Dual-Metal Sites Boosting Polarization of Nitrogen Molecules for Efficient Nitrogen Photofixation

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Constructing nitrogen ($\text{N}_2$) adsorption and activation sites on semiconductors is the key to achieving efficient $\text{N}_2$ photofixation. Herein, Mn–W dual-metal sites on WO$_3$ are designed toward efficient $\text{N}_2$ photoreduction via controlled Mn doping. Impressively, the optimal 2.3% Mn-doped WO$_3$ (Mn-WO$_3$) exhibits a remarkable ammonia ($\text{NH}_3$) production rate of 425 µmol $\cdot$ g$_{\text{cat.}}^{-1}$ $\cdot$ h$^{-1}$, representing the best catalytic performance among the ever-reported tungsten oxide-based photocatalysts for $\text{N}_2$ fixation. Quasi in situ synchrotron radiation X-ray spectroscopy directly identifies that the Mn–W dual-metal sites can enhance the polarization of the adsorbed $\text{N}_2$, which is beneficial to the $\text{N}_2$ activation. Further theoretical calculations reveal that the increased polarization is originated from the electron back-donation into the antibonding orbitals of the adsorbed $\text{N}_2$, hence lowering the reaction energy barrier toward the $\text{N}_2$ photofixation. The concept of dual sites construction offers a powerful platform toward rational design of highly efficient catalysts for nitrogen fixation and beyond.

1. Introduction

Ammonia ($\text{NH}_3$) is one of the most important chemical products in modern industry to serve as the precursor of fertilizers, guaranteeing the subsistence of billions of people.[1–3] The synthesis of NH$_3$ in traditional industry is typically operated at high temperature and pressure via the Haber–Bosch process, which accounts for 1–2% of global energy consumption each year.[4–6] In recent years, photocatalysts have been widely considered as energy harvest antennas for renewable energy conversion.[7–12] Driven by solar energy, photocatalytic nitrogen ($\text{N}_2$) reduction paves a green and sustainable avenue to the synthesis of NH$_3$ under mild reaction conditions.[13–16] Due to the extremely stable N≡N triple bonds of $\text{N}_2$ molecules with the bond energy of 941 kJ mol$^{-1}$, efficient activation of $\text{N}_2$ molecules over catalysts is generally regarded as the bottleneck toward $\text{N}_2$ reduction.[17–21] To this end, various catalysts have been developed for photocatalytic $\text{N}_2$ fixation. For instance, Ye et al. constructed frustrated-Lewis-pairs by doping boron (Lewis acid) to capture and activate $\text{N}_2$ molecules.[22] Zhang et al. created oxygen vacancies with localized electrons on the surface of BiOBr nanosheets for activating $\text{N}_2$ molecules,[23] in which the NH$_3$ production rate reached 223.3 µmol $\cdot$ g$_{\text{cat.}}^{-1}$ $\cdot$ h$^{-1}$. Moreover, Yu and coworkers reported that hot electrons generated from plasmon excitation of the Au nanocrystals can facilitate the fracture of the...
N≡N bond to boost NH₃ synthesis. Although some progress has been achieved on N₂ photofixation, active photocatalysts with efficient N₂ adsorption and activation sites are still urgently desired.

Since the essence of the molecule activation is stemmed from the electron back-donation into the antibonding orbitals of the adsorbate, constructing superior adsorption sites is the key to achieve highly efficient N₂ photofixation. Generally, N₂ molecules are adsorbed on the single-metal sites of semiconductors through side-on or end-on configuration (Figure 1A). The absorption of N₂ molecules is through the electronic coupling between the d orbitals of the metal sites and the p orbitals of the N₂ molecules, where N₂ molecules could accept electrons from metal sites and thus induce polarization for the adsorbed N₂. Based on the adsorption configuration, the impact of the single metal on the molecular polarization might not be high enough for the activation of inert N₂ molecules. In this regard, dual-metal sites with different metallicity and d orbitals can induce polarization in N₂ molecules to a larger extent (Figure 1B). Therefore, constructing dual-metal sites could provide new opportunities to develop highly efficient catalysts for N₂ fixation.

