Wavelength-Dependent Solar N₂ Fixation into Ammonia and Nitrate in Pure Water

Wenju Ren,1,2 Zongwei Mei,1 Shisheng Zheng,1 Shunning Li,1 Yuanmin Zhu,3,4 Jiaxin Zheng,1 Yuan Lin,5 Haibiao Chen,1 Meng Gu,3 and Feng Pan1

1School of Advanced Materials, Peking University, Shenzhen Graduate School, China
2School of Advance Manufacturing Engineering, Chongqing University of Posts and Telecommunications, Chongqing, China
3Department of Materials Science and Engineering, Southern University of Science and Technology, China
4SUSTech Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, China
5Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Correspondence should be addressed to Feng Pan; panfeng@pkusz.edu.cn

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Solar-driven N₂ fixation using a photocatalyst in water presents a promising alternative to the traditional Haber-Bosch process in terms of both energy efficiency and environmental concern. At present, the product of solar N₂ fixation is either NH₄⁺ or NO₃⁻. Few reports described the simultaneous formation of ammonia (NH₄⁺) and nitrate (NO₃⁻) by a photocatalytic reaction and the related mechanism. In this work, we report a strategy to photocatalytically fix nitrogen through simultaneous reduction and oxidation to produce NH₄⁺ and NO₃⁻ by W₁₈O₄₉ nanowires in pure water. The underlying mechanism of wavelength-dependent N₂ fixation in the presence of surface defects is proposed, with an emphasis on oxygen vacancies that not only facilitate the activation and dissociation of N₂ but also improve light absorption and the separation of the photoexcited carriers. Both NH₄⁺ and NO₃⁻ can be produced in pure water under a simulated solar light and even till the wavelength reaching 730 nm. The maximum quantum efficiency reaches 9% at 365 nm. Theoretical calculation reveals that disproportionation reaction of the N₂ molecule is more energetically favorable than either reduction or oxidation alone. It is worth noting that the molar fraction of NH₄⁺ in the total product (NH₄⁺ plus NO₃⁻) shows an inverted volcano shape from 365 nm to 730 nm. The increased fraction of NO₃⁻ from 365 nm to around 427 nm results from the competition between the oxygen evolution reaction (OER) at W sites without oxygen vacancies and the N₂ oxidation reaction (NOR) at oxygen vacancy sites, which is driven by the intrinsically delocalized photoexcited holes. From 427 nm to 730 nm, NOR is energetically restricted due to its higher equilibrium potential than that of OER, accompanied by the localized photoexcited holes on oxygen vacancies. Full disproportionation of N₂ is achieved within a range of wavelength from ~427 nm to ~515 nm. This work presents a rational strategy to efficiently utilize the photoexcited carriers and optimize the photocatalyst for practical nitrogen fixation.

1. Introduction

Ammonia (NH₃) and nitrate are widely used for agricultural and chemical synthesis purposes [1–4]. Due to the environmental issues and energy crisis in recent years, NH₃ has also gained growing interest as a liquid fuel for fuel cells due to its high energy density and easy storage [5]. However, the industrial production of NH₃ is mainly based on the traditional Haber-Bosch process, which consumes nearly 2% of global energy and emits about 1% of greenhouse gases [6, 7]. Extra energy is needed for the production of nitrate from NH₃ [1, 8]. As a green and environmentally friendly alternative for ammonia and nitrate synthesis, solar-driven nitrogen fixation in aqueous media using a photocatalyst at room temperature and atmospheric pressure presents a tantalizing approach [9–13]. However, the current efficiency of synthesizing NH₃ and nitrate (NO₃⁻) by a photocatalytic approach is still far from practical purpose [2].

Either NH₄⁺ or NO₃⁻ as a solar N₂ fixation product has been reported based on a tungsten oxide photocatalyst [8, 14], in which only the photogenerated electrons or holes are utilized. Few studies have exhibited the simultaneous coproduction of NH₄⁺ and NO₃⁻ and a mechanism of wavelength-dependent solar N₂ fixation. This process utilizes...
both photogenerated electrons and holes more efficiently. During the N₂ reduction reaction (NRR) process, oxygen evolution reaction (OER) will participate in pure water without sacrificial reagents, which occurs throughout the photocatalytic N₂ fixation process and consumes the photoexcited holes. Therefore, the overall reaction is as follows:

\[
2\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 3\text{O}_2
\]  

(1)

The voltage per electron is 1.13 V for the above reaction. Previous work has indicated that N₂ can also be oxidized to NO₃⁻ over pothole-rich ultrathin WO₃ nanosheets [8]. It is reasonable that NO₃⁻ and NH₃ could be produced simultaneously, with N₂ fixation proceeding through the following reactions:

\[
5\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 6\text{NO}
\]  

(2)

\[
4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3
\]  

(3)

The voltage per electron is 1.57 V for Reaction (2), meaning that this reaction route is thermodynamically unfavorable as compared to Reaction (1). However, nitrogen fixation on defected surfaces can be controlled by the reaction kinetics on the catalytic sites like oxygen vacancies on the surfaces of transition metal oxides. It should be noted that Reaction (3), i.e., the oxidation of NO, can occur spontaneously in aqueous solution [15]. Since the oxygen in Reaction (3) can only come from Reaction (1) when the external O₂ is removed from the reaction system, the maximization of NO₃⁻ will correspond to the consumption of all produced oxygen, which gives the overall reaction as follows:

\[
4\text{N}_2 + 9\text{H}_2\text{O} \rightarrow 5\text{NH}_3 + 3\text{HNO}_3
\]  

(4)

