# Defect Engineering of Air-Treated WO<sub>3</sub> and Its Enhanced Visible-Light-Driven Photocatalytic and Electrochemical Performance

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#### **Supporting Information**

**ABSTRACT:** In this paper, we reported that oxygen vacancies could be introduced in tungsten oxide hierarchical nanostructures through air treatment at certain temperatures. The production of oxygen vacancies may be due to two mechanisms, i.e., critical phase transition and nanoscale inhomogeneous deformation, depending on the annealing temperature or time and the size of the building block. The oxygen vacancies can be introduced at 300 and 350 °C when critical phase transformation from orthorhombic WO<sub>3</sub>· 0.33H<sub>2</sub>O to hexagonal WO<sub>3</sub> takes place or 350 and 400 °C when nanoscale inhomogeneous deformation occurs in the nanobelts. Moreover, the oxygen vacancy concentration is also influenced by the annealing time. For comparison, the oxygen



vacancies are also introduced by hydrogen treatment. It is found that a certain amount of oxygen vacancies introduced by air treatment could trap and transfer electrons, thus decreasing the electron-hole recombination rate and improving the conductivity, while an abundance of oxygen vacancies introduced by hydrogen treatment could facilitate the electron-hole pair recombination and destroy the hexagonal tunnel structure, resulting in lower photocatalytic activity and electrochemical performance. Through air treatment, the constant rate of photocatalytic performance in degrading rhodamine B under visible light irradiation can reach 0.0300 min<sup>-1</sup>, and the specific capacitance can improve to 166.7 F/g. It is suggested that both photocatalytic activity and electrochemical performance can be greatly improved by introducing a proper concentration of oxygen vacancies through air treatment.

# 1. INTRODUCTION

Tungsten oxides are of great interest for various technological applications: electrochromic and optochromic devices, gas sensors, and catalysts, and so on. $^{1-4}$  Particularly, tungsten oxides with a band gap at 2.5-2.8 eV could utilize visible light and they also exhibit high resistance against photocorrosion and good chemical stability in acidic aqueous solution (pH <4).5 Meanwhile, tungsten oxides are great electrochemically active materials for energy storage.<sup>6–9</sup> Among the different crystal structures of tungsten oxide, hexagonal tungsten oxide (h- $WO_3$ ) would be the most desirable one for pseudocapacitors, because it provides larger hexagonal tunnels in addition to the typical tetragonal tunnels. These precise tunnels could benefit the insertion of guest ions into the h-WO<sub>3</sub>.<sup>7</sup> However, one of the greatest challenges that impedes tungsten oxide from being an excellent photocatalyst is its high electron-hole recombination rate.<sup>10</sup> To improve the electrochemical performance, the conductivity and activity of electrodes must be upgraded. Nowadays, it has been demonstrated that a number of distinct properties of oxides can be controlled not only by their geometric/electronic structures but more significantly by defects in the structure.<sup>11,12</sup> Among all the defects, oxygen vacancies are supposed to be the most prevalent point defects in oxides.<sup>13</sup> Theoretical calculations and experimental characterizations revealed that oxygen vacancies in oxides (e.g.,  $TiO_2$ ) serving as photoinduced charge traps enhance the photocatalytic activity.<sup>14,15</sup> Oxygen vacancies could improve both the conductivity and activity of electrodes or even act as the key factor for electrode reactions.<sup>16</sup> Therefore, it is desirable to introduce defects, especially oxygen vacancies, in the tungsten oxide to improve its photocatalytic activity and electrochemical performance.

Tungsten oxides usually have five crystal structures: tetragonal ( $\alpha$ -WO<sub>3</sub>, >740 °C), orthorhombic ( $\beta$ -WO<sub>3</sub>, 330– 740 °C), monoclinic I ( $\gamma$ -WO<sub>3</sub>, 17–330 °C), triclinic ( $\delta$ -WO<sub>3</sub>, -43 to 17 °C), and monoclinic II ( $\epsilon$ -WO<sub>3</sub>, <-43 °C).<sup>17</sup> Monoclinic I is most stable at room temperature. The h-WO<sub>3</sub> obtained by dehydration of the tungsten oxide hydrate WO<sub>3</sub>.

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 $0.33H_2O$  is also stable at room temperature.<sup>18</sup> It is known that crystal structures and defect states of semiconductors can regulate light response, electrical, and chemical properties. Therefore, it is of significance to control the crystal structures and defect states of tungsten oxides to achieve high-performance photocatalytic activity and good electrochemical performance. The most common way to introduce oxygen vacancies is through hydrogen treatment.<sup>19-22</sup> If WO<sub>3</sub> is treated in hydrogen, oxygen loss induces new structural features, giving rise to the  $WO_{3-x}$  phase.<sup>21,23</sup> This structure consists of blocks of [WO<sub>6</sub>] octahedral sharing corners regularly separated by defect planes. These defect planes usually contain a number of oxygen vacancies and  $[WO_6]$  octahedra share their edges.<sup>24,25</sup> Commonly, it is thought that a semiconductor annealed in air at certain temperatures could change its crystal structure and especially would decrease the concentration of oxygen vacancies.<sup>26-30</sup> However, there are reports that the phase transformations through air treatment could introduce oxygen or sulfur vacancy in  $In_2O_3$  nanocubes or ultrathin nano-sheets<sup>31,32</sup> and ZnS nanoparticles.<sup>33</sup> Oxygen vacancies can also form in the air-calcined  $Y_2WO_6$ .<sup>34</sup> As for WO<sub>3</sub>, it was reported that annealing a WO<sub>3</sub> thin film deposited on Al<sub>2</sub>O<sub>3</sub> substrate at 250-400 °C in air could also result in the WO3-x oxygendeficient structure, in which oxygen vacancies were concentrated in well-ordered defect planes. However, it was found that when WO3 film was annealed without substrate, no obvious defect planes were observed, and it was thought that the substrate played an important role for oxygen vacancy generation.<sup>35</sup> Meanwhile, many researchers had also observed defect structures including oxygen vacancies in tungsten oxide thin films, <sup>24,25,35–38</sup> and the thinner the film, the more obvious of the defects,<sup>24</sup> suggesting that defect generation might be sizedependent. These reports all indicate that it is possible to introduce oxygen vacancies in nanoscale tungsten oxides by heat-treatment in air. Since nanomaterials have large surface-tovolume atom ratios, their behaviors, including phase transition and defect generation, are quite different from their bulk ones.<sup>5</sup> However, there is still a lack of investigations about the oxygen vacancy generation of free-standing nanoscale tungsten oxides (such as tungsten oxide without substrate) upon air treatment. Among all the dimensional tungsten oxides, the one-dimensional (1D) nanostructure, which can facilitate the charge transportation,<sup>10</sup> and the three-dimensional (3D) structure assembled with 1D nanosized building blocks, which can provide more active sites, receive more attention.<sup>39</sup> Moreover, introducing defects through air treatment for the visible-lightdriven photocatalysis and electrochemical performance of 1D or 3D tungsten oxides is rarely reported.

Herein, the oxygen vacancies introduced by air treatment were reported and confirmed by ESR spectra, XPS spectra and TEM images. The hydrothermally synthesized 3D orthorhombic WO<sub>3</sub>·0.33H<sub>2</sub>O (o-WO<sub>3</sub>·0.33H<sub>2</sub>O) assembled with 1D nanorods and 3D h-WO<sub>3</sub> hierarchical nanostructures assembled with 1D nanobelts were annealed at different temperatures and times in air. The production of oxygen vacancies is perhaps ascribed to two mechanisms—critical phase transition and nanoscale inhomogeneous deformation—dependent on annealing temperature or time and the size of the building block. It is suggested that both photocatalytic activity and electrochemical performance can be greatly improved by introducing a proper concentration of oxygen vacancies through air treatment.

## 2. EXPERIMENTAL SECTION

**2.1.** Synthesis of  $WO_3 \cdot 0.33H_2O$  or  $WO_3$  with Hierarchical Nanostructures. All the chemicals (Sinopharm Chemical Reagent Co., Ltd.) were of analytical reagent grade and used without further purification. All the aqueous solutions were prepared using deionized water.

