Enhanced photocatalytic performance of tungsten oxide through tuning exposed facets and introducing oxygen vacancies

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Abstract

It is known that the exposed facet and defect state are crucial to the photocatalytic performance. Here, we report that the exposed facets of the building blocks in the tungsten oxide hierarchical nanostructures could be controlled by adjusting the amount of formamide in the hydrothermal precursor solution and the oxygen vacancies were successfully introduced through the post-air annealing. It is found that exposing high percentage (020) facet is unbeneficial for the photocatalytic performance and (200) and (002) facets should be the photocatalytic active facets of the hexagonal tungsten oxide. The hexagonal tungsten oxide with oxygen vacancies and maximum (200) and (002) facets archives highest photocatalytic performance in degrading rhodamine B under simulated solar light irradiation, which the rate constant per specific surface area (k/S_{BET}) is 7.3 times as high as the sample without oxygen vacancies and minimum (200) and (002) facets. Both introducing oxygen vacancies and exposing (200) and (002) facets can enhance the separation efficiency of photo-generated charges, thus improving the photocatalytic performance.

Key Words

1 Tungsten oxide; exposed facet tuning; oxygen vacancy; solar light photocatalysis; charge transfer

2 **1. Introduction**

3 Photocatalysis is an effective strategy to deal with the increasingly serious environment problems.
4 Tungsten oxide has received considerable attention in the field of photocatalysis due to its earth-
5 abundance, highly tunable composition, high chemical stability at appropriate pH value, and excellent
6 electrical conductivity.[1] Tungsten oxide is made up of perovskite units and is one of the most-attractive
7 candidates for photocatalysis, as it exhibits approximately absorption of 12% of the solar spectrum ($E_g =$
8 $2.5\text{-}2.8\text{ eV}$), a moderate hole-diffusion length (150-500 nm) compared with $\alpha\text{-Fe}_2\text{O}_3$ (2-4 nm), and better
9 electron transport ($\sim 12\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) compared with TiO_2 ($\sim 0.3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$).[1, 2] However, bulk tungsten
10 oxide often has some drawbacks such as insufficient quantum efficiency and high recombination rate of
11 the photoproducted electron-hole pairs, which limit its practical application on photocatalytic field.

12 The reactivity of a photocatalyst is basically influenced by its surface atomic and linked electron
13 structure. Tuning exposed facet is becoming an important strategy to optimize the reactivity of a
14 photocatalyst.[3, 4] Abundant references have reported the determinant effects of exposed facets on the
15 performance of TiO_2 . [3, 5-7] However, the photocatalytic activity dependent on the exposed facets of
16 tungsten oxide has been preliminarily investigated.[8-21] The photoactive facets are usually phase-
17 dependent. Among the different crystal structures of tungsten oxides, the previously reported highly
18 active facets for tungsten oxides were mainly toward monoclinic tungsten oxide,[8-16] it may because
19 monoclinic tungsten oxide is the most stable tungsten oxides in the room temperature and easily
20 prepared.[12] Recently, hexagonal tungsten oxide (h-WO_3) are received great attention in many fields
21 especially photocatalysis due to its unique structural features such as long, hexagonal prism channels
22 parallel to the c-axis and layered oxygen octahedral.[17, 22-26] Moreover, h-WO_3 is also stable in the

room temperature.[27] However, exposed facet-dependent photocatalysis of tungsten oxides especially hexagonal tungsten oxide is still not well established or systematically studied.

Besides exposed facets, defect state especially oxygen vacancy is another important factor that influencing the photocatalytic performance, because the electronic configurations, charge transfer and surface properties of semiconductor based photocatalyst are closely related to the oxygen vacancies.[28] Many researchers reported that oxygen vacancies especially surface oxygen vacancies would appear above and partly overlap the valence band (VB), thus leading to the rising of the valence band maximum (VBM) and the narrowing of the band gap width, expanding the photoresponse wavelength range.[29-33] The rising of VBM can also expand the VB width, which would increase the transport rate of photo-generated carriers, resulting in the enhancement of the separation efficiency of photoinduced electron-hole pairs.[31] There are many approaches to introduce oxygen vacancies, such as hydrogen treatment,[34, 35] ball milling[36] and air annealing.[37, 38] Among them, air annealing through control the annealing temperature and time is a very convenient and effective method for introducing oxygen vacancies.