2. Results and Discussion

\(\text{W}_{18}\text{O}_{49}\) nanowires were prepared using a solvothermal method, and a reference sample was prepared by subsequently annealing the as-synthesized \(\text{W}_{18}\text{O}_{49}\) nanowires at 300°C in air for 30 min to eliminate oxygen vacancies from the surface. The crystal structure and phase purity of the as-synthesized blue velvet-like product (Figure 1(a)) were revealed by X-ray diffraction (XRD) to be consistent with the standard monoclinic \(\text{W}_{18}\text{O}_{49}\) (P2/m) (PDF 05-0392) as previously reported [31–33]. No visible changes in XRD patterns can be observed after annealing (Figure S1). The scanning electron microscopy (SEM) images indicate that the as-synthesized \(\text{W}_{18}\text{O}_{49}\) consists of ultrathin nanowires (Figure 1(b)), while the transmission electron microscopy (TEM) image (Figure 1(c)) further confirms that the diameters and the lengths of the as-synthesized nanowires are <10 nm and >2 μm, respectively. The selected area electron diffraction (SAED) pattern demonstrates that the diffraction rings belong to the (010, 020) planes of the \(\text{W}_{18}\text{O}_{49}\) structure (inset in Figure 1(c)), consistent with XRD. The interplanar spacing of the (010) planes is ~3.8 Å, and the nanowire grows along the [010] direction (Figure 1(d)). After annealing, the nanowire becomes shorter and thicker (Figures S2a and S2b); however, the interplanar spacing remains 3.8 Å (Figure S2c), which further confirms that the crystal structure remains unchanged after annealing.
The photocatalytic nitrogen fixation performance of the W$_{18}$O$_{49}$ nanowires under simulated solar irradiation (AM 1.5G, 400 nm-1100 nm) is presented in Figure 2(a). The yield rates of NH$_4^+$ and NO$_3^-$ within 12 h were about 22.8 μmol L$^{-1}$ g$_{\text{cat}}^{-1}$ h$^{-1}$ and 0.54 μmol L$^{-1}$ g$_{\text{cat}}^{-1}$ h$^{-1}$, respectively. W$_{18}$O$_{49}$ nanowires were also tested under irradiation of a 300 W xenon light (872 mW/cm$^2$). The average NH$_3$ production rate was about 65.2 μmol L$^{-1}$ g$_{\text{cat}}^{-1}$ h$^{-1}$, and the yield rate of NO$_3^-$ was nearly 0.57 μmol L$^{-1}$ g$_{\text{cat}}^{-1}$ h$^{-1}$ for the as-synthesized W$_{18}$O$_{49}$ nanowires (Figure S3a). In comparison, the average NH$_3$ production rate decreased to ~1.6 μmol L$^{-1}$ g$_{\text{cat}}^{-1}$ h$^{-1}$, and no NO$_3^-$ was produced during the test process using the annealed photocatalyst at 300°C for 30 min (Figure S3b). The dependence of photocatalytic performances on oxygen vacancy concentrations is shown in Figure S4, and ultraviolet LED with high power was used to produce more NO$_3^-$ for activity comparison. The yields of NH$_4^+$ and NO$_3^-$ reduce as the annealing time (1.5, 3, and 30 min) increases at 300°C under a 300 W xenon lamp and 5 W of 370 nm LED illumination, respectively. The standard curves for quantifying ammonia and nitrate concentrations were calibrated using ion chromatography, which is a precise measurement for most anions and cations. The correlation coefficient values are 0.9993 and 0.9974 for ammonia and nitrate calibration curves (Figure S5), respectively. The peak signal from the lowest calibrated concentration (0.05 ppm) is very sharp and clean (Figures S5e and S5f), indicating that the instrument is capable of reliably measuring low concentrations at this level. Though some measured values for ammonia or nitrate listed in Table S1 are below the lowest calibrated concentration, the linear relationship between the peak area and the concentration of ammonia or nitrate should persist down to the origin. In other words, the calibrations in Figure S5 are acceptable to quantify the amount of ammonia and nitrate produced in the photocatalytic N$_2$ fixation of this work.

To evaluate the photocatalytic stability, the suspension of the as-synthesized W$_{18}$O$_{49}$ nanowires was irradiated using a 300 W xenon lamp and tested for ten 12-hour cycles. After each cycle, the catalyst was carefully cleaned by filtration using a copious amount of distilled water to wash off the
dissolved NH$_4^+$ and nitrate products. Even if a layer of NH$_4^+$ might strongly adsorb on the surface of the W$_{18}$O$_{49}$ catalyst and even if they are carried over to the next cycle, it is expected that the adsorbed NH$_4^+$ cannot easily desorb and only the NH$_4^+$ in the bulk solution can be extracted and measured. It is found that the as-synthesized W$_{18}$O$_{49}$ nanowires are relatively stable during the cycle test (Figure S3c). The UV-vis absorption spectrum of the sample after one cycle test (12 h) exhibits lower tail absorption intensity compared with that of the as-synthesized W$_{18}$O$_{49}$ nanowires (Figure S6), indicating that the concentration of oxygen vacancies decreases slightly. It can be speculated that the number of oxygen vacancies gradually decreased after each cycle according to the reduced photocatalytic activities as shown in Figure S3c. The total turnover number is greater than 114.7% after ten cycles, which confirms the photocatalytic reaction for N$_2$ fixation.

In order to understand the wavelength-dependent catalytic process for N$_2$ fixation, the as-synthesized photocatalyst suspension was irradiated under LED lights of different wavelengths: 365, 384.3, 400, 427, 468.4, 498, 515, 590, 620, 730, and 850 nm. It was found that the as-synthesized W$_{18}$O$_{49}$ nanowires can photocatalytically fix N$_2$ to NH$_4^+$ and NO$_3^-$ at wavelengths from ultraviolet up to 730 nm (Figure 2(b) and Figure S7 and Table S1). Although there have been some visible light-sensitive photofixation catalysts reported, our photocatalyst appears to be the one with the widest absorption range so far [14, 34, 35].
Figure 2(c) demonstrates the molar percentage ratio of NH$_4^+$ and NO$_3^-$ to the total production. The ratio of NH$_4^+$ gradually decreases from 365 nm to 427 nm and increases from 427 nm to 730 nm with a high NO$_3^-$ yield (35–40%) during 427–515 nm; the reason will be discussed herein below.