The o-WO<sub>3</sub>·0.33H<sub>2</sub>O (WH) and h-WO<sub>3</sub> (W) hierarchical nanostructures assembled with 1D nanorods or nanobelts were synthesized through hydrothermal reaction by adjusting the amount of urea based on a previous study.40 In a typical process, 0.875 g of tungstic acid was added into 18 mL of  $H_2O_2$ , and the mixture stirred at 90 °C for 1.5 h before converting into a transparent sol. The resulting clear sol was diluted using deionized water to 210 mL, and then 14 mL of 3 M HCl was added to the as-prepared solution. After stirring for another 20 min, 30 mL of the precursor solution was transferred into a 50 mL Teflon-lined autoclave followed by adding 0.072 or 0.18 g of urea to obtain sample WH or W. Finally, the autoclave was sealed and maintained at 180 °C for 12 h. The as-synthesized precipitate was washed with deionized water three times and ethanol two times by centrifugation and then dried in vacuum at 80 °C for 3 h.

To introduce oxygen vacancies, the as-prepared o-WO<sub>3</sub>·  $0.33H_2O$  was subsequently annealed in air at 250, 300, 350, 400, and 450 °C or in 95% Ar + 5% H<sub>2</sub> at 350 °C for 2 h, which were labeled as WH-A250, -A300, -A350, -A400, -A450, and WH-H350, respectively; the samples WH annealed at 300 °C for 0.5, 2, 4, 6, and 8 h were marked as WH-A300-0.5h, -2h, -4h, -6h, -8h, respectively (WH series samples). Meanwhile, the obtained h-WO<sub>3</sub> was annealed at 300, 350, 400, 450, and 600 °C or in 95% Ar + 5% H<sub>2</sub> at 350 °C for 2 h, which were recorded as W-A300, -A350, -A400, -A450, -A600, and W-H350, repectively; samples W annealed at 350 °C for 0.5, 2, 4, 6, and 8 h were marked as W-A350-0.5h, -2h, -4h, -6h, and -8h, respectively (W series samples). If not otherwise specified, the annealing time was 2 h, such as for sample W-A300.

**2.2. Photocatalytic Activity Measurements.** The photocatalytic properties of the samples were evaluated by measuring the concentration of rhodamine B (RhB) in aqueous solution after equilibration in the dark and irradiation with the visible light produced by a 300 W xenon lamp through a cutoff filter ( $\lambda$  > 400 nm). Typically, a 20 mg sample was dispersed in 40 mL of RhB aqueous solution (15 mg L<sup>-1</sup>). Before the sample was exposed to visible-light irradiation, the suspension was stirred overnight to ensure the equilibrium of dye adsorption on the surface of the sample. About 3 mL of the solution was taken every 20 min during the photocatalysis, the powder sample was separated from the solution via centrifugation, and the RhB concentration was measured by UV–vis spectroscopy.

**2.3. Electrochemical Measurements.** The working electrodes were prepared by mixing the as-obtained samples, carbon black (Super P), and polyvinylidene fluoride (PVDF) at a weight ratio of 8:1:1 and coating on Ni foam. The resulting electrodes were dried at 80 °C overnight. The electrochemical properties were characterized using a standard three-electrode cell in an aqueous 1 M Li<sub>2</sub>SO<sub>4</sub> electrolyte at room temperature. A saturated Ag/AgCl electrode and a platinum sheet were used as reference and counter electrodes, respectively. Cyclic voltammograms (CVs) tests were performed in the potential range from -0.5 to 0 V (vs Ag/AgCl) at various scan rates. Specific capacitances of different scan rates can be calculated from the CVs by using the following equation:  $C = \int I \, dV/$ 

 $vm\Delta V$ , where *m* is the weight of the active material, v is the scan rate,  $\Delta V$  is the potential range, and *I* is the current at certain potential. The electrochemical impedance spectroscopy (EIS) data at room temperature were collected at frequencies from 10 mHz to 100 kHz with a magnitude of 5 mV at the open-circuit potential. Both CVs and EIS were tested on a Zahner IM6 electrochemical workstation.

**2.4. Characterization of Materials.** Crystallographic structures of the as-prepared materials were characterized by powder X-ray diffraction (XRD) (Cu K $\alpha$ , Rigaku D/max-V2500). Morphologies and microstructures were studied by scanning electron microscopy (SEM) (ZEISS) and transmission electron microscopy (TEM) (JEOL-2100). UV–vis absorption spectra were recorded with an U-3900 spectrophotometer (Hitachi). The X-ray photoelectron spectroscopy (XPS) was determined on an ESCALAB 250Xi instrument (Thermo Fisher Scientific). The Raman spectra (excited at 633 nm) were recorded with a high-resolution Raman spectrometer (HR800, HORIBA Jobin Yvon). Electron spin resonance spectroscopy (ESR) measurements were performed with a JEOL FA200 ESR spectrometer.

## 3. RESULTS AND DISCUSSION

**3.1. Structure and Morphology.** The XRD patterns of the tungsten oxides prepared under different conditions are



Figure 1. XRD patterns of (a) WH series samples and (b) W series samples.

presented in Figures 1 and S1 (Supporting Information, SI). The main peaks of all samples are very strong and narrow, indicating that all samples exhibit high crystallographic quality. As shown in Figure 1a, the diffraction peaks of sample WH can

be well-indexed to the orthorhombic structure of  $WO_3$ . 0.33H<sub>2</sub>O (JCPDS no. 72-0199). The (111) diffraction peak at about  $18^{\circ}$  is the characteristic peak of o-WO<sub>3</sub>·0.33H<sub>2</sub>O, while there is no peak in this position for h-WO<sub>3</sub>. When annealed at 250 °C in air, the sample WH-A250 maintains almost the same crystal structure as the unannealed one. While the temperature rises to 300 °C, the intensity of the (111) diffraction peak decreases obviously. When temperature increases to 350 °C, the (111) diffraction peak disappears and the sample transforms to the h-WO<sub>3</sub> phase (JCPDS no. 85-2460) and remains as such until 450 °C, where a small peak (marked by an asterisk) belonging to monoclinic WO<sub>3</sub> appears. When the annealing time varies from 0 to 8 h at 300 °C, the (111) diffraction peaks of the WH series of samples decrease. Besides, the orthorhombic  $WO_3 \cdot 0.33H_2O$  is the major phase within 2 h and then the hexagonal WO<sub>3</sub> is the major phase in the last 6 h, as shown in Figure S1a (SI). These results indicate that the phase transformations have been in progress under airannealing conditions at about 300 °C. The sample W can be indexed to the h-WO3 phase (JCPDS no. 85-2460) and the samples annealed in air at 300-450 °C have the same crystal phase as the unannealed one (Figure 1b). When the temperature rises to 600 °C, the sample transforms to the monoclinic phase completely (JCPDS no. 72-0677), as shown in Figure 1b. When the sample W was annealed at 350 °C for 0.5-8 h, the samples can be indexed to the same crystal phase as sample W (h-WO<sub>3</sub>), as shown in Figure S1b (SI). But the intensity ratios of  $I_{(100)}/I_{(002)}$  gradually increase, suggesting that there might exist some changes, such as the orientation of nanobelts, since the nanobelts grow along [002].<sup>40</sup> In addition, both samples WH and W annealed in hydrogen at 350 °C have the same hexagonal phase (see Figure 1). In general, as for WH series samples, the crystal phase gradually changes with the annealing temperature and time, while the crystal phase is maintained until the temperature rose up to 450  $\,^{\circ}\text{C}$  for W series samples.

The information on the o-WO<sub>3</sub>·0.33H<sub>2</sub>O hierarchical nanostructures assembled with nanorods and h-WO3 hierarchical nanostructures assembled with ultrathin nanobelts has been fully discussed in our previous study.<sup>40</sup> The SEM images of the samples prepared under different annealing conditions are shown in Figures S2 and S3 (SI) and the selective enlarged images are shown in Figure 2. As for the WH series samples shown in Figures 2a–c and S2 (SI), the morphology of samples (WH-A250, WH-A300-0.5h/2h/4h/6h/8h, WH-A350, and WH-A400) undergo little change when the annealing temperature is below 400 °C and the annealing time is less than 8 h, compared with the unannealed sample. But Figure 2d shows that the building blocks of WH-A450 hierarchical nanostructure become shorter and thicker nanorods or even nanoparticles compared with the thinner ones in the unannealed sample, indicating a process where nanorods collapse at 450 °C. Similarly, Figures 2e-i and S3 (SI) show that the W series samples maintain similar morphology with the unannealed sample when the annealing temperatures are below 400 °C. The sample exhibits serious deformation when annealed at 450 °C (Figure 2h), where the nanobelts become small nanoparticles and the nanoparticles become bigger when the temperature increases to 600 °C (Figure 2i). Besides, when prolonging the annealing time from 0.5 to 8 h at 350 °C (Figure S3, SI), part of the nanobelts begins to transform into nanoparticles after 4 h, suggesting that the nanobelts gradually deform upon annealing. These phenomena suggest that the



Figure 2. SEM images of samples WH or W annealed under different conditions: (a) WH-A300 (2 h), (b) WH-A300-8h, (c) WH-A350, (d) WH-A450, (e) W-A300, (f) W-A350, (g) W-A400, (h) W-A450, and (i) W-A600.