Herein, the hexagonal tungsten oxide hierarchical nanostructures synthesized via hydrothermal reaction for application in photocatalysis is reported. The exposed facets of the building block were controlled by adjusting the amount of formamide and the oxygen vacancies were introduced through post-air annealing. The exposed facets and oxygen vacancies dependent-photocatalytic performance and photoelectrochemical property were investigated.

2. Experimental

2.1 Synthesis of materials

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Deionized water was used for all experiments.

1 The tungsten oxide hierarchical nanostructures were synthesized through hydrothermal reaction by
2 adjusting the amount of formamide. Typically, 0.875 g tungstic acid was added into 18 mL H_2O_2 , stirred
3 at 90 °C for 1.5 h before converting into a transparent sol. The resulting clear sol was diluted using
4 deionized water to 210 mL, and then 14 mL of 3 M HCl was added to the as-prepared solution. After
5 stirring for another 20 min, 30 mL of the precursor solution was transferred into a 50 mL Teflon-lined
6 autoclave followed by adding a certain volume of formamide. Finally, the autoclave was sealed and
7 maintained at 180 °C for 12 h. The as-synthesized precipitate was washed with deionized water for three
8 times and ethanol for two times, and then dried in vacuum at 80 °C for 5 h. The as-prepared tungsten
9 oxide was subsequently annealed in air at 350 °C for 2 h. The samples prepared by adding different
10 amount of formamide were devoted as WF40 (40 μL formamide), WF120 (120 μL formamide), and
11 WF160 (160 μL formamide) and the corresponding samples annealed in air at 350 °C were marked as
12 WF40-A350, WF120-A350 and WF160-A350.

13 **2.2 Measurements of photocatalytic property and photoelectrochemical property**

14 The photocatalytic properties of the samples were evaluated by measuring the concentration of rhodamine
15 B (RhB) in aqueous solution after irradiation with simulated solar light produced by a 300 W Xenon lamp.
16 Typically, 20 mg sample was dispersed in 40 mL RhB aqueous solution (15 mg L^{-1}). Prior to irradiation,
17 the suspension was stirred over night to ensure the equilibrium of dye adsorption on the surfaces of the
18 sample. The RhB concentration was measured by UV-Vis spectroscopy.

19 The photocurrent and electrochemical impedance spectrum (EIS) were measured on an electrochemical
20 workstation (CHI-660E, China) and carried out in a three-electrode system with a working electrode, a
21 platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode. 0.1 M
22 Na_2SO_4 was used as the electrolyte solution. The photoelectric responses of the photocatalysts were
23 measured at 0.0 V (vs. SCE). The working electrodes were prepared by a dip-coating method: 10 mg
24 photocatalyst was suspended in 1 mL 1-methyl-2-pyrrolidinone (NMP) to make a slurry, and the slurry

1 was then dip-coated onto a 2×3.5 cm fluorine-tin oxide (FTO) glass. The as-prepared electrodes were
2 dried at 80 °C for 10 h in air.

3 **2.3 Characterization of materials**

4 The X-ray diffraction patterns were obtained on a Rigaku D/max-V2500 (Cu K α radiation). The
5 morphology and microstructure were studied by scanning electron microscopy (SEM, Zeiss, Germany)
6 and transmission electron microscopy (TEM, JEOL-2100, Japan). UV-Vis spectrophotometer (U-3010,
7 Hitachi, Japan) were used to record UV/Vis absorption spectra. The surface areas of the samples were
8 measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption isotherms
9 at 77 K with a Contador QuadraSorb SI-MP instrument. High-resolution Raman spectroscopy (HR800,
10 Horiba Jobin Yvon, France) were used to collect the Raman spectra. Electron spin resonance
11 spectroscopy (ESR) measurements were performed with a JEOL FA200 ESR spectrometer.