The wavelength-dependent quantum efficiencies (QE) can also be evaluated based on the amount of photofixation products under LED light illumination using the equations [1, 2] in the experimental part. The calculated QE values are closely related to the wavelength and the light absorption ability. The trend of the photon-to-product efficiency vs. wavelength follows an inverted volcano shape in the range from 365 to 498 nm (Figure 2(d)). In this range, the highest and lowest efficiencies are 9% at the wavelength of 365 nm and 5% at 427 nm, respectively, where the light absorption ability is weakest. On the other hand, the absorption edge of the as-synthesized W$_{18}$O$_{49}$ nanowires is about 428 nm because the band gap was close to the incident energy of the light source (Figure S8a). The absorption in longer wavelengths must be caused by the defect levels (DLs). According to the density of states (DOS) calculation, there are some defect levels located below the conduction band in the presence of oxygen vacancies in W$_{18}$O$_{49}$ (Figures S8b and S8c). The DLs explain why the as-synthesized W$_{18}$O$_{49}$ nanowires exhibit tail absorption in the UV-vis absorption spectrum transformed from the Kubelka-Munk formula (Figures S6 and S8a). Since the density of defects is expected to decrease after annealing, the absorption in the tail range for the annealed sample for 30 min is lower (Figure S8a), suggesting that the photocatalytic activity above 428 nm wavelength originates from the DLs. Photon-to-product efficiency gradually decreases in the wavelength range from 498 nm to 730 nm, possibly due to the relatively lower energy of the photoexcited carriers. This trend is proven by the real production of NH$_4^+$ and NO$_3^-$ under different wavelength LED irradiation with approximate light intensity (Figure S7).

In order to determine the source of the oxygen element in the nitrate product, appropriate H$_2^{18}$O in normal distilled water was used as the reagent. After 5 h of xenon lamp irradiation, the $^{18}$O isotope was quantified by the denitrification method using Delta V-Precon (Thermo Fisher Scientific, Germany, with the detailed measurement method described in Supplementary Materials) to be about 0.20% in NO$_3^-$.

The measured peak position, peak area, and atomic percentage are shown in Figure S9 and Table S2, and all the calculation values were based on the equipped software on the test instrument. For additional confirmation, control experiments were carried out to prove the photocatalytic nitrogen fixation ability and exclude possible interference from any contaminants. Firstly, neither ammonia nor nitrate can be detected in pure water (100 mL) with the as-synthesized W$_{18}$O$_{49}$ photocatalyst (0.05 g) and Ar gas bubble under 300 W xenon lamp irradiation at 25°C (Figure S10a). This result demonstrates that the nitrogen element in the ammonia and nitrate is from the N$_2$ flow through photocatalytic fixation. Secondly, ammonia and nitrate are also undetectable in pure water (100 mL) with the as-synthesized W$_{18}$O$_{49}$ photocatalyst (0.05 g) and N$_2$ gas bubble without irradiation at 25°C (Figure S10b). Then, light illumination is required for N$_2$ fixation and the fixation products are not from environmental contaminations. These results unequivocally confirm that the photocatalytic reaction of N$_2$ fixation to ammonia and nitrate indeed happens in this process, and the oxygen element in nitrate originates from water.

The surface defects of the as-synthesized and annealed W$_{18}$O$_{49}$ nanowires are analyzed using atomic scale HAADF Z-contrast images. Lattice distortion, polycrystalline, and amorphous regions are revealed on the surface of the as-synthesized W$_{18}$O$_{49}$ nanowires (Figure 3(a)). However, all the surface irregularities disappear and the surface becomes smooth after annealing (Figure 3(b) and Figure S11). The electron energy loss spectroscopy (EELS) edges, which are sensitive to the unoccupied local density of states, provide useful information of local oxidation states and coordination chemistry of the W$_{18}$O$_{49}$ nanowires [36]. The W and O EELS results of the as-synthesized W$_{18}$O$_{49}$ nanowires are plotted in Figure 3(c), where peak A corresponds to the vacant density of states in the hybridized O 2p and W 5d orbitals. Therefore, the intensity of peak A is closely related to the oxidation state of W. As shown in the spectra collected inside the bulk and near the surface of the as-synthesized W$_{18}$O$_{49}$ nanowires, there is a significant drop in the intensity of peak A, which indicates a decrease in the valence state of W at the surface of W$_{18}$O$_{49}$ nanowires. For the W$_{18}$O$_{49}$ nanowires after annealing for 30 min, no visible change was observed in the EELS signals from the surface to the inside.

The chemical composition and the valence states of the as-synthesized and annealed W$_{18}$O$_{49}$ nanowires were examined with an X-ray photoelectron spectrometer (XPS). In the full range of XPS spectra, peaks at binding energies corresponding to O and W elements are clearly observed, and no impurities other than carbon are observed in the spectra (Figure S12a). The W 4f core-level spectrum of the as-synthesized sample could be fitted into two doublets with two different oxidation states. The main peaks of W 4f5/2 at 38 eV and W 4f7/2 at 36 eV are attributed to the W$^{5+}$ oxidation state. The second doublet with a lower binding energy at 34.5 eV and 36.7 eV arises from W 4f5/2 and W 4f7/2 core levels of the W$^{5+}$ oxidation state. These binding energies belong to the typical oxidation states found in W$_{18}$O$_{49}$ nanowires as reported previously [24, 37–39]. The above results further confirm that the as-synthesized catalyst is W$_{18}$O$_{49}$ rather than WO$_3$. However, the peaks attributed to the W$^{5+}$ oxidation state disappear after annealing, indicating that the concentration of surface oxygen vacancies decreases significantly after annealing, which is consistent with the EELS (Figure 2(c)).