Tungsten oxides have been widely used toward photocatalytic N₂ photofixation for low cost and stability. However, tungsten oxides generally lack efficient reaction sites for activating N₂. Meanwhile, Mn element has been regarded as a relatively active transition metal for N₂ reduction due to the coexistence of empty and occupied d orbitals. Herein, we designed and fabricated Mn–W dual catalytic sites on WO₃ semiconductor toward N₂ photoreduction by Mn doping. Impressively, the optimal 2.3% Mn-doped WO₃ (Mn–WO₃) delivers an NH₃ production rate of 425 µmol g⁻¹ h⁻¹, which is the best catalytic activity among the reported tungsten oxide-based photocatalysts for N₂ fixation. More importantly, quasi in situ X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge spectroscopy (XANES) directly demonstrate that N₂ molecules are highly polarized at Mn–W dual sites, which greatly contributes to the activation of N₂. Further theoretical analysis reveals that the increased molecular polarization is stemmed from the electron back-donation from the Mn–W dual sites to the antibonding orbitals of the adsorbed N₂ molecules, thus lowering the energy barrier of the N₂ fixation.

2. Results and Discussion

With regard to the synthesis of Mn–WO₃, 1.0 g of commercial W₂O₅·Mn₂O₃ powders were etched by sulfuric acid solution (H₂SO₄, 0.31 m) at 353 K for 2 h, followed by thermal treatment in muffle furnace at 873 K for 1 h, and 2.3% Mn–WO₃ was obtained with the mass percentage of Mn element being 2.3%. In addition, WO₃, 0.7% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃ were also prepared by the similar synthetic procedure by varying the concentration of H₂SO₄ solution. The scanning electron microscopy images of as-obtained samples show similar morphology with aggregated nanocrystalline structure (Figure S1, Supporting Information). Figure 2A displays the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of 2.3% Mn–WO₃. The fringes with interplanar spacing of 3.6 Å are assigned to the (200) plane of WO₃ nanocrystals. Besides, STEM energy-dispersive X-ray elemental mapping images of 2.3% Mn–WO₃ indicate the homogeneous distribution of W, O, and Mn elements (Figure 2B). Moreover, the 3D image of 2.3% Mn–WO₃ was revealed by soft X-ray computed tomography, exhibiting the morphology of irregular nanoparticles (Figure 2C). The Raman spectra of the samples are similar to that of commercial WO₃ (JCPDS#71-2141) (Figure 2D). As for 2.7% Mn–WO₃ and 5.0% Mn–WO₃, new peaks attributed to monoclinic MnWO₄ (JCPDS#13-0434) appear. As a result, WO₃, 0.7% Mn–WO₃, and 2.3% Mn–WO₃ are regarded as WO₃ nanocrystals doped by Mn atoms, while MnWO₄ phase is formed for 2.7% Mn–WO₃ and 5.0% Mn–WO₃.

Figure S2, Supporting Information, shows the XPS spectra of W 4f for different catalysts, where the peaks at 35.3 and 37.4 eV correspond to W 4f½ and 4f½ of W⁶⁺ species, respectively. As for the XPS spectra of O 1s, the peaks located at 530.1 and 532.8 eV are assigned to lattice oxygen and surface hydroxyl group, respectively (Figure S3, Supporting Information). The W species are in W⁵⁺ state for all samples, while these catalysts mainly contain the lattice oxygen species. Meanwhile, the XPS analysis also reveals that the nitrogen impurity is negligible in these catalysts (Figure S4, Supporting Information). When it comes to the XPS spectra of Mn 2p, Mn²⁺ species with two peaks located at 641.4 and 653.1 eV can be clearly observed for 2.3% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃ (Figure S5, Supporting Information). XANES was further measured to explore the electronic properties of these samples. Mn species in 0.7% Mn–WO₃, 2.3% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃ exhibit the characteristic of oxidation state in Mn K-edge XANES spectra (Figure 2E). In addition, the W L₃-edge XANES spectra of the samples are similar to that of commercial WO₃ (Figure 2F), which is consistent with the XPS results.