12 **3. Results and discussion**

13 **3.1. Structure and morphology**

14 The XRD patterns of the as-prepared tungsten oxides are presented in Fig. 1. The peaks of the sample
15 WF40 can be indexed to the orthorhombic structure of WO₃·0.33H₂O (JCPDS no. 72-0199). When
16 adding 160 μ L formamide, the sample WF160 yields a hexagonal WO₃ phase (h-WO₃), with the XRD
17 pattern corresponding to JCPDS no. 85-2460. However, the sample WF120 prepared using 120 μ L
18 formamide has a small diffraction peak at 18.1°, which belongs to orthorhombic WO₃·0.33H₂O (o-
19 WO₃·0.33H₂O). All of the other diffraction peaks can be indexed to h-WO₃, showing that this sample
20 possesses a mixed phase with both h-WO₃ and o-WO₃·0.33H₂O. Besides the additive, post-air annealing
21 also affects the crystal phase of the samples. When WF40 and WF120 were annealed at 350 °C, they can
22 transfer to h-WO₃ completely, and WF160-A350 still keep the same hexagonal crystal structure with the
23 unannealed one, as shown in Fig. 1. To sum up, the amount of formamide would influence the crystal

1 structure of tungsten oxides, while after the post-air annealing at 350 °C in air, all the samples have the
2 same phase of h-WO₃.

3 The crystal structure of samples can also be investigated by Raman spectra. As shown in Fig. 2, the
4 peaks centered at about 685, 804, 918 and 950 cm⁻¹ (the black dash line) are assigned to the o-
5 WO₃·0.33H₂O. The peaks at around 685 and 804 cm⁻¹ are attributed to the stretching vibration of O-W-O
6 [ν (O-W-O)].[39] The peaks around 918 and 950 cm⁻¹ are assigned to the stretching mode of the terminal
7 W=O bond, which are the typical peaks for all types of tungsten oxide hydrates.[40] The peaks at 254,
8 691, 786 and 815 cm⁻¹ (the red dash line) belong to h-WO₃. [41] The peak at 254 cm⁻¹ is assigned to the
9 W-O-W bending vibration of the bridging oxygen [δ (W-O-W)]. The other three peaks are ascribed to ν
10 (O-W-O). The Raman peaks belonging to o-WO₃·0.33H₂O can be observed in the sample WF40, while
11 the Raman peaks owing to h-WO₃ can be observed in the samples WF160 and all the annealed samples.
12 And both peaks of o-WO₃·0.33H₂O and h-WO₃ can be observed in the sample WF120. The Raman
13 spectra suggest that the hydrothermal synthesized samples have transformed to h-WO₃ after annealing.

14 The morphology information of the samples were obtained from SEM images as shown in Fig. 3.
15 Fig. 3a presents that the sample WF40 ascribed to o-WO₃·0.33H₂O appears with a uniform flower-like
16 shape. The flowers with a diameter at about 1-2 μm are assembled with many rectangle cross-section
17 nanorods. When the sample prepared using 160 μL formamide (WF160), the thick nanorods disappear
18 and only microspheres composed of numerous thin nanowires are observed (Fig. 3c). The nanorods and
19 nanowires can be observed in the sample WF120, simultaneously (Fig. 3b). Additionally, when the
20 samples WF40, WF120 and WF160 were annealed at 350 °C, the morphologies keep same with their
21 unannealed ones, as shown in Figs. 3d-f. The morphology evolution can be reflected from the variation of
22 the specific surface areas of the as-prepared samples. As Table 1 shows, with the amount of formamide
23 increasing, the specific surface areas have a tendency to increase. The specific surface area of WF40-
24 A350 slightly decreases, while those of WF120-A350 and WF160-A350 obviously decline, compared

1 with their unannealed ones. It may be the smaller size of the nanowires that makes them more easily
2 aggregate than the nanorods during the annealing process. Above all, increasing the amount of formamide
3 could make the building blocks of tungsten oxides hierarchical structures transform from thick nanorods
4 to thin nanowires and post-air annealing could keep the similar appearance of nanorods or nanowires.