The high-resolution XPS spectra of W$_{18}$O$_{49}$ can be described as the deconvolution into two peaks by the Gaussian distribution (Figures S12b and S12c), where the one at 530.7 and 530.8 eV can generally be assigned to the bridging oxygen on the W$_{18}$O$_{49}$ surface, while the peak at 531.5 eV is attributed to O-H in the oxygen defects [40–42].
Electron paramagnetic resonance (EPR) spectroscopy and temperature-programmed desorption of N\textsubscript{2} (N\textsubscript{2}-TPD) were used to investigate the oxygen vacancies and N\textsubscript{2} adsorption on the surface oxygen vacancies. In Figure 3(e), a signal exists at around $g = 2.003$ caused by oxygen vacancies in the as-synthesized and annealed sample for 30 min [12]. Thus,
there are still some oxygen vacancies in the annealed sample. In Figure 3(f), a single desorption peak of N₂ begins at 450 K and centers at 604.6 K, of which the positions suggest chemisorption of nitrogen on the surface. A first-order process was indicated with the N₂ peak unchanged with coverage for adsorption at 545 K. N₂ was the major desorption product, with a peak at 650 K on Ru/Al₂O₃ [43–46]. Since the weights of samples were identical to these two TDPS runs, the difference in peak areas can be used to compare the amount of N₂ desorbed. For the annealed sample, the N₂ TCD signal of the annealed W₁₈O₄₉ significantly decreases in comparison with that of the as-synthesized sample, suggesting that there was a significant drop in the population of surface oxygen vacancies after annealing. In combination with the EPR and TCD results, it can be concluded that the surface oxygen vacancies are reduced but still expected to exist inside the annealed sample.

The PL emission spectra of the as-synthesized and annealed W₁₈O₄₉ nanowires for 30 min were examined in the wavelength range of 330–500 nm with an excitation wavelength of 280 nm at room temperature (Figure 3(g)). The blue emission peak at 421 nm is attributed to the oxygen vacancies in tungsten oxide nanowires and nanorods [47, 48], and the green emission peak centered at 483 nm is usually related to the intrinsic defect structures reduced particularly from oxygen deficiency [49]. The increased PL intensity demonstrates that more photogenerated electron-hole recombination occurs in the annealed sample. The PL result reveals that oxygen vacancies assist the separation of the photoexcited carriers, possibly by functioning as trapping sites.

The specific surface area is a key factor for the photocatalytic performance. The N₂ adsorption and desorption isotherms of the as-synthesized and annealed W₁₈O₄₉ nanowires for 30 min were measured to evaluate their BET surface areas. The isotherms of both samples are of classical type IV with a hysteresis loop (Figure S13). The BET surface areas of the original W₁₈O₄₉ and annealed W₁₈O₄₉ were calculated to be 437.1 and 93.2 m² g⁻¹, respectively. Apparently, the annealing process resulted in a significant reduction in the surface area, most likely due to the change in the shape of the nanowires with the reconstruction of the rough surface. Although the specific surface area of the annealed sample was below one-fourth that of the as-synthesized sample, the photocatalytic activity turned out to be below 1/30 of the as-synthesized sample (Figure S3b). Therefore, the reduction in the specific surface area of the annealed sample alone cannot account for the significant decrease in the photocatalytic performance. It is the surface oxygen vacancy that primarily determines the performance of photoxidation of N₂.

In order to better understand the mechanisms for nitrogen fixation on the W₁₈O₄₉ nanowire from a microscopic point of view, density function theory calculation was carried out. The unit cell of W₁₈O₄₉ was optimized (Figure S14), and the relaxed lattice parameters (a = 18.50 Å, b = 3.82 Å, c = 14.19 Å, and β = 115.62°) are consistent with previous work [14]. The (001) surface was modelled with a 1 x 2 x 1 supercell to investigate the N₂ fixation process. We found that the N₂ molecule cannot be chemically adsorbed on a perfect W₁₈O₄₉ surface (Figure S15), in which case the bond length of the adsorbed N₂ is nearly identical to that of the gaseous phase. When an oxygen vacancy was introduced (Figure 4(a)), however, the Bader charge analysis showed that 0.85 e⁻ is localized on each of the two W atoms around the oxygen vacancy. Therefore, both N atoms of N₂ could form strong bonds with the W atoms around the oxygen vacancy, and the N-N bond length is significantly stretched from 1.11 Å to 1.21 Å with adsorption energy of -1.70 eV, indicating the activation of the N₂ triple bond. The charge difference analysis with Bader charge analysis was performed to analyze the charge of N₂ adsorption configuration (Figure S16 and Table S3). It is found that the adsorbed N₂ gain 0.74 e⁻ and the charges accumulate in the area between the bonded N and W atoms, while a charge depletion region is created between both N atoms, indicating that the N₂ triple bond is weakened, thus facilitating the following nitrogen fixation reactions [50]. Free energy profiles toward different products were calculated under pH = 7 (Figures 4(b)–4(f)), and the optimized geometries for the reaction intermediates are presented in Figures S17–S22. For NRR, the most energetically favorable pathway is shown in Figure 4(b). In this process, the potential-determining step (PDS) is the last hydrogenation step (*NH₂−*NH₃) and the corresponding energy (ΔG_PDS) is 1.71 eV. In NOR, N₂ can be oxidized to produce two NO molecules (Figure 4(d)) with ΔG_PDS of 1.20 eV. Intriguingly, it is found that N₂ can also disproportionate at a single oxygen vacancy, forming NH₃ and NO successively (Figure 4(c)). The PDS is that the hydroxyl attacks the *N intermediate to form the *NOH intermediate and ΔG_PDS is 1.18 eV, demonstrating that such disproportionation reaction probably prevails in the N₂ fixation process. The pathways for the OER on the W₁₈O₄₉ (001) with an oxygen vacancy and the pristine W₁₈O₄₉ (001) are conceived from studies of OER on other metal oxides and depicted in Figures 4(e) and 4(f). According to the calculated ΔG_PDS for both pathways, OER appears to be more feasible on a facet without an oxygen vacancy. The formation of H₂O₂ was also examined (Figure S23), and it turned out that H₂O₂ can hardly take part in the reactions of our system.