Figure 3. W 4f XPS spectra of (a) WH (unannealed), (b) WH-A350, (c) WH-H350, (d) W (unannealed), (e) W-A350, and (f) W-H350.

intensity variation of  $I_{(100)}/I_{(002)}$  of the XRD patterns with the annealing time in Figure S1b (SI) is perhaps attributed to the deformation of the nanobelts. To sum up, the morphology of WH series samples annealed in air or hydrogen for 0.5–8 h shows no obvious change until the temperature was raised to 450 °C, while as for W series samples, the nanobelts would undergo a process of deformation during the annealing.

**3.2. The Existence of Oxygen Vacancies.** Figure 3 is the XPS spectra of o-WO<sub>3</sub>.0.33H<sub>2</sub>O (WH) and h-WO<sub>3</sub> (W) crystals and samples annealed at 350 °C in air or hydrogen. As

shown in the W 4f XPS spectra of WH (Figure 3a) and WH-A350 (Figure 3b), two peaks centered at 35.8 and 37.9 eV correspond to the characteristic W  $4f_{5/2}$  and W  $4f_{7/2}$  peaks of W<sup>6+</sup>.<sup>21</sup> In comparison to sample WH, which only has the binding energies of the W<sup>6+</sup> state, the peaks of the WH-A350 are slightly broader with a shoulder at the lower binding energy region. The two extra peaks centered at 37.0 and 34.6 eV correspond to the typical binding energies of W<sup>5+</sup>.<sup>21</sup> W<sup>5+</sup> usually has a great relationship with oxygen vacancies.<sup>21,23</sup> In addition, the sample WH-H350 only has the binding energies



Figure 4. ESR spectra (T = 108 K) of the as-prepared tungsten oxides: sample WH annealed at different temperatures (a) and times (c) and the corresponding intensity of the ESR signal (b and d) and sample W annealed at different temperatures (e) and times (g) and the corresponding intensity of the ESR signal (f and h) (/2 and/4 mean dividing the intensity of the ESR signal by two or four; In = intensity).



Figure 5. TEM images of (a) WH, (b) WH-A350, (c) W, and (d) W-A350.

(centered at 37.1 and 34.9 eV) of the W5+ state, indicating a high degree of reduction in the hydrogen atmosphere. Similarly, the sample W only has the binding energies of the W<sup>6+</sup> state, while in the sample W-A350, besides the peaks centered at 35.8 and 38.0 eV ( $W^{6+}$ ), the peaks at 37.2 and 34.7 eV can also be observed, suggesting the appearance of W<sup>5+</sup>, as shown in Figure

3d,e. As for W-H350, the intensities of peaks representing  $W^{5+}$ are higher than that of W-A350 (Figure 3f). In summary, the XPS results show that not only samples annealed in hydrogen but also samples annealed in air at 350 °C have W<sup>5+</sup>. The W<sup>5+</sup> may mainly distribute on the surface of the samples, since XPS spectra are surface-sensitive.<sup>41</sup>

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Figure 6. Curves of the UV-vis absorbance spectra (a, c) and Kubelka–Munk function plotted against the photon energy (b, d): (a, b) sample WH and WH annealed in air or hydrogen at 350 °C and (c, d) sample W and W annealed in air or hydrogen at 350 °C.



Figure 7. (a) Three different crystal structures of tungsten oxide. (b) The possible phase transition process of tungsten oxide. (c) Schematic models of three different free-standing nanomaterials with tensile surface stress resulting in intrinsic compressive stress in the cores.

To further confirm the existence of defects, verify the formation of defects, and identify the defect species in annealed samples, the ESR spectroscopy was employed, as displayed in Figure 4. Since the ESR signal intensity is related to the density of the defects, we can compare the contents of the defects in different samples through measuring the intensity of the signal.<sup>33</sup> The calculated ESR signals are shown in Figure 4b,d,f,i. As shown in Figure 4a, similar to the sample annealed in hydrogen (WH-H350), a signal located at g = 2.003 also appears in the samples WH-A300 and WH-A350, suggesting that there exist oxygen vacancies in the air-treatment

samples.<sup>33,42</sup> The sample WH-H350 has expectedly the highest intensity signal, followed by the sample annealed in air at 300 °C (WH-A300), which has a much stronger signal than the sample WH-A350. No signals were detected for either the unannealed sample (WH) or WH-A400, as shown in Figure 4a,b. As for hydrothermally synthesized h-WO<sub>3</sub> (W) and its annealed samples, the signal located at g = 2.003 also appears in air-treated sample W-A350 and W-A400, as shown in Figure 4e. The sample W annealed at 350 °C (W-A350) in air contains more oxygen vacancies than the sample W annealed at 400 °C (Figure 4f). Beside the annealing temperature, the annealing



Figure 8. Raman spectra of the samples prepared under different annealing conditions.



Figure 9. Photodegradation of RhB by sample WH (a) annealed at different temperatures and (b) at 300  $^{\circ}$ C for 0.5–8 h and sample W (c) annealed at different temperatures and (d) at 350  $^{\circ}$ C for 0.5–8 h.

time also would influence the oxygen vacancy concentration. As shown in Figure 4c,d,g,h, the WH and W series samples show similar variation, i.e., when prolonging the annealing time from 0.5 to 8 h, the ESR signal at g = 2.003 first intensifies, reaching the maximum at 2 h, and then weakens with time. The ESR results suggest that the W<sup>5+</sup> observed in the XPS spectra may be due to the presence of oxygen vacancies. In summary, annealing in air at a certain temperature could introduce oxygen vacancies in tungsten oxide hierarchical structures assembled with 1D nanostructure, and high temperature and long annealing time usually would decrease the oxygen vacancies.

Further information about the defect structures of the samples can be investigated through the high-resolution

transmission electron microscopy (HRTEM) images, as shown in Figure 5. The sample WH shows a lattice spacing of about 0.386 nm, corresponding to the (002) plane of orthorhombic WO<sub>3</sub>·0.33H<sub>2</sub>O, and the lattice spacing of WH-A350 (about 0.382 nm) is assigned to the (002) plane of hexagonal WO<sub>3</sub>. Differently, the unannealed sample WH displays a perfect lattice feature, but the edge of the nanorod in WH-A350 containing oxygen vacancies becomes disordered (about 4 nm thick), indicating that the surface structure is damaged. Moreover, the lattice fringe with a spacing of 0.266 nm indexed to the (202) plane of o-WO<sub>3</sub>·0.33H<sub>2</sub>O is also observed in the nanorods of the sample WH-A350 from the enlarged picture of the square-enclosed area shown in Figure



Figure 10. Recyclability of W-A350.

S4a,b (SI). However, the XRD pattern shows that the sample WH-A350 has transformed to h-WO<sub>3</sub>. Besides, near the lattice fringe of (202) (the two rectangular frames in the Figure S4b, SI), the mismatch of adjacent fringes are also observed, suggesting that this area might be a transition region.<sup>43,44</sup> The mismatched fringes in the transition region are usually related to planar oxygen vacancies.<sup>35,45</sup> There may also exist oxygen vacancies in the bulk, but further study is needed. Similarly, W-A350 nanobelt also shows a lattice-disordered layer (about 2 nm thick). This suggests that the oxygen vacancies are formed on the surface of the nanorods or nanobelts.<sup>42,46–49</sup> Additionally, the top of the nanobelt in sample W (Figure 4c) is angular, but that of W-A350 (Figure 5d) become smooth and deformed. Thus, by considering the SEM images, the process of the deformation of nanobelts over varying annealing temperatures and times can be illustrated in Scheme S1 (SI).