5 Further information on the microstructure of the samples were obtained from TEM and high
6 resolution transmission electron microscopy (HRTEM) images shown in Fig. 4 and Fig. S2. As for WF40
7 belonging to α - $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$, the lattice fringe spacing and FFT spots in Fig. 4a indicate that the nanorod
8 with a diameter at about 110 nm exposes three facets-(002), (020) and (200). The nanowires in the sample
9 WF160 have a width about 10 nm and a length of several hundred nanometers, as shown in Fig. S2b and
10 Fig. 4d. Moreover, the images also show that the nanowires are ultrathin, suggesting that the
11 microspheres in WF160 are assembled with ultrathin nanobelts rather than nanowires. The lattice fringe
12 spacing and FFT spots in Fig. 4d reveal that the ultrathin nanobelts almost expose one facet-(020). Fig.
13 S2a and Figs. 4b and c are the TEM and HRTEM images of WF120. Fig. S2a shows that WF120 contains
14 two kinds of building blocks, i.e. ultrathin nanobelts and thick nanorods, corresponding to the SEM
15 images in Fig. 3b. The spacing of the lattice fringes of nanobelts are found to be about 0.383 and 0.317
16 nm, indexing to (002) and (200) planes of the α - WO_3 crystal, as shown in Fig. 4c. While the spacing of
17 the lattice fringes of nanorods are found to be about 0.387 and 0.370 nm, corresponding to the (002) and
18 (200) planes of α - $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$, as shown in Fig. 4b, further confirming the mixed phases of WF120.
19 The crystal phase and morphology change of tungsten oxide may be due to the intercalation and
20 hydrolysis of formamide, i.e. the NH proton donor and C=O proton acceptor enable formamide to insert
21 into the layers of tungsten hydrates and the weak basicity allows it to cause the change of pH values
22 during hydrothermal reaction through hydrolysis, thereby realizing phase-control and exposed facets-
23 control. The detailed mechanism has been reported in the previous articles. [20, 42, 43] Based on above
24 analysis, it can conclude that the nanorods are exposed with (200), (020) and (002) facets and the

1 nanobelts are exposed with (020) facet. Meanwhile, the HRTEM images of WF40-A350 and WF160-
2 A350 were also taken and shown in Figs. 4e and f, respectively. From the HRTEM images of the
3 annealed samples, it is known that the building blocks of the annealed samples show same exposed facets
4 with their unannealed ones. However, the unannealed sample WF40 displays perfect lattice feature, but
5 the edge of the nanorod in WF40-A350 becomes disordered (marked by the orange dots and circles in Fig.
6 4e), indicating that the surface structure is damaged. Similarly, the nanobelt in WF160-A350 also shows a
7 layer of lattice disorder (marked by orange dots in Fig. 4f). The lattice disorder on the surface of nanorod
8 or nanobelt suggest that there may exist oxygen defects on the surface. [30,32,37] Therefore, WF40 and
9 WF40-A350 are exposed with maximum (002) and (200) facets but least (020) facet; WF160 and WF160-
10 A350 exposed with most (020) facet but minimum (002) and (200) facets. WF120 and WF120-A350
11 exposed with middle (002), (200) and (020) facet. The summary of exposed facets variation is illustrated
12 in the Scheme 1.

13 To identify the defect states of the samples, low temperature electron spin resonance (ESR) was used.
14 No signal can be observed in the unannealed samples (WF40, WF120 and WF160), while a strong ESR
15 signal at $g=2.003$ are found in the air-annealed samples (WF40-A350, WF120-A350 and WF160-A350),
16 as shown in Fig. 5a. It is suggested that the oxygen vacancies are successfully introduced by air
17 annealing.[44] It can indicate that the lattice disorder on the surface of nanorod or nanobelt (Fig. 4e and f
18) is attributed to the introduction of oxygen vacancies. This suggests that the oxygen vacancies are formed
19 on the surface of the nanorods or nanobelts. The almost same strong signal intensity of WF40-A350,
20 WF120-A350 and WF160-A350 indicate that these three annealed samples have same concentration of
21 oxygen vacancies. The mechanism of introducing oxygen vacancies by air annealing was discussed in
22 detail in the previous articles.[45,46] The introduction of oxygen vacancies in the air-annealed samples
23 can be further confirmed by EIS and UV-Vis absorbance spectra. The Nyquist arc radii of the air-
24 annealed samples are much smaller than the unannealed ones, suggesting a much better conductive (Fig.

5b). And the introduction of oxygen vacancies also influences the absorption edges of the air-annealed samples (Fig. S1). These all prove that the existence of oxygen vacancies in the air-annealed samples.