Although many factors may play a role in the entire photocatalytic process of N₂ fixation on the W₁₈O₄₉ nanowires, we believe that the oxygen vacancies on the nanowire surface are essential in promoting the chemical adsorption of N₂ molecules and providing catalytic-active sites for both ammonia and nitrate formations. Here, we propose the wavelength-controlled mechanism of photocatalytic N₂ fixation on W₁₈O₄₉ nanowires (Figure 5). Under the whole range light irradiation from 365 to 730 nm used in this work, the photoexcited electrons transfer to the surface oxygen vacancies and reduce the chemisorbed N₂ molecule to NH₃ (Figure 5(a)). However, in the short wavelength range from 365 nm to around 427 nm, intrinsic absorption of light is valid and the photoexcited holes are generated in the bulk and near the surfaces. In this case, the highly mobile holes are delocalized over the surface regions and can reach the W sites either with or without a nearby oxygen vacancy.

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Owing to the favorable OER at the W sites without a nearby oxygen vacancy (Figures 4(e) and 4(f)), only a small portion of photoexcited holes are injected to the oxygen vacancies where NOR takes place. The OER takes more advantage under the shorter wavelength light irradiation (Figure 5(c)), which corresponds to the increase in the ratio of NO$_3^-$ at wavelength from 365 nm to around 427 nm (Figure 2(c)). In the long wavelength from around 427 nm to 730 nm (Figure 5(d)), intrinsic absorption is not available; hence, all the reactions are most likely to occur on oxygen vacancies due to light absorption by DLs. Since the equilibrium potential of the N$_2$/NO redox couple is 0.44 eV higher than that of…
the H2O/O2 redox couple (Figure 5(b)), OER will be more thermodynamically favorable than NOR at longer wavelength. As a result, the ratio of NO3− decreases in this range of wavelength (Figure 2(c)). It is worth mentioning that for wavelength from 427 nm to 515 nm, the ratio between the produced NH4+ and NO3− is close to 5 : 3. Given that the valence changes of N from N2 to NH4+ and NO3− are -3 and 5, respectively, we can deduce that nearly all the O2 molecules produced by OER are consumed by the oxidation of NO to NO3−, i.e., through Reaction (4). Under this condition, O2 should be regarded as a reaction intermediate rather than a reaction product, and all the photoexcited holes that participate in reactions will take part in the oxidation of N2. In other words, the photogenerated carriers are most efficiently utilized in this wavelength range.

3. Conclusions

In summary, we have developed oxygen vacancy-rich W18O49 ultrathin nanowires as an excellent photocatalyst for N2 fixation into ammonia and nitrate. Our investigation revealed that the oxygen vacancies promote the light absorption from the visible to the NIR region, improve the separation ability of the photoexcited electrons and holes, and also serve as the active sites for N2 chemisorption and the bridging between the photogenerated carriers from the catalyst to the N2 molecules. The total quantum efficiency can reach 9% at the irradiation wavelength of 365 nm. Theoretical results show that the oxygen vacancies are the catalytic sites for the formation of both ammonia and nitrate. Interestingly, the molar percentage ratio of NH4+ to the total production (NH4+ and NO3−) shows a gradual decrease from 365 nm to 427 nm, followed by an increase from 427 nm to 730 nm. This trend can be rationalized as follows: in the short wavelength range, the energetically favorable OER predominates at the W sites without a nearby oxygen vacancy due to the intrinsic absorption of the catalyst and the delocalized nature of the photoexcited holes; in long wavelength ranges, NOR becomes more energetically challenging as compared with OER at oxygen vacancies according to the equilibrium potential for both reactions. The photogenerated carriers are most efficiently utilized in the wavelength range from ~427 nm to ~515 nm. This work presents a new insight into the role of oxygen vacancies in the wavelength-dependent photocatalytic nitrogen fixation and demonstrates the underlying mechanisms that could guide the design of future photocatalysts of higher efficiencies.

Conflicts of Interest

The authors declare no competing interests.
**Authors’ Contributions**

Wenju Ren, Zongwei Mei, Shisheng Zheng, and Shunning Li contributed equally to this work.