To examine the effects of oxygen vacancies on the light absorbability and band gap energy of the air-treated and hydrogen-treated samples, UV-vis absorbance spectra and plots of  $(\alpha h\nu)^2$  versus photoenergy  $h\nu$  of the absorbed light are Article

Scheme 1. Illustration of the Photocatalytic Mechanism for Air-Treated WO<sub>3</sub> Containing Oxygen Vacancies



generated and shown in Figure 6. It shows that the absorption edges are red-shifted and the band gaps are narrowed both for air-treated and hydrogen-treated samples compared with unannealed samples, and the hydrogen-treated samples show stronger visible-light absorption and a more obviously narrowed band gap compared with the air-treated samples. These results clearly show that the oxygen vacancies successfully introduced by air and hydrogen treatment could effectively extend the visible-light absorption of tungsten oxide.<sup>29</sup>

**3.3. The Formation Mechanism of Defects in Air-Treated Samples.** From the above analysis, it is certain that there exist oxygen vacancies in the samples annealed in air or hydrogen at certain temperatures. It is well-known that hydrogen treatment can introduce oxygen vacancies.<sup>23,50,51</sup> It is thought that oxygen vacancies would decrease through airannealing;<sup>26,51,52</sup> however, oxygen vacancies were found in our air-treated samples. As for the WH series samples, the processes that introduce oxygen vacancies take place in the samples annealed at 300 and 350 °C. The SEM images in Figure 2a–c show that the samples' morphology undergoes little change, and the XRD patterns in Figures 1a and S1a (SI) reveal the critical phase transitions from o-WO<sub>3</sub>·0.33H<sub>2</sub>O to h-WO<sub>3</sub> at



**Figure 11.** ESR spectroscopy of DMPO (DMPO- $\bullet$ OH) with the samples WH, WH-A350, WH-A450, and WH-H350 (a, b) and the samples W, W-A350, and WH-H350 (c, d) in aqueous solution with visible- or UV-light irradiation.



Figure 12. CVs and specific capacitance calculated at different scan rates of (a, b) samples WH, WH-A350, WH-A400, and WH-H350 and (c, d) samples W, W-A350, W-A600, and W-H350. Specific capacitance of (e) sample WH annealed at 300 °C for 0.5-8 h and (f) sample W annealed at 350 °C for 0.5-8 h.

these two temperatures. Some references reported that phase transformation could introduce the oxygen vacancies in air-treatment materials such as ZnS and  $In_2O_3$ .<sup>32,33</sup> Therefore, it is suggested that the phase transition could be an important cause for the appearance of oxygen vacancies in the air-treated tungsten oxide. A scheme for the phase transformations of tungsten oxides from orthorhombic to hexagonal then to monoclinic is suggested in Figure 7a. The o-WO<sub>3</sub>·0.33H<sub>2</sub>O structure consists of layers in which [WO<sub>6</sub>] octahedra share their corners and form six-membered rings along the (001) plane. These layers stack along the [001] direction, with every other layer shifted by a/2, as shown in Figure 7a(I). The h-WO<sub>3</sub> has structure similar to the orthorhombic one but without a displacement of 1/2a, thus forming a hexagonal tunnel structure [Figure 7a(II)]. The monoclinic structure is composed of [WO<sub>6</sub>] octahedra connected by covalent bonds in every corner, also forming a stacked layer structure [Figure 7a(III). Besides the  $[WO_6]$  octahedron in which all bonds are W–O [see Figure 7a(I) position 1 and Figure 7b(II)], o-WO<sub>3</sub>.  $0.33H_2O$  has another octahedron,  $[WO_5(H_2O)]$ , in which the other two W-O are substituted by a shorter terminal W=O bond and a longer W–OH<sub>2</sub> bond [see Figure 7a(I) position 2 and Figure 7b(I)].<sup>53</sup> As for the other two structures, they only have the  $[WO_6]$  octahedron, in which all bonds are W–O. In general, the phase transformation originates from the atomic displacement in going from orthorhombic to hexagonal then to monoclinic tungsten oxide, driven by thermal energy. In these transition processes, the rearrangement of W-O atom pairs opportunistically leaves some delocalized atoms and dangling bonds behind ascribed to the crystalline mismatch of two

phases with different lattice constants, giving rise to crystal defects.<sup>33,35,36</sup> The detailed transition processes are shown in Figure 7b. The transition process may include the process of  $[WO_5(H_2O)]$  dehydration, the disruption of W–O bonds in  $[WO_6]$ , and the reconstruction to a new network. As illustrated in Figure 7b(I), before  $[WO_5(H_2O)]$  reconstructs to a new  $[WO_6]$ , it may have an intermediate state that generates  $[WO_5]$ with a dangling bond or oxygen vacancy, occurring in the transformation from o-WO<sub>3</sub>·0.33H<sub>2</sub>O to h-WO<sub>3</sub>. Meanwhile, the disruption of W-O bonds during transformation is also shown in Figure 7b(II). When the W–O atom pair in position A disrupts, a W–O atom pair can move from B position to C position during the layer shifting in order to complete structure reconstruction. If the temperature is not high enough and time is not long enough, the process cannot be finished completely, thus leaving some [WO<sub>5</sub>] octahedra in a transition state. Once the temperature rises and time prolongs, the process can be finished, with the concentration of defects decreasing. This process can happen in the transition of orthorhombic to hexagonal and hexagonal to monoclinic. The transition from o-WO<sub>3</sub>·0.33H<sub>2</sub>O to h-WO<sub>3</sub> could more easily introduce defects, since dehydration produces more dangling bonds or oxygen vacancies and happens at relatively lower temperature, at which the defects can be maintained. Correspondingly, WH-A300 shows a much stronger ESR signal than WH-A350 and WH-A300-4h/6h/8h (see Figure 4).

The critical phase transition mechanism could be further confirmed by the Raman spectra. Raman spectroscopy is an effective way to study subtle changes of the crystal structure, since Raman spectra are very sensitive to the bond vibration changes that may be caused by the phase transition and the defects.<sup>54</sup> The peaks centered at about 251, 685, 803, and 950  $cm^{-1}$  in sample WH are assigned to the orthorhombic WO<sub>3</sub>.  $0.33H_2O_1$ , as shown in Figure 8a. The peak at 251 cm<sup>-1</sup> is assigned to the W-O-W bending vibration of the bridging oxygen  $[\delta(W-O-W)]$ . The peaks at around 685 and 803 cm<sup>-1</sup> are attributed to the stretching vibration of O–W–O [ $\nu$ (O– W-O]<sup>40</sup> The peaks around 950 cm<sup>-1</sup> are assigned to the stretching mode of the terminal W=O bond, which is a typical peak for all types of tungsten trioxide hydrates.<sup>55</sup> WH-A250 maintains spectra similar to those of WH but with stronger intensity. Remarkably, the peak of WH-A300 red shifts from 803 to 806 cm<sup>-1</sup> and the peak around 950 cm<sup>-1</sup> is declined compared with that of WH, suggesting the change of the hydrous structure of WH-A300. Moreover, when the annealing time varies from 0.5 to 8 h at 300 °C, the peaks originally at about 803, 685, and 950 cm<sup>-1</sup> gradually red shift within 2 h and then the position of the peaks remains unchanged in the last 6 h, suggesting that the crystal structure becomes stable in the last 6 h (Figure S5a, SI). As the temperature increases to 350 °C, the peak originally at 685 cm<sup>-1</sup> shifts to 691 cm<sup>-1</sup> and the peak originally at about 803 cm<sup>-1</sup> splits into two peaks: the peak at 816 cm<sup>-1</sup> belongs to the stretching vibration of O-W-O of h-WO<sub>3</sub><sup>56</sup> and a new peak at about 788 cm<sup>-1</sup> is present for WH-A350, but it is not seen for the samples WH-A400 and WH-A450 (all are h-WO<sub>3</sub>). The appearance of the new peak may be related to the oxygen vacancies.<sup>23,29,47</sup> The peaks (685, 803, and 950 cm<sup>-1</sup>) belonging to o-WO<sub>3</sub>·0.33H<sub>2</sub>O disappear, suggesting that the sample has transformed to h-WO<sub>3</sub> or quasi-h-WO3 at 350 °C. The transition process, including the process of  $[WO_5(H_2O)]$  dehydration, the disruption of W–O bonds in  $[WO_6]$ , and reconstruction to a new network, would cause the variation of the Raman spectra, such as the position variation and decreased symmetry, which correlate with the production of oxygen vacancies.<sup>21,47</sup>