3.2 Photocatalytic performance

The solar-light-driven photocatalytic activities of the samples with oxygen vacancies and different exposed facets were measured by decolourization of the RhB solution. As shown in Figs. 6a-c, the photodegradation rates of RhB decrease as the amount of formamide increasing, which can photodegrade 88.3%, 78.1% and 68.7% of RhB within 100 min under simulated solar light irradiation for WF40, WF120 and WF160, respectively. Notably, the performances of the samples are significantly enhanced after air annealing at 350 °C. Furthermore, the photocatalytic performances of the annealed samples followed the sequence of WF40-A350 > WF120-A350 > WF160-A350. WF40-A350 shows most excellent performance among all the samples, which can photodegrade 95.3% RhB in 100 min and its apparent constant rate (k) could reach 0.0314 min^{-1} (Figs. 6b-c). Meanwhile, WF40-A350 also shows good stability with only slight decrease after 4 cycles (Fig. 7). The slight decrease of photocatalytic performance may be due to the recovery of the oxygen vacancies, as the ESR signal of oxygen vacancies has a small decline after 4 cycles (Fig. S3).

There are many factors leading to the results of Fig. 6. The factors can be the specific surface area, the crystal structure, the exposed facet and the defect state. In order to exclude the factor of specific surface area, the column diagram of rate constants per specific surface area (k/SBET) is also presented in Fig. 6d. It shows similar variation to Fig. 6c but different tendency to table 1, suggesting that specific surface area is not the main factor. The samples give rise to a remarkable improvement of the photocatalytic performance after air-annealing. The significant photocatalytic enhancement should mainly due to the introduction of oxygen vacancies, which can increase the efficient separation of electron-hole pairs.[47] The decreasing photocatalytic performances of WF40-A350, WF120-A350 and WF160-A350 suggest that the different expose facets can effectively influence the photocatalytic performance. These

three samples all belong to h-WO₃ and have same amount of oxygen vacancies but with different exposed facets. The WF40-A350 is assembled with nanorods exposing maximum (200), (002) facets but least (002) facet, WF160-A350 assembled with nanobelts has most percentage of (020) exposed facet and WF120-A350 has both nanorods and nanobelts exposing mild (200), (020) and (002) facets. The tendency of photocatalytic performance variation is consistent with the decrease of (020) facet or the increase of (200) and (002) facets, indicating that (200) and (002) facet should be the active facet of h-WO₃. Therefore, WF40-A350 with oxygen vacancies and maximum (200) and (002) facets archives highest photocatalytic performance, which the rate constant per specific surface area (k/SBET) is 7.3 times as high as WF160 without oxygen vacancies and minimum (200) and (002) facets.

3.3 Mechanism of enhancement of photocatalytic activity

The separation efficiency of photo-generated electrons and holes has a significant influence on the photocatalytic performance.[31] Therefore, the photoelectrochemical performances of the samples with oxygen vacancies and different exposed facets were studied using photocurrent-time curves. A higher photocurrent means a much quicker migration rate and a higher separation efficiency of photo-generated carriers.[47] As shown in Fig. 8, the photocurrent is remarkably enhanced between the unannealed sample and air-annealed sample (WF40 and WF40-A350, WF120 and WF120-A350, WF160 and WF160-A350), confirming that the oxygen vacancies can promote the quick separation of the photo-generated charges. Furthermore, among the annealed samples, the WF40-A350 shows highest photocurrent density, followed by WF120-A350 and WF160-A350, corresponding to the variation of expose facets of (200) and (002). It is known that photogenerated carriers prefer to flow to the specific facets.[6] Therefore, the exposed facets with different atom configurations are crucial to the separation of the photo-generated charges. Exposing more active facets would lead to a high separation efficiency of photo-generated carriers, thus resulting in the high efficiency of photodegrading RhB. In addition, the photocurrent densities of the annealed samples are gradually decreasing with the irradiation time prolonging, which may be attributed

to recovery of oxygen vacancies, as shown in Fig. 8 and Fig. S3. In order to further study the photodegradation mechanism, the trapping experiments using t-BuOH ($\bullet$ OH scavenger),[31] EDTA-2Na (hole scavenger)[31] and p-benzoquinone ($\bullet$ O₂⁻ scavenger)[30] were carried out. Fig. 9 shows that the photodegradation process of the sample WF40 can be greatly prevented by adding t-BuOH, while the addition of EDTA-2Na and p-benzoquinone cause a small change on the photocatalytic performance. However, the photocatalytic performance of WF40-A350 decreases obviously after adding EDTA-2Na. The results suggest that the $\bullet$ OH should be the main reactive species for WF40 and the holes are the main reactive species for WF40-A350 in the process of photodegradation of RhB.

