Hydrogen-treated WO ₃ nanoflakes	Hydrothermal / > 7 h	0.5 M Na ₂ SO ₄ AM 1.5 G	0.88 mA cm ⁻² at 1.6 V vs. RHE	5e
WO ₃ nanosheet array	Hydrothermal / > 6 h	0.01M Na ₂ SO ₄ AM 1.5 G	~0.68 mA cm ⁻² at 1.23 V vs. RHE	5h
WO ₃ NWs	Flame vapor deposition / > 2.5 h	0.5 M potassium phosphate (pH = 8) AM 1.5 G	1.1 mA cm ⁻² at 1.23 V vs. RHE	5g
WO ₃ nanorods	Glancing angle deposition / > 7 h	0.5 M Na ₂ SO ₄ (pH = 7), AM 1.5 G	0.55 mA cm ⁻² at 1.23 V vs. RHE	17a
Dual etched/reduced WO ₃ Nanoflakes	Hydrothermal / > 8 h	1M H ₂ SO ₄ AM 1.5 G	~1.10 mA cm ⁻² at 1.23 V vs. RHE	17b
Pristine WO ₃	Hydrothermal / > 4 h		~0.62 mA cm ⁻² at 1.23 V vs. RHE	
Fe-doped WO ₃ nanoflakes	Hydrothermal / > 7 h	0.1 M Na ₂ SO ₄ AM 1.5 G	0.88 mA cm ⁻² at 1.23 V vs. RHE	17c
Pristine WO ₃ nanoflakes	Hydrothermal / > 7 h		0.69 mA cm ⁻² at 1.23 V vs. RHE	
Gd-doped-WO ₃ vertical arrays	Hydrothermal / > 13 h	0.2 M Na ₂ SO ₄ AM 1.5 G	2.28 mA cm ⁻² at 1.6 V vs. RHE	17d
pristine WO ₃ vertical arrays			0.90 mA cm ⁻² at 1.6 V vs. RHE	
WO ₃ nanomultilayers	Hydrothermal / > 8 h	0.5 M Na ₂ SO ₄ AM 1.5 G	~ 0.88 mA cm ⁻² at 1.23 V vs. RHE	17e
Porous WO ₃ nanorod array	Hydrothermal / > 8 h	0.5 M Na ₂ SO ₄ AM 1.5 G	~ 0.6 mA cm ⁻² at 1.23 V vs. RHE	17f
Tree-like nanoporous WO ₃	Pulsed laser deposition / >2.5 h	0.5 M phosphate buffer solution (pH 7.0)	1.8 mA cm ⁻² at 1.23V vs. RHE	10

WO ₃ plate-like array	Hydrothermal / > 18 h	0.1M H ₂ SO ₄ AM 1.5 G	3.7 mAcm ⁻² at 1.23V vs. RHE	2c
WO ₃ nanoplate arrays	Hydrothermal / > 6 h	0.5 M Na ₂ SO ₄ AM 1.5 G	~ 1 mA cm ⁻² at 1.23 V vs. RHE	17g

COMMUNICATION

One-step ultra-rapid scalable method for the fabrication of efficient WO_3 photoanodes were fabricated through flame-made nanoparticle aerosols. A short deposition time of 10 s was sufficient for the fabrication of robust WO_3 films that do not require post-calcination treatment and achieve a photocurrent density for water oxidation of 0.91 mAcm^{-2} at 1.24 V vs RHE in $0.1 \text{ M H}_2\text{SO}_4$, and an IPCE of $\sim 61\%$ at 360 nm.



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One-step Rapid and Scalable Flame Synthesis of Efficient WO_3 Photoanodes for Water Splitting