The critical phase transition may explain the defect formation introduced by air treatment in the WH series samples. However, it cannot well explain the formation of oxygen vacancies in the W series samples, in which the oxygen-vacancycontaining samples do not experience a phase transition [Figures 1b and S1b (SI)]. In order to further investigate the oxygen vacancy formation mechanism in the W series samples, the Raman spectra shown in Figures 8b and S5b (SI) are studied. The nanorod-like sample WH-A400 and nanoparticlelike sample W-A450 are both h-WO3 and have the same Raman peaks positioned at about 251 cm<sup>-1</sup> [ $\delta$ (W–O–W)], 691 cm<sup>-1</sup>  $[\nu(O-W-O)]$ , and 816 cm<sup>-1</sup>  $[\nu(O-W-O)]$ , while the Raman spectrum of the nanobelt-like sample W (h-WO<sub>3</sub>) has only one weak peak at about 780 cm<sup>-1</sup>, suggesting the unique structure of the nanobelt (such as ultrathin character and small diameter).<sup>40</sup> With the annealing temperature increasing from 300 to 450  $^{\circ}\mathrm{C}$  and annealing time varing from 0.5 to 8 h, the Raman peaks of the W series samples gradually changed along with the deformation of the nanobelts [Figures 8b, S5b (SI), 2e-i, and S3 (SI)]. Since the other peaks only change the intensity (251 and 691 cm<sup>-1</sup>), the peak shifts of 788 and 815  $cm^{-1}$  may be related to the deformation of nanobelts: (1) samples W-A300 and W-A350, with a peak at 788  $\rm cm^{-1}$  but without a peak at 816  $\text{cm}^{-1}$ , keep the nanobelt morphology; (2) in W-A400, which has peaks at 788 and 815 cm<sup>-1</sup>, some nanobelts have collapsed and aggregated; and (3) the stronger the peak at 816 cm<sup>-1</sup>, the more serious the deformation of the nanobelts; for example, the nanobelts in the sample W-A450

completely change to nanoparticles. The relation between the deformation of nanobelts and the variation of the peaks at 788 and 815 cm<sup>-1</sup> can be further confirmed by the Raman spectra of samples annealed at 350 °C for various times (Figure S5b, SI). The intensity ratio of 815/788 increases as the annealing time increases. Both the peaks at 788 and 815 cm<sup>-1</sup> can be assigned to the stretching vibration of O–W–O of hexagonal WO<sub>3</sub>. The variation of Raman spectra, including the change of peak intensity ratios and peak positions, suggests the change of W–O bonds, which may be related to deformation-induced lattice disorder on the surface of nanobelts (Figure 5d).<sup>47,55,58</sup>

The lattice disorder on the surface of nanobelts, suggesting the existence of oxygen vacancies, may be due to the inhomogeneous deformation of the nanobelts upon raising the annealing temperature and time.<sup>42,46</sup> Nanomaterials usually have large surface-to-volume atom ratios, thus making them have more dangling atoms on the surface, which increases the surface energy and the broken atomic symmetry on the surface. The surface energy is usually orientation-dependent and anisotropic.<sup>59</sup> As shown in Figure 7c, a zero-dimensional (0D) nanoparticle [Figure 7c(III)] has hydrostatic stress, a 1D nanorod is subjected to triaxial stress with a larger component along the rod axis (Figure 7c(I)), and an ultrathin 1D nanobelt may also be regarded as a 2D film, which experiences in-plane biaxial stress [Figure 7c(II)]. This suggests that different dimensional nanomaterials may have different surface conditions.<sup>60</sup> When subjected to some driving force, such as high temperature and long annealing time, they may behave differently. Because the nanobelts in our samples are ultrathin and the diameter is small, the deformation of nanobelts would be more unsynchronized in different parts than other dimensional materials (nanorods and nanoparticles). It can be confirmed by the phenomenon that the oxygen vacancies signal was found in the sample W-A400 assembled with nanobelts but not in the sample WH-A400 assembled with nanorods. Moreover, the deformation occurs more easily on surfaces of the nanobelts, which have much higher energy and are more unsymmetrical than the bulk, thus generating a disordered layer on the surface, as shown in Figure 5d.<sup>59</sup> This nanoscale inhomogeneous deformation induced lattice disorder should be one important cause of the variation of the (100) and (002)diffraction peaks of XRD and the shifts of Raman peaks at 788 and 815 cm<sup>-1</sup>. Meanwhile, the oxygen vacancies could only exist at certain temperature where the lattice disorder may occur and be maintained without obvious morphology change. Once the morphology changes substantially, the oxygen vacancies would decrease (W-A350-4h/6h/8h) or even disappear (W-A450). From the above analysis, it is inferred that the nanoscale inhomogeneous deformation derived by a proper heat treatment introduces the oxygen vacancies in the W series samples. To sum up, both critical phase transition and nanoscale inhomogeneous deformation would introduce oxygen vacancies, and it seems that the critical phase transition is more effective in introducing oxygen vacancies, since WH-A300 shows much stronger ESR signals than other air-treated samples (Figure 4).

**3.4. Photocatalytic Performance.** On the basis of the above results and discussions, it is imperative to study the overall effect of the introduced oxygen vacancies on the photocatalytic property of tungsten oxides under visible-light illumination. The visible-light-driven photocatalytic performances of the WH and W series samples to degrade RhB are shown in Figure S6 (SI). The degradation processes are fitted

to pseudo-first-order kinetics, and the value of the rate constants  $\kappa$  are equal to the corresponding slope of the fitting lines (Figure S6b,d,f,h, SI) and are presented in Figure 9, respectively. As for WH annealed at different temperatures shown in Figure 9a, the photodegradation efficiency increases with the annealing temperature rising to 350 °C. When the temperature is higher than 400 °C, the performance decreases obviously. Besides, the sample WH-H350 annealed in hydrogen shows a significant photocatalytic activity decline compared with the unannealed samples. Besides the annealing-temperature-related photocatalytic activity of WH series samples, the annealing-time-dependent photocatalytic activity is also presented in Figure 9b. The photocatalytic performance increases in the first 2 h and then decreases. Among the WH series samples, the sample WH-A350 shows the highest photocatalytic performance, which can degrade 95% RhB in 100 min (see Figure S6a, SI) with a rate constant reaching  $0.0300 \text{ min}^{-1}$ . Figure 9c,d presents the visible-light-driven photocatalytic performance of the W series samples. As shown in Figure 9c, the samples exhibit enhanced performance as the temperature increases to 350 °C. When the temperature continues to increase, the performance decreased rapidly. The same variation occurs for W-H350 compared with WH-H350. In addition, when sample W was annealed at 350 °C for 0.5-8 h, the performances of all the samples are higher than that of sample W, and the highest performance is achieved at 2 h (Figure 9d). Among the W series samples, W-A350, which can degrade 94% of RhB (see Figure S5e, SI) with a rate constant of 0.0267  $\min^{-1}$ , shows the best performance. Figure 10 shows the recyclability of W-A350 in the photocatalytic decomposition of RhB. W-A350 shows high performance stability with only a slight decrease after six cycles.

There are many factors that influence the photocatalytic performance. As for sample WH annealed at different temperatures, the highest performance is achieved in the sample WH-A350, which has similar morphology to sample WH but with slightly decreased specific surface area (Table S1, SI) and different crystal phase (WH-A350, hexagonal; WH, orthorhombic). It seems that the hexagonal phase performs better than the orthorhombic phase. However, WH-A400 also has hexagonal phase and a morphology similar to that of sample WH, but it demonstrates significantly declined performance. Besides, orthorhombic WH shows much greater photocatalytic performance than the hexagonal sample W, although sample W has a much higher specific surface area than WH (Table S1, SI). Moreover, the W series samples, except W-A600, all have the same hexagonal phase but exhibit different performances. This all indicates that crystal phase does not directly determine the photocatalytic performance. From the SEM images, it is known that when the temperature is below 400 °C, the samples (both WH and W series samples) maintain a morphology similar to that of the unannealed sample. In addition, the specific surface areas decrease upon increasing the annealing temperature and prolonging the annealing time, which does not follow the same trend as the photocatalytic performance. On the contrary, the trend of the photocatalytic activities is similar to that of the density variation of oxygen vacancies. Moreover, when excluding the contribution of specific surface areas, the rate constants per specific surface area (Figure S7, SI) also show a variation similar to that of the concentration change of oxygen vacancies (Figure 4). These facts suggest that the highly improved performance of WH-A300, WH-A350, W-A350, and W-A400 is attributed to the proper amount of oxygen vacancies

being introduced by air treatment. Too many defects have a negative effect, as seen, for example, in the hydrogen annealed samples WH-H350 and W-H350. Additionally, from Figure S7 and Table S1 (SI), it may be inferred that the obvious decreased specific surface areas mainly lead to the remarkably decreased performance of WH-A450 and W-A600. Similarly, when prolonging the annealing time, the number of oxygen vacancies first increases and then decreases, showing a trend similar to that of the photocatacalytic performances. These results demonstrate that the number of oxygen vacancies determined the visible-light photocatalytic activities of our defective tungsten oxide systems.