The as-obtained samples were applied as the photocatalysts toward N₂ photofixation. Each reaction was performed in 20 mL of water under 1 atm of N₂ at 25℃ with 10 mg of catalysts. The generated NH₃ was analyzed spectrophotometrically using Nessler’s reagent, ion chromatography, and ¹H nuclear magnetic resonance (¹H-NMR) methods (Figures S6–S8 and Table S1, Supporting Information). In the absence of catalysts, no product
**Figure 2.** A) Magnified HAADF-STEM image. B) EDS elemental mapping images, and C) synchrotron X-ray 3D computed tomography image of 2.3% Mn–WO₃. D) XRD patterns of the obtained samples. E) Mn K-edge XANES spectra of 0.7% Mn–WO₃, 2.3% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃. Mn foil and MnO were used as references. F) W L₃-edge XANES spectra of WO₃, 0.7% Mn–WO₃, 2.3% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃. The commercial WO₃ was used as a reference.

was observed (Table S2, entry 1, Supporting Information). Figure 3A illustrates the NH₃ production rate under full-spectrum irradiation (320–780 nm) of Xenon lamp (250 mW cm⁻²). WO₃, 0.7% Mn–WO₃, 2.3% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃ exhibit the NH₃ production rate of 81, 249, 425, 316, and 176 µmol g⁻¹ h⁻¹, respectively. Besides, the NH₃ production rate for 2.3% Mn–WO₃ under visible light still reaches 5.7, 2.1, 1.7, and 4.1 times as high as that for WO₃, 0.7% Mn–WO₃, 2.7% Mn–WO₃, and 5.0% Mn–WO₃, respectively. Thus, 2.3% Mn–WO₃ exhibits superior catalytic activity for N₂ photoreduction, which also represents the best catalytic performance among the ever-reported tungsten oxide-based photocatalysts (Figure S9 and Tables S3 and S4, Supporting Information). Furthermore, controlled experiments were carried out to confirm the authenticity of the reaction. As shown in Table S2, Supporting Information, no NH₃ was detected without light irradiation over 2.3% Mn–WO₃, confirming that the N₂ reduction process is driven by light. Besides, replacing H₂O with CH₃CN also...
inhibits the formation of NH$_3$, suggesting that H$_2$O is the proton source of NH$_3$ (Table S2, entry 3, Supporting Information). In addition, the disappearance of NH$_3$ after replacing N$_2$ with Ar proves that NH$_3$ originates from N$_2$ fixation (Table S2, entry 4, Supporting Information). Moreover, neither N$_2$H$_4$ nor NO$_3^-$ was detected during the photocatalytic process. Furthermore, we also simultaneously detected the production of H$_2$ and O$_2$ during the N$_2$ fixation process (Figure S10, Supporting Information).

To further corroborate the origin of obtained NH$_3$, we designed an isotopic labeling study by using $^{15}$N$_2$ as the purging gas.\cite{44} The obtained $^{15}$NH$_4^+$ was measured by NMR spectroscopy. As shown in $^1$H NMR spectra (Figure 3B), the isotopically labeled sample exhibits the doublets of $^{15}$NH$_4^+$, reaffirming that the generated NH$_3$ indeed originates from N$_2$ fixation. To evaluate the light utilization efficiency, the apparent quantum efficiency (AQE) of 2.3% Mn–WO$_3$ was measured under their radiation of monochromatic light (Figure 3C). Specifically, the AQE is calculated to be 0.18% at 450 nm for 2.3% Mn–WO$_3$. We further assessed the solar-to-ammonia (STA) efficiency of 2.3% Mn–WO$_3$ in pure water under simulated AM1.5G irradiation. The STA efficiency was calculated to be $\approx 0.019\%$, which was comparable to the results reported recently.\cite{45,46} Furthermore, the stability of 2.3% Mn–WO$_3$ was studied by recycling the catalyst (Figure 3D). After five successive reaction rounds, nearly $\approx 100\%$ of initial activity was retained, indicating remarkable catalytic stability.