Based on the above analysis, a schematic diagram of the mechanism of charge separation and photocatalytic reaction of the hydrothermal synthesized tungsten oxide (unannealed) and post-air annealed tungsten oxide are presented in Scheme 2. The hydrothermal synthesized tungsten oxide can transform to h-WO₃ after post-air annealing and then be equipped with oxygen vacancies and photoactive facets. Compared with the unannealed tungsten oxide which the RhB is mainly photodegraded by $\bullet$ OH, the main reactive species of the annealed sample are holes. Because of the introduction of oxygen vacancies, the valence band maximum (VBM) is raised and the valence band (VB) width is expanded, which would accelerate the separation of the photoinduced electron-hole pairs.[29-33] Moreover, the exposing of (200) and (002) facets also facilitates the transformation of photogenerated charges, thus decreasing the recombination rate of the electron-hole pairs in annealed sample.[6] Therefore, the hexagonal tungsten oxide with oxygen vacancies and maximum (200) and (002) exposed facets archives excellent photocatalytic performance.

4 Conclusions

Tungsten oxides architectures assembled with nanorods or nanobelts were synthesized by adjusting the amount of formamide via hydrothermal reaction. Through post-air-annealing, the oxygen vacancies were

successfully introduced and the photocatalytic performances were significantly enhanced. The variation of exposed facets of the building blocks of the tungsten oxides architectures were investigated. It is found that exposing high percentage of (020) facet is unbeneficial for the photocatalytic performance and (200) and (002) facets should be the photocatalytic active facets of the hexagonal tungsten oxide. The results of photoelectrochemical performances show that the introduction of oxygen vacancies and the exposing of active facets would increase the separation efficiency of photo-generated charges. The main oxidative species of photocatalysts transform from hydroxyl radicals to the holes after post-air annealing.

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Caption of Figures

Fig. 1 XRD patterns of the tungsten oxides prepared with different amount of formamide and post-air annealed at 350 °C in air.

Fig. 2 Raman spectra of the tungsten oxides prepared with different amount of formamide and post-annealed at 350 °C in air (H: Hexagonal WO₃, O: Orthorhombic WO₃.0.33H₂O).

1 **Fig. 3** SEM images of the as-prepared tungsten oxides prepared with different volume of formamide: (a)
2 WF40, (b) WF120 (the rectangular frame shows the thick nanorod), and (c) WF160 and the samples
3 annealed at 350 °C: (d) WF40-A350, (e) WF120-A350 and (f) WF160-A350.

4 **Fig. 4** HRTEM images of (a) WF40; (b) and (c) WF120; (d) WF160; (e) WF40-A350; (f) WF160-A350
5 (The insets are the corresponding FFT spots and the low magnification image).

6 **Scheme 1** Illustration of the exposed facets variation after hydrothermal reaction and after air annealing.

7 **Fig. 5** (a) ESR spectra (T=108 K) and (b) EIS spectra (measured in dark) of the unannealed samples and
8 the corresponding annealed samples.

9 **Fig. 6** (a) concentration change of RhB solution versus irradiation time; (b) corresponding pseudo-first-
10 order linear fitting results; (c) the apparent kinetic rate constant (k) calculated from Fig. b and (d) the rate
11 constants per specific surface area (k/S_{BET}) of the samples prepared by adding different volume of
12 formamide and their annealed samples.

13 **Fig. 7** Recyclability of WF40-A350.

14 **Fig. 8** Photocurrent response of the samples.

15 **Fig. 9** the plots of photogenerated carriers trapping in the system of photodegradation of RhB over the
16 samples WF40 (a) and WF40-A350 (b) under simulated solar light.

17 **Scheme 2** The mechanism of charge separation and photocatalytic reaction of the unannealed tungsten
18 oxide and post-air-annealed tungsten oxide with oxygen vacancies and active facets.

(a) unannealed WO_3

(b) air-annealed WO_3 with oxygen vacancies and active facets

Table 1. BET specific surface areas of the samples

sample	WF40	WF120	WF160	WF40-A350	WF120-A350	WF160-A350
BET(m ² g ⁻¹)	22.8	49.3	56.1	20.7	28.8	36.4

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

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