The results can also be confirmed by ESR spectroscopy, as shown in Figure 11. DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) is a nitrone spin trap generally used for trapping radicals, i.e., DMPO-hydroxyl radical (DMPO-•OH) and DMPO-superoxide radical (DMPO $-\bullet O_2^-$ ). A quartet signal characteristic of the DMPO-•OH adduct with an intensity of 1:2:2:1 is observed under visible- and UV-light irradiation at room temperature for all the samples, as presented in Figure 11. The samples annealed in air at 350 °C (WH-A350 and W-A350) show the strongest signal of DMPO-•OH among the samples that contain few (WH, W, and W-A450) or too many oxygen vacancies (WH-H350 or W-H350) under visible- or UV-light irradiation, suggesting a consistent variation with the photocatalytic performance shown in Figure 9. Meanwhile, the signal of superoxide radicals ( $\bullet O_2^-$ ) was also detected by ESR, as shown in Figure S6 (SI). No obvious signals were observed in the samples W, W-A350, and W-H350, suggesting that the single-electron reduction of  $O_2$  to  $\bullet O_2^-$  may not be feasible for the present samples and that •OH plays the major role in photodegrading the RhB.

The mechanism for air-treatment-introduced oxygen-vacancy-dependent visible-light-driven photocatalytic activity is illustrated in Scheme 1. Many researchers reported that the introduction of oxygen vacancies, especially surface oxygen vacancies, would appear above and partly overlap the valence band (VB), thus resulting in the rising of the valence band maximum (VBM) and the narrowing of the band gap width, expanding the photoresponse wavelength range.<sup>29,42,46-48</sup> The rising of the VBM can also expand the VB width, which contributes to increasing the transport rate of photoinduced carriers, leading to enhancement of the separation efficiency of photoinduced electron-hole pairs; thus, more electrons and holes can participate in the photodegradation process.<sup>47</sup> For the samples annealed in hydrogen containing an abundance of oxygen vacancies, the excess oxygen vacancies in tungsten oxide could be recombination centers of photoelectrons and holes.<sup>32</sup>

**3.5. Electrochemical Performance.** In order to investigate the electrochemical performance of the materials, CVs and EIS were carried out within the potential range from -0.5 to 0 V (vs Ag/AgCl) in a three-electrode cell. CVs at scan rate of 20 mV s<sup>-1</sup> shown in Figure 12a,c present a near-rectangular and symmetric shape, indicating a typical pseudocapacitive behavior. The calculated specific capacitances of the samples at different scan rates are shown in Figure 12b,d. W-A350 with a specific capacitance of 166.7 F/g at 2 mV s<sup>-1</sup> performs best. For the samples WH-A350, WH-A400, and WH-H350, which are all h-WO<sub>3</sub> and have similar morphology, the specific capacitances follow the sequence WH-A350 > WH-H350 > WH-A400, suggesting that the oxygen vacancies contained in the materials play a significant role in their electrochemical performance, since oxygen vacancies with a proper concen-

tration could improve both the conductivity and activity of electrodes, while superabundant oxygen vacancies might destroy the hexagonal tunnel structure, which is unbeneficial for the electrochemical performance.<sup>16,61</sup> The rule also applies to W, W-A350, and W-H350. When the sample WH was annealed at 300 °C, the specific capacitance first decreases (0.5 h), then increases (2-4 h), and finally decreases (6-8 h), as shown in Figure 12e. The annealed samples contain abundant oxygen vacancies, but the crystal structure that changed (Figure S1a, SI) during the annealing may destroy the ion channel, thus leading to the decreased electrochemical performance.<sup>61</sup> As the annealing time increases, the phase transition gradually completes and the crystal structure becomes stable. As a result, the specific capacitances increase in the last 6 h compared with the first 2 h. For the W series samples, the crystal phases show inconspicuous change. The variation of the specific capacitance follows the same trend as the change in the density of oxygen vacancies when the sample W was annealed at 350 °C for 0.5-8 h (Figure 12f). Remarkably, the samples obtained by heattreating h-WO<sub>3</sub> (W) perform better than those by obtained by heat-treating o-WO3.0.33H2O (WH) using the same procedure, i.e., the specific capacitances WH < W, WH-A350 < W-A350 and WH-H350 < W-H350. There may be two factors leading to these results: (1) the sample assembled with nanobelts has a bigger surface area and could provide more active sites than the samples assembled with nanorods or nanoparticles (Table S1, SI); (2) the hexagonal tunnel structure can readily facilitate the inset of Li+, followed by an orthorhombic structure.9 Thereby, W-A350 presents the best performance, benefiting from its hierarchical nanostructures assembled with nanobelts, hexagonal tunnel structure, and a proper concentration of oxygen vacancies. Figure S8 (SI) shows the EIS of the WH and W and their annealed samples. It is noted that the values of  $R_{ct}$  follow the sequence WH-H350 < WH-A350 < WH < WH-A400 and W-H350 < W-A350 < W< W-A600, suggesting that a high concentration of oxygen vacancies would result in a high conductivity.

## 4. CONCLUSION

In summary, the defective tungsten oxides are constructed by critical phase transition or nanoscale inhomogeneous deformation through air treatment at different temperatures and times. The oxygen vacancies could be produced in the process of o-WO<sub>3</sub>·0.33H<sub>2</sub>O transforming to h-WO<sub>3</sub> through air-annealing at 300 and 350 °C. Meanwhile, the nanoscale inhomogeneous deformation of tungsten oxide nanobelts via air-annealing at 350 and 400 °C also can introduce oxygen vacancies. The photocatalysis experiment results show that the photocatalytic property can be enhanced by introducing a proper amount of oxygen vacancies. Moreover, the oxygen vacancies introduced by air-annealing could effectively improve the electrochemical performance of tungsten oxides.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00457.

XRD patterns and SEM images of samples WH and W annealed at different temperatures and times, TEM of samples WH-A350 and W, an illustration of the deformation process of nanobelts, the Raman spectra of sample WH annealed at 300 °C or W annealed at 350 °C for 0.5–8 h, concentration change of RhB solution versus irradiation time and corresponding pseudo-first-order linear fitting results, specific rate constants ( $k/S_{BET}$ ) of the samples in degrading RhB,  $S_{BET}$  of samples, ESR spectra of radical adduct trapped by DMPO (DMPO– $\bullet$ O<sub>2</sub><sup>-</sup>), and EIS curves of samples (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) Santos, L.; Wojcik, P.; Pinto, J. V.; Elangovan, E.; Viegas, J.; Pereira, L.; Martins, R.; Fortunato, E. Structure and Morphologic Influence of WO<sub>3</sub> Nanoparticles on the Electrochromic Performance of Dual-Phase a-WO<sub>3</sub>/WO<sub>3</sub> Inkjet Printed Films. *Adv. Electron. Mater.***2015**, *1*, DOI: 10.1002/aelm.201570001.

(2) Rettie, A. J. E.; Klavetter, K. C.; Lin, J.; Dolocan, A.; Celio, H.; Ishiekwene, A.; Bolton, H. L.; Pearson, K. N.; Hahn, N. T.; Mullins, C.
B. Improved Visible Light Harvesting of WO<sub>3</sub> by Incorporation of Sulfur or Iodine: A Tale of Two Impurities. *Chem. Mater.* 2014, 26, 1670–1677.

(3) Yao, M.; Li, Q.; Hou, G.; Lu, C.; Cheng, B.; Wu, K.; Xu, G.; Yuan, F.; Ding, F.; Chen, Y. Dopant-Controlled Morphology Evolution of WO<sub>3</sub> Polyhedra Synthesized by RF Thermal Plasma and Their Sensing Properties. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2856–2866.

(4) Huang, Z. F.; Song, J. J.; Pan, L.; Zhang, X. W.; Wang, L.; Zou, J. J. Tungsten Oxides for Photocatalysis, Electrochemistry, and Photo-therapy. *Adv. Mater.* **2015**, *27*, 5309–5327.

(5) Liu, X.; Wang, F. Y.; Wang, Q. Nanostructure-Based WO<sub>3</sub> Photoanodes for Photoelectrochemical Water Splitting. *Phys. Chem. Chem. Phys.* 2012, 14, 7894–7911.