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**Supplementary Materials**

Preparation of W$_{18}$O$_{49}$ nanowires. Material characterizations. Photocatalytic activity evaluations. Isotope test. Figure S1: the XRD patterns of the original and annealed W$_{18}$O$_{49}$ nanowires. Figure S2: (a) SEM, (b) TEM, and (c) HRTEM images of the annealed W$_{18}$O$_{49}$ nanowires. Figure S3: the photocatalytic NH$_4^+$ and NO$_x$ production ability of the (a) as-synthesized W$_{18}$O$_{49}$ nanowires and (b) annealed W$_{18}$O$_{49}$ nanowires for 30 min under a xenon lamp. (c) Stability of W$_{18}$O$_{49}$ nanowires for N$_2$ reduction under a xenon lamp (light source: 300 W xenon lamp; 25ºC). Figure S4: (a) NH$_4^+$ yield under 300 W of xenon lamp illumination and (b) NO$_x$ yield under 5 W of 370 nm LED illumination for photocatalytic N$_2$ fixation of the as-synthesized W$_{18}$O$_{49}$ nanowires (0.05 g) and the sample annealed for different times at 300 ºC. Figure S5: standard curve of (a) nitrate and (b) ammonia with high-performance ion chromatography. (c) Measurement curves of NH$_4^+$ from 0.05 ppm to 1 ppm tested by ion chromatography. (d) Measurement curves of NO$_3^-$ and NO$_2^-$ from 0.05 ppm to 1 ppm tested by ion chromatography. (e) The enlarged curves of (c). (f) The enlarged curves of (d). Figure S6: the UV-vis absorption spectra of the as-synthesized W$_{18}$O$_{49}$ nanowires and the as-synthesized sample after one cycle test of photocatalytic N$_2$ fixation for 12 h. Figure S7: the photocatalytic NH$_4^+$ and NO$_x$ production ability of the as-synthesized W$_{18}$O$_{49}$ nanowires under different wavelength LED irradiation: (a) 384.3 nm; (b) 400 nm; (c) 427 nm; (d) 468.4 nm; (e) 498 nm; (f) 515 nm; (g) 590 nm; (h) 620 nm; (i) 850 nm. Figure S8: (a) the UV/vis absorption spectra of W$_{18}$O$_{49}$ nanowires and annealed W$_{18}$O$_{49}$ nanowires. (b) Density of states for W$_{18}$O$_{49}$. (c) Density of states for W$_{18}$O$_{49}$ with an oxygen vacancy. Figure S9: the typical measurement peaks of different N$_2$O. Figure S10: (a) the ammonia and nitrate concentration curves with the as-synthesized W$_{18}$O$_{49}$ photocatalyst (0.05 g) and Ar gas bubble in water (100 mL) under 300 W of xenon lamp irradiation (25 ºC). (b) The ammonia and nitrate concentration curves with the as-synthesized W$_{18}$O$_{49}$ (0.05 g) photocatalyst and N$_2$ gas bubble in water (100 mL) without irradiation (25 ºC). Figure S11: the HRTEM image of W$_{18}$O$_{49}$ nanowires after annealing. Figure S12: (a) XPS full-range spectra of the original and annealed W$_{18}$O$_{49}$ nanowires for 30 min. High-resolution XPS O 1s of (b) W$_{18}$O$_{49}$ nanowires. (c) Annealed W$_{18}$O$_{49}$ nanowires for 30 min. Figure S13: N$_2$ adsorption/desorption isotherms at 77 K of W$_{18}$O$_{49}$ nanowires and annealed W$_{18}$O$_{49}$ nanowires. Figure S14: the top view, side view, and lattice parameters of the bulk unit cell of W$_{18}$O$_{49}$. Figure S15: the adsorption configuration of the N$_2$ molecule on the perfect W$_{18}$O$_{49}$ (001) facet without an oxygen vacancy. Figure S16: the different oxygen vacancies on the W$_{18}$O$_{49}$ nanowires. Figure S17: the charge difference analysis of the N$_2$ adsorption configuration on the W$_{18}$O$_{49}$ (001) facet with one oxygen vacancy; blue represents charge accumulation while red indicates charge depletion. Figure S18: the optimized geometries for reaction intermediates during the nitrogen fixation process to the NH$_3$ product over W$_{18}$O$_{49}$ (001) with one oxygen vacancy. Figure S19: the optimized geometries for reaction intermediates during the nitrogen fixation process to the NO product over W$_{18}$O$_{49}$ (001) with one oxygen vacancy. Figure S20: the optimized geometries for reaction intermediates during the nitrogen fixation process to NH$_3$ and NO products over W$_{18}$O$_{49}$ (001) with one oxygen vacancy. Figure S21: the optimized geometries for reaction intermediates during the OER process over W$_{18}$O$_{49}$ (001) with one oxygen vacancy. Figure S22: the optimized geometries for reaction intermediates during the OER process over the pristine W$_{18}$O$_{49}$ (001). Figure S23: formation of H$_2$O$_2$ on the W$_{18}$O$_{49}$ (001) facet (a) with and (b) without one O vacancy and (c) the 2*OH and 4*O$_2$H$_2$ intermediates on the surface without an O vacancy. Table S1: the area of characteristic peak and corresponding ammonia and nitrate concentration. Table S2: the delta value of atomic percentage of $^{18}$O. (Supplementary Materials)

**References**

[1] J. G. Chen, R. M. Crooks, L. C. Seefeldt et al., “Beyond fossil fuel–driven nitrogen transformations,” *Science*, vol. 360, no. 6391, article eaar6611, 2018.

[2] A. J. Medford and M. C. Hatzell, “Photon-driven nitrogen fixation: current progress, thermodynamic considerations, and future outlook,” *ACS Catalysis*, vol. 7, no. 4, pp. 2624–2643, 2017.

[3] J. A. Pool, E. Lobkovsky, and P. J. Chirik, “Hydrogenation and cleavage of dinitrogen to ammonia with a zirconium complex,” *Nature*, vol. 427, no. 6974, pp. 527–530, 2004.

[4] B. M. Lindley, R. S. Van Alten, M. Finger et al., “Mechanism of chemical and electrochemical N2 splitting by a rhodium pincer complex,” *Journal of the American Chemical Society*, vol. 140, no. 25, pp. 7922–7935, 2018.

[5] R. G. Boothroyd, “A proposed Australian transition to an anhydrous ammonia fuel transport economy to replace liquid petroleum fuels,” *WIT Transactions on Ecology and the Environment*, vol. 186, pp. 443–456, 2015.

[6] H. Liu, “Ammonia synthesis catalyst 100 years: practice, enlightenment and challenge,” *Chinese Journal of Catalysis*, vol. 35, no. 10, pp. 1619–1640, 2014.

[7] S. L. Foster, S. I. P. Bakovic, R. D. Duda et al., “Catalysts for nitrogen reduction to ammonia,” *Nature Catalysis*, vol. 1, no. 7, pp. 490–500, 2018.

[8] Y. Liu, M. Cheng, Z. He et al., “Pothole-rich ultrathin WO3 nanosheets that trigger N≡N bond activation of nitrogen for...
direct nitrate photosynthesis,” Angewandte Chemie, International Edition, vol. 58, no. 3, pp. 731–735, 2019.

[9] H. Hirakawa, M. Hashimoto, Y. Shiraishi, and T. Hirai, “Photocatalytic conversion of nitrogen to ammonia with water on surface oxygen vacancies of titanium dioxide,” Journal of the American Chemical Society, vol. 139, no. 31, pp. 10929–10936, 2017.

[10] G. N. Schrauwer and T. D. Guth, “Photolysis of water and photo-reduction of nitrogen on titanium dioxide,” Journal of the American Chemical Society, vol. 99, no. 22, pp. 7189–7193, 2002.

[11] M. M. T. Khan, R. C. Bhardwaj, and C. Bhardwaj, “Catalytic fixation of nitrogen by the photocatalytic CdS/Pt/RuO2 particulate system in the presence of aqueous [Ru(Hedta)N2]3+ complex,” Angewandte Chemie (International Ed. in English), vol. 27, no. 7, pp. 923–925, 1988.

[12] S. Wang, X. Hai, X. Ding et al., “Light-switchable oxygen vacancies in ultrafine Bi5O7Br nanotubes for boosting solar-driven nitrogen fixation in pure water,” Advanced Materials, vol. 29, no. 31, article 1701774, 2017.

[13] J. W. Peters, A. Rasmussen, L. C. Seefeldt et al., “Light-driven dinitrogen reduction catalyzed by a CdS:nitrogenase MoFe protein biohybrid,” Science, vol. 352, pp. 448–450, 2016.

[14] N. Zhang, A. Jalil, D. Wu et al., “Defining defect states in W18O49 by Mo doping: a strategy for tuning N2 activation towards solar-driven nitrogen fixation,” Journal of the American Chemical Society, vol. 140, no. 30, pp. 9434–9443, 2018.

[15] S. Yuan, J. Chen, Z. Lin, W. Li, G. Sheng, and H. Yu, “Nitrate formation from atmospheric nitrogen and oxygen photocatalysed by nano-sized titanium dioxide,” Nature Communications, vol. 4, no. 1, pp. 2249, 2013.

[16] M. Kitano, Y. Inoue, Y. Yamazaki et al., “Ammonia synthesis using a stable electrode as an electron donor and reversible hydrogen store,” Nature Chemistry, vol. 4, no. 11, pp. 934–940, 2012.

[17] D. Kumar, S. Pal, and S. Krishnamurty, “N2 activation on Al metal clusters: catalyzing role of BN-doped graphene support,” Physical Chemistry Chemical Physics, vol. 18, no. 40, pp. 27721–27727, 2016.

[18] H. Li, J. Shang, Z. Ai, and L. Zhang, “Efficient visible light nitrogen fixation with BiOBr nanosheets of oxygen vacancies on the exposed [001] facets,” Journal of the American Chemical Society, vol. 137, no. 19, pp. 6393–6399, 2015.

[19] Y. Liu, T. Zhou, Y. Zheng et al., “Local electric field facilitates high-performance Li-ion batteries,” ACS Nano, vol. 11, no. 8, pp. 8519–8526, 2017.

[20] X. Chen, N. Li, Z. Kong, W. J. Ong, and X. Zhao, “Photocatalytic fixation of nitrogen to ammonia: state-of-the-art advancements and future prospects,” Materials Horizons, vol. 5, no. 1, pp. 9–27, 2018.

[21] M. Li, H. Huang, J. Low, C. Gao, R. Long, and Y. Xiong, “Recent progress on electrocatalyst and photocatalyst design for nitrogen reduction,” Small Methods, vol. 3, no. 6, article 1800388, 2018.

[22] S. Hu, X. Chen, Q. Li, Y. Zhao, and W. Mao, “Effect of sulfur vacancies on the nitrogen photofixation performance of ternary metal sulfide photocatalysts,” Catalysis Science & Technology, vol. 6, no. 15, pp. 5884–5890, 2016.

[23] S. Hu, Y. Li, F. Li et al., “Construction of g-\(\text{g-C}_3\text{N}_4/Z\text{Sn}_{0.11}\text{S}_{\text{11/12}}\text{Cd}_{\text{688/112}}\) hybrid heterojunction catalyst with outstanding nitrogen photofixation performance induced by sulfur vacancies,” ACS Sustainable Chemistry & Engineering, vol. 4, pp. 2269–2278, 2016.

[24] H. Ma, Z. Shi, S. Li, and N. Liu, “Large-scale production of graphitic carbon nitride with outstanding nitrogen photofixation ability via a convenient microwave treatment,” Applied Surface Science, vol. 379, pp. 309–315, 2016.

[25] H. Ma, Z. Shi, Q. Li, and S. Li, “Preparation of graphitic carbon nitride with large specific surface area and outstanding N2 photofixation ability via a dissolve-regrowth process,” Journal of Physics and Chemistry of Solids, vol. 99, pp. 51–58, 2016.

[26] G. Wu, Y. Gao, and B. Zheng, “Template-free method for synthesizing sponge-like graphitic carbon nitride with a large surface area and outstanding nitrogen photofixation ability induced by nitrogen vacancies,” Ceramics International, vol. 42, no. 6, pp. 6985–6992, 2016.

[27] Y. C. Zhang, N. Afzal, L. Pan, X. Zhang, and J. J. Zou, “Structure-activity relationship of defective metal-based photocatalysts for water splitting: experimental and theoretical perspectives,” Advancement of Science, vol. 6, no. 10, article 1900053, 2019.

[28] G. Xi, S. Ouyang, P. Li et al., “Ultrathin \(\text{W}_{18}\text{O}_{49}\) nanowires with diameters below 1 nm: synthesis, near-infrared absorption, photoluminescence, and photochemical reduction of carbon dioxide,” Angewandte Chemie, International Edition, vol. 51, no. 10, pp. 2395–2399, 2012.

[29] Z. Mei, B. Zhang, J. Zheng et al., “Tuning Cu dopant of \(\text{Zn}_{0.5}\text{C}_{0.5}\) nanocrystals enables high-performance photocatalytic \(\text{H}_2\) evolution from water splitting under visible-light irradiation,” Nano Energy, vol. 26, pp. 405–416, 2016.

[30] S. Cong, F. Geng, and Z. Zhao, “Tungsten oxide materials for optoelectronic applications,” Advanced Materials, vol. 28, no. 47, pp. 10518–10528, 2016.

[31] H. Bai, W. Yi, J. Liu et al., “Large-scale synthesis of ultrathin tungsten oxide nanowire networks: an efficient catalyst for aerobic oxidation of toluene to benzaldehyde under visible light,” NanoScale, vol. 8, no. 28, pp. 13545–13551, 2016.

[32] R. Ganesan, I. Perelshtein, and A. Gedanken, “Biotemplated synthesis of single-crystalline \(\text{W}_{18}\text{O}_{49}\)@\(\text{C}\) core-shell nanorod and its capacitance properties,” Journal of Physical Chemistry C, vol. 112, no. 6, pp. 1913–1919, 2008.

[33] M. Govender, L. Shikwambana, B. W. Mwakikunga, E. Sideras-Haddad, R. M. Eramus, and A. Forbes, “Formation of tungsten oxide nanostructures by laser pyrolysis: stars, fibres and spheres,” Nanoscale Research Letters, vol. 6, no. 1, pp. 166, 2011.

[34] J. Ding, Q. Zhong, and H. Gu, “Iron-titanium dioxide composite nanoparticles prepared with an energy effective method for efficient visible-light-driven photocatalytic nitrogen reduction to ammonia,” Journal of Alloys and Compounds, vol. 746, pp. 147–152, 2018.

[35] Y. Zhao, Y. Zhao, G. I. N. Waterhouse et al., “Layered-double-hydroxide nanosheets as efficient visible-light-driven photocatalysts for dinitrogen fixation,” Advanced Materials, vol. 29, pp. 1–10, 2017.

[36] D. A. Muller, “Structure and bonding at the atomic scale by scanning transmission electron microscopy,” Nature Materials, vol. 8, no. 4, pp. 263–270, 2009.

[37] X. Chang, L. Dong, Y. Yin, and S. Sun, “A novel composite photocatalyst based on in situ growth of ultrathin tungsten oxide nanowires on graphene oxide sheets,” RSC Advances, vol. 3, no. 35, pp. 15005–15013, 2013.
[38] C. Guo, S. Yin, M. Yan, M. Kobayashi, M. Kakihana, and T. Sato, “Morphology-controlled synthesis of $W_{18}O_{49}$ nanostructures and their near-infrared absorption properties,” Inorganic Chemistry, vol. 51, no. 8, pp. 4763–4771, 2012.

[39] J. Guo, Y. Shi, H. Zhou, X. Wang, and T. Ma, “A novel composite of W18O49 nanorods on reduced graphene oxide sheets based on in situ synthesis and catalytic performance for oxygen reduction reaction,” RSC Advances, vol. 7, no. 4, pp. 2051–2057, 2017.

[40] T. Kunyapat, F. Xu, N. Neate et al., “Ce-doped bundled ultrafine diameter tungsten oxide nanowires with enhanced electrochromic performance,” Nanoscale, vol. 10, no. 10, pp. 4718–4726, 2018.

[41] H. C. Lin, C. Y. Su, Y. H. Yu, and C. K. Lin, “Non-catalytic and substrate-free method to titania-doped $W_{18}O_{49}$ nanorods: growth, characterizations, and electro-optical properties,” Journal of Nanoparticle Research, vol. 14, 2012.

[42] D. Y. Lu, J. Chen, S. Z. Deng, N. S. Xu, and W. H. Zhang, “The most powerful tool for the structural analysis of tungsten suboxide nanowires: Raman spectroscopy,” Journal of Materials Research, vol. 23, no. 2, pp. 402–408, 2008.

[43] J. A. Schwarz, “Temperature-programmed desorption and reaction: applications to supported catalysts,” Catalysis Reviews, vol. 25, pp. 141–227, 1983.

[44] Y. Chan, “Temperature-programmed desorption of $N_2$, Ar, and $CO_2$ encapsulated in 3A zeolite,” Journal of Catalysis, vol. 50, pp. 319–329, 2004.

[45] B. Fastrup, “Temperature-programmed adsorption and desorption of nitrogen on iron ammonia synthesis catalysts,” Journal of Catalysis, vol. 150, no. 2, pp. 345–355, 1994.

[46] B. Fastrup, M. Mühler, H. N. Nielsen, and L. P. Nielsen, “The interaction of $H_2$ and $N_2$ with iron catalysts used for NH$_3$ synthesis: a temperature-programmed desorption and reaction study,” Journal of Catalysis, vol. 142, no. 1, pp. 135–146, 1993.

[47] W. Hu, Y. Zhao, Z. Liu, C. W. Dunnill, D. H. Gregory, and Y. Zhu, “Nanostructural evolution: from one-dimensional tungsten oxide nanowires to three-dimensional ferberite flowers,” Chemistry of Materials, vol. 20, no. 17, pp. 5657–5665, 2008.

[48] H. C. Lin, C. Y. Su, and C. K. Lin, “High-yield fabrication of $W_{18}O_{49}$@TiO$_2$ core-shell nanoparticles: microstructures and optical-thermal properties,” Journal of Nanoparticle Research, vol. 13, no. 10, pp. 4549–4555, 2011.

[49] B. Moschosky and T. Mokari, “Length and diameter control of ultrathin nanowires of substoichiometric tungsten oxide with insights into the growth mechanism,” Chemistry of Materials, vol. 25, no. 8, pp. 1384–1391, 2013.

[50] M. Falcone, L. Chatelain, R. Scopelliti, I. Živković, and M. Mazzanti, “Nitrogen reduction and functionalization by a multimetalltic uranium nitride complex,” Nature, vol. 547, no. 7663, pp. 332–335, 2017.