To explore the catalytic mechanism, we investigated the energy band structures of the obtained catalysts. As indicated by diffuse reflectance ultraviolet–visible (UV–vis) spectra, the intrinsic UV–vis absorption edges of prepared samples are similar (Figure S11, Supporting Information). In addition, the values of band gaps are determined to be 2.60 and 2.58 eV for WO$_3$ and 2.3% Mn–WO$_3$, respectively (Figure S12, Supporting Information). The positions of valence band (VB) for these samples were measured by synchrotron radiation photoemission spectroscopy with a photon energy of 169.96 eV (Figures S13 and S14, Supporting Information). As a result, the values of VB for WO$_3$ and 2.3% Mn–WO$_3$ are 2.23 and 2.02 eV below Fermi level ($E_F$), respectively. Considering the value of normal hydrogen electrode (NHE), 4.50 eV, versus vacuum level (Figure S15, Supporting Information), the electronic band structures versus NHE of WO$_3$ and 2.3% Mn–WO$_3$ are illustrated in Figure 4A. Apparently, Mn doping elevates the CB of WO$_3$ nanocrystals, ensuring sufficient driving force to trigger N$_2$ reduction. By contrast, commercial WO$_3$ is thermodynamically unfavorable for N$_2$ reduction (Figures S16–S19, Supporting Information).

The photoinduced charge-separation efficiency was further explored for these photocatalysts. Figure S20, Supporting Information, shows the transient photocurrent responses spectra of WO$_3$, 2.3% Mn–WO$_3$, and 5.0% Mn–WO$_3$ under Ar atmosphere, where 2.3% Mn–WO$_3$ exhibits the strongest photocurrent density. The high photoinduced charge-separation efficiency of 2.3% Mn–WO$_3$ is further proved by room-temperature photoluminescence spectroscopy (Figure S21, Supporting Information). Meanwhile, 5.0% Mn–WO$_3$ displays the highest intensity among
Figure 4. A) The illustration of band structures of WO$_3$ and 2.3% Mn–WO$_3$. B) Transient photocurrent responses spectra under Ar or N$_2$ atmosphere of WO$_3$ and 2.3% Mn–WO$_3$. C) Quasi in situ XPS spectra of Mn 2p and D) quasi in situ XANES spectra of Mn L-edge of 2.3% Mn–WO$_3$ before and after N$_2$ treatment. E) Quasi in situ XANES spectra of N K-edge of WO$_3$ and 2.3% Mn–WO$_3$ after N$_2$ treatment. F) Schematic illustration for the polarization of adsorbed N$_2$ molecules at Mn–W dual sites through strong electrons transfer.

all the samples, which may suggest the rapid recombination of the charge carrier for excessive Mn doping. In addition, as can be seen from the O K-edge X-ray absorption spectroscopy (Figure S22, Supporting Information), the peak located at 533 eV is related to W/Mn–O hybridization, originating from the electron transfer from O to W/Mn atoms. 2.3% Mn–WO$_3$ displays enhanced covalency between metal and O atoms due to the strongest intensity of the peak at 533 eV. As the metal–oxygen covalency promotes the electron transfer from metal active sites to adsorbed molecules, the adsorbed N$_2$ molecules are expected to facilely accept electrons from 2.3% Mn–WO$_3$. This point is confirmed by transient photocurrent responses of the catalysts (Figure 4B). When the electrolyte was saturated N$_2$, the transient photocurrent responses declined, which can be attributed to the competitive interfacial electron transfer to adsorbed N$_2$ molecules. Apparently, the photocurrent responses
of 2.3% Mn–WO3 under N2 decreases by ≈39.1% compared with those under Ar atmosphere, which further confirms the active electron transfer from 2.3% Mn–WO3 to adsorbed N2 molecules over the photocatalysis process.\[16\]

To further clarify the promotion effect of Mn–W dual sites on N2 activation, quasi in situ XPS and quasi in situ XANES were performed. After treated with N2 gas, the binding energies of Mn 2p spectrum for 2.3% Mn–WO3 displays a positive shift of ≈0.5 eV (Figure 4C). Meanwhile, a similar shift of 0.4 eV to higher energy region is also observed in Mn L-edge spectra. As displayed in Figure 4D, the Mn L-edge spectra of 2.3% Mn–WO3 own two photon energy peaks of L1 and L2, located at 640.8 and 652.3 eV, corresponding to the electron transition from Mn 2p1/2 and 2p1/2 to 3d, respectively.\[48\] The variation of the electronic state of Mn indicates that the Mn sites spontaneously inject electrons into the adsorbed N2 molecules.\[49\] We further applied N K-edge spectra to monitor the evolution of adsorbed N2 molecules. As shown in Figure 4E, the peaks in the range of 395 to 405 eV are assigned to multi-electron excitations associated with the prominent N 1s→\(\pi^*\) transition, while the peak at ≈418 eV is called \(\sigma^*\) shape resonance.\[50\] A fact which has been discussed extensively is that the energy position and strength of the \(\sigma^*\) resonance are very sensitive to the internuclear distance, namely bond length. Specifically, the longer bond length results in lower position and higher intensity of \(\sigma^*\) resonance for first-row diatomics.\[51\] Apparently, the \(\sigma^*\) resonance of adsorbed N2 for 2.3% Mn–WO3 shows a sharp position movement and an increased intensity compared with that for WO3. It clearly indicates that the N≡N triple bond is asymmetrically elongated and efficiently polarized over 2.3% Mn–WO3, as illustrated in Figure 4F.

Furthermore, density functional theory (DFT) calculations were conducted to gain in-depth insights into the reaction process over Mn–WO3. Based on the experimental results shown in Figure 2A,D, the WO3(200) and Mn-doped WO3(200) models were built as shown in Figure S23, Supporting Information. The stability of the Mn-doped model was first studied. As displayed in Figure S24, Supporting Information, the model of Mn–WO3(200) still maintained its geometric structure even after 500 steps in 5ps simulation. Moreover, the adsorption configurations and energies of N2 molecules on these models were calculated. As for WO3(200), N2 molecule is weakly adsorbed on WO3(200) through end-on configuration with an adsorption energy of −0.56 eV (Figure 5A). As for side-on configuration of N2 on WO3(200), the corresponding adsorption energy is determined to be endothermic.
dual sites is also beneficial for the polarization of adsorbed N2 molecules. The difference of electron density between two nitrogen atoms in adsorbed N2 molecule over Mn–WO3(200) is much higher than that over WO3(200). Thus, N2 molecules are obviously polarized by Mn–W dual sites, leading to elongated bond length of N=N triple bond. Moreover, the reaction pathways over WO3(200) and Mn–WO3(200) were also screened. The simultaneous activation of two nitrogen atoms through side-on configuration greatly optimizes subsequent hydrogenation steps over Mn–WO3(200) (Figure S26, Supporting Information). Meanwhile, the other possibilities of reaction paths were also considered and studied in Figures S27 and S28, Supporting Information. As a result, the N2 fixation over WO3(200) undergoes distal pathway, while Mn–WO3(200) favors associative alternating pathway (Figure 5G). More importantly, due to the inertness and stability of the N2 molecules, the