(6) Sun, P.; Deng, Z. W.; Yang, P. H.; Yu, X.; Chen, Y. L.; Liang, Z. M.; Meng, H.; Xie, W. G.; Tan, S. Z.; Mai, W. J. Freestanding CNT-WO<sub>3</sub> Hybrid Electrodes for Flexible Asymmetric Supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 12076–12080.

(7) Zhu, M.; Meng, W.; Huang, Y.; Huang, Y.; Zhi, C. Proton-Insertion-Enhanced Pseudocapacitance Based on the Assembly Structure of Tungsten Oxide. *ACS Appl. Mater. Interfaces* **2014**, *6*, 18901–18910.

(8) Salmaoui, S.; Sediri, F.; Gharbi, N.; Perruchot, C.; Jouini, M. Hexagonal Hydrated Tungsten Oxide Nanomaterials: Hydrothermal Synthesis and Electrochemical Properties. *Electrochim. Acta* **2013**, *108*, 634–643.

(9) Sun, W.; Yeung, M. T.; Lech, A. T.; Lin, C.; Lee, C.; Li, T.; Duan, X.; Zhou, J.; Kaner, R. B. High Surface Area Tunnels in Hexagonal WO<sub>3</sub>. *Nano Lett.* **2015**, *15*, 4834–4838.

(10) An, X.; Yu, J. C.; Wang, Y.; Hu, Y.; Yu, X.; Zhang, G. WO<sub>3</sub> Nanorods/Graphene Nanocomposites for High-Efficiency Visible-Light-Driven Photocatalysis and NO<sub>2</sub> Gas Sensing. *J. Mater. Chem.* **2012**, *22*, 8525–8531.

(11) Royer, S.; Duprez, D.; Can, F.; Courtois, X.; Batiot-Dupeyrat, C.; Laassiri, S.; Alamdari, H. Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality. *Chem. Rev.* **2014**, *114*, 10292–10368.

(12) Naldoni, A.; Allieta, M.; Santangelo, S.; Marelli, M.; Fabbri, F.; Cappelli, S.; Bianchi, C. L.; Psaro, R.; Dal Santo, V. Effect of Nature and Location of Defects on Bandgap Narrowing in Black TiO<sub>2</sub> Nanoparticles. J. Am. Chem. Soc. **2012**, 134, 7600–7603.

(13) Pan, X.; Yang, M.; Fu, X.; Zhang, N.; Xu, Y. Defective TiO<sub>2</sub> with Oxygen Vacancies: Synthesis, Properties and Photocatalytic Applications. *Nanoscale* **2013**, *5*, 3601–3614.

(14) Zhang, L.; Wang, S.; Lu, C. Detection of Oxygen Vacancies in Oxides by Defect-Dependent Cataluminescence. *Anal. Chem.* **2015**, 87, 7313–7320.

(15) Tian, J.; Zhao, Z.; Kumar, A.; Boughton, R. I.; Liu, H. Recent Progress in Design, Synthesis, and Applications of One-Dimensional  $TiO_2$  Nanostructured Surface Heterostructures: A Review. *Chem. Soc. Rev.* 2014, 43, 6920–6937.

(16) Chen, C.; Xu, K.; Ji, X.; Zhang, B.; Miao, L.; Jiang, J. Enhanced Electrochemical Performance by Facile Oxygen Vacancies from Lower Valence-State Doping for Ramsdellite-MnO<sub>2</sub>. *J. Mater. Chem. A* **2015**, *3*, 12461–12467.

(17) Manthiram, K.; Alivisatos, A. P. Tunable Localized Surface Plasmon Resonances in Tungsten Oxide Nanocrystals. J. Am. Chem. Soc. 2012, 134, 3995–3998.

(18) Murphy, S.; Manai, G.; Shvets, I. V. Oxygen-Induced  $P(3 \times 1)$ Reconstruction of the W(100) Surface. *Surf. Sci.* **2005**, *579*, 65–72.

(19) Kim, H. S.; Kang, S. H. Effect of Hydrogen Treatment on Anatase  $TiO_2$  Nanotube Arrays for Photoelectrochemical Water Splitting. *Bull. Korean Chem. Soc.* **2013**, *34*, 2067–2072.

(20) Liu, Y.; Liu, C.; Li, J. Flexible Free-Standing Hydrogen-Treated Titanium Dioxide Nanowire Arrays as a High Performance Anode for Lithium Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 15746–15751.

(21) Wang, G.; Ling, Y.; Wang, H.; Yang, X.; Wang, C.; Zhang, J. Z.; Li, Y. Hydrogen-Treated WO<sub>3</sub> Nanoflakes Show Enhanced Photostability. *Energy Environ. Sci.* **2012**, *5*, 6180–6187.

(22) Wheeler, D. A.; Ling, Y.; Dillon, R. J.; Fitzmorris, R. C.; Dudzik, C. G.; Zavodivker, L.; Rajh, T.; Dimitrijevic, N. M.; Millhauser, G.; Bardeen, C.; et al. Probing the Nature of Bandgap States in Hydrogen-Treated TiO<sub>2</sub> Nanowires. J. Phys. Chem. C 2013, 117, 26821–26830.

(23) Cheng, L.; Hou, Y.; Zhang, B.; Yang, S.; Guo, J. W.; Wu, L.; Yang, H. G. Hydrogen-Treated Commercial WO<sub>3</sub> as an Efficient Electrocatalyst for Triiodide Reduction in Dye-Sensitized Solar Cells. *Chem. Commun.* **2013**, *49*, 5945–5947.

(24) LeGore, L. J.; Lad, R. J.; Moulzolf, S. C.; Vetelino, J. F.; Frederick, B. G.; Kenik, E. A. Defects and Morphology of Tungsten Trioxide Thin Films. *Thin Solid Films* **2002**, *406*, 79–86.

(25) Li, M.; Altman, E. I.; Posadas, A.; Ahn, C. H. Surface Phase Transitions and Related Surface Defect Structures upon Reduction of Epitaxial WO<sub>3</sub>(100) Thin Films: A Scanning Tunneling Microscopy Study. *J. Vac. Sci. Technol., A* **2004**, *22*, 1682–1689.

(26) Smith, A. M.; Kast, M. G.; Nail, B. A.; Aloni, S.; Boettcher, S. W. A Planar-Defect-Driven Growth Mechanism of Oxygen Deficient Tungsten Oxide Nanowires. *J. Mater. Chem. A* **2014**, *2*, 6121–6129.

(27) Wei, S. F.; Lian, J. S.; Wu, H. Annealing Effect on the Photoluminescence Properties of ZnO Nanorod Array Prepared by a PLD-assistant Wet Chemical Method. *Mater. Charact.* **2010**, *61*, 1239–1244.

(28) Ghosh, S.; Khan, G. G.; Mandal, K.; Samanta, A.; Nambissan, P. Evolution of Vacancy-Type Defects, Phase Transition, and Intrinsic Ferromagnetism during Annealing of Nanocrystalline TiO<sub>2</sub> Studied by Positron Annihilation Spectroscopy. *J. Phys. Chem. C* **2013**, *117*, 8458–8467.

(29) Wang, J.; Wang, Z.; Huang, B.; Ma, Y.; Liu, Y.; Qin, X.; Zhang, X.; Dai, Y. Oxygen Vacancy Induced Band-Gap Narrowing and Enhanced Visible Light Photocatalytic Activity of ZnO. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4024–4030.

(30) Chen, D.; Wang, Z.; Ren, T.; Ding, H.; Yao, W.; Zong, R.; Zhu, Y. Influence of Defects on the Photocatalytic Activity of ZnO. *J. Phys. Chem. C* **2014**, *118*, 15300–15307.

(31) Lei, F.; Sun, Y.; Liu, K.; Gao, S.; Liang, L.; Pan, B.; Xie, Y. Oxygen Vacancies Confined in Ultrathin Indium Oxide Porous Sheets

(32) Gan, J. Y.; Lu, X. H.; Wu, J. H.; Xie, S. L.; Zhai, T.; Yu, M. H.; Zhang, Z. S.; Mao, Y. C.; Wang, S.; Shen, Y.; et al. Oxygen Vacancies Promoting Photoelectrochemical Performance of  $In_2O_3$  Nanocubes. *Sci. Rep.* **2013**, *3*, 1021.

(33) Fang, Z. B.; Weng, S. X.; Ye, X. X.; Feng, W. H.; Zheng, Z. Y.; Lu, M. L.; Lin, S.; Fu, X. Z.; Liu, P. Defect Engineering and Phase Junction Architecture of Wide-Band gap ZnS for Conflicting Visible Light Activity in Photocatalytic H<sub>2</sub> Evolution. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13915–13924.

(34) Ding, B.; Qian, H.; Han, C.; Zhang, J.; Lindquist, S.; Wei, B.; Tang, Z. Oxygen Vacancy Effect on Photoluminescence Properties of Self-Activated Yttrium Tungstate. *J. Phys. Chem. C* **2014**, *118*, 25633– 25642.

(35) Al Mohammad, A.; Gillet, M. Phase Transformations in WO<sub>3</sub> Thin Films during Annealing. *Thin Solid Films* **2002**, *408*, 302–309.

(36) Ramana, C. V.; Utsunomiya, S.; Ewing, R. C.; Julien, C. M.; Becker, U. Structural Stability and Phase Transitions in WO<sub>3</sub> Thin Films. *J. Phys. Chem. B* **2006**, *110*, 10430–10435.

(37) Li, M.; Posadas, A.; Ahn, C. H.; Altman, E. I. Scanning Tunnelling Microscopy Study of Terminal Oxygen Structures on  $WO_3(100)$  Thin Films. *Surf. Sci.* **2005**, *579*, 175–187.

(38) Li, M.; Gao, W.; Posadas, A.; Ahn, C. H.; Altman, E. I. Reactivity of 1-Propanol on P (N x 2) Reconstructed  $WO_3(100)$  Thin Films. J. Phys. Chem. B 2004, 108, 15259–15265.

(39) Xu, D.; Jiang, T.; Wang, D.; Chen, L.; Zhang, L.; Fu, Z.; Wang, L.; Xie, T. pH-Dependent Assembly of Tungsten Oxide Three-Dimensional Architectures and Their Application in Photocatalysis. *ACS Appl. Mater. Interfaces* **2014**, *6*, 9321–9327.

(40) Li, Y.; Tang, Z.; Zhang, J.; Zhang, Z. Exposed Facet and Crystal Phase Tuning of Hierarchical Tungsten Oxide Nanostructures and their Enhanced Visible-Light-Driven Photocatalytic Performance. *CrystEngComm* **2015**, *17*, 9102–9110.

(41) Li, H.; Chen, J.; Xia, Z.; Xing, J. Microwave-Assisted Preparation of Self-Doped TiO<sub>2</sub> Nanotube Arrays for Enhanced Photoelectrochemical Water Splitting. *J. Mater. Chem. A* **2015**, *3*, 699–705.

(42) Lv, Y.; Zhu, Y.; Zhu, Y. Enhanced Photocatalytic Performance for the  $BiPO_{4x}$  Nanorod Induced by Surface Oxygen Vacancy. J. Phys. Chem. C 2013, 117, 18520–18528.

(43) Suzuki, T.; Wakabayashi, H.; Nishi, Y.; Fujimoto, M. Transmission Electron Microscopy Study of Defect Structure in Epitaxial  $\text{SnO}_2$  Rutile Thin Film. Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi **2002**, 110, 86–91.

(44) Huang, F.; Banfield, J. F. Size-Dependent Phase Transformation Kinetics in Nanocrystalline ZnS. J. Am. Chem. Soc. 2005, 127, 4523–4529.

(45) Zhou, J.; Ding, Y.; Deng, S. Z.; Gong, L.; Xu, N. S.; Wang, Z. L. Three-Dimensional Tungsten Oxide Nanowire Networks. *Adv. Mater.* **2005**, *17*, 2107.

(46) Wang, J.; Jiang, W.; Liu, D.; Wei, Z.; Zhu, Y. Photocatalytic Performance Enhanced via Surface Bismuth Vacancy of  $Bi_6S_2O_{15}$  Core/Shell Nanowires. *Appl. Catal., B* **2015**, *176-177*, 306–314.

(47) Lv, Y.; Liu, Y.; Zhu, Y.; Zhu, Y. Surface Oxygen Vacancy Induced Photocatalytic Performance Enhancement of a BiPO<sub>4</sub> Nanorod. J. Mater. Chem. A **2014**, 2, 1174–1182.

(48) Lv, Y.; Pan, C.; Ma, X.; Zong, R.; Bai, X.; Zhu, Y. Production of Visible Activity and UV Performance Enhancement of ZnO Photocatalyst via Vacuum Deoxidation. *Appl. Catal., B* **2013**, *138-139*, 26–32.

(49) Lv, Y.; Yao, W.; Ma, X.; Pan, C.; Zong, R.; Zhu, Y. The Surface Oxygen Vacancy Induced Visible Activity and Enhanced UV Activity of a ZnO<sub>1-x</sub> Photocatalyst. *Catal. Sci. Technol.* **2013**, *3*, 3136–3146.

(50) Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y. Hydrogen-Treated TiO<sub>2</sub> Nanowire Arrays for Photoelectrochemical Water Splitting. *Nano Lett.* **2011**, *11*, 3026–3033.

(51) Cooper, J. K.; Ling, Y.; Longo, C.; Li, Y.; Zhang, J. Z. Effects of Hydrogen Treatment and Air Annealing on Ultrafast Charge Carrier

Dynamics in ZnO Nanowires Under in Situ Photoelectrochemical Conditions. J. Phys. Chem. C 2012, 116, 17360–17368.

(52) Wang, J. P.; Wang, Z. Y.; Huang, B. B.; Ma, Y. D.; Liu, Y. Y.; Qin, X. Y.; Zhang, X. Y.; Dai, Y. Oxygen Vacancy Induced Band-Gap Narrowing and Enhanced Visible Light Photocatalytic Activity of ZnO. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4024–4030.

(53) Kalanur, S. S.; Hwang, Y. J.; Chae, S. Y.; Joo, O. S. Facile Growth of Aligned WO<sub>3</sub> Nanorods on FTO Substrate for Enhanced Photoanodic Water Oxidation Activity. *J. Mater. Chem. A* **2013**, *1*, 3479–3488.

(54) Zhang, J.; Li, M. J.; Feng, Z. C.; Chen, J.; Li, C. UV Raman Spectroscopic Study on TiO<sub>2</sub>. I. Phase Transformation at the Surface and in the Bulk. *J. Phys. Chem. B* **2006**, *110*, 927–935.

(55) Santato, C.; Odziemkowski, M.; Ulmann, M.; Augustynski, J. Crystallographically Oriented Mesoporous WO<sub>3</sub> Films: Synthesis, Characterization, and Applications. *J. Am. Chem. Soc.* **2001**, *123*, 10639–10649.

(56) Rajagopal, S.; Nataraj, D.; Mangalaraj, D.; Djaoued, Y.; Robichaud, J.; Khyzhun, O. Y. Controlled Growth of  $WO_3$  Nanostructures with Three Different Morphologies and their Structural, Optical, and Photodecomposition Studies. *Nanoscale Res. Lett.* **2009**, *4*, 1335–1342.

(57) Zheng, Y.; Chen, G.; Yu, Y.; Zhou, Y.; He, F. Synthesis of Carbon Doped WO<sub>3</sub> Center Dot 0.33H<sub>2</sub>O Hierarchical Photocatalyst with Improved Photocatalytic Activity. *Appl. Surf. Sci.* **2016**, *362*, 182–190.

(58) Wei, Z.; Liu, Y.; Wang, J.; Zong, R.; Yao, W.; Wang, J.; Zhu, Y. Controlled Synthesis of A Highly Dispersed BiPO<sub>4</sub> Photocatalyst with Surface Oxygen Vacancies. *Nanoscale* **2015**, *7*, 13943–13950.

(59) Ma, F.; Xu, K.; Chu, P. K. Surface-Induced Structural Transformation in Nanowires. *Mater. Sci. Eng., R* **2013**, *74*, 173–209. (60) Gall, K.; Diao, J. K.; Dunn, M. L.; Haftel, M.; Bernstein, N.; Mehl, M. J. Tetragonal Phase Transformation in Gold Nanowires. *J.* 

Eng. Mater. Technol. 2005, 127, 417–422. (61) Song, J.; Shin, D. W.; Lu, Y.; Amos, C. D.; Manthiram, A.;

Goodenough, J. B. Role of Oxygen Vacancies on the Performance of Li[Ni<sub>0.5-x</sub>Mn<sub>1.5+X</sub>]O<sub>4</sub> (X = 0, 0.05, and 0.08) Spinel Cathodes for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24*, 3101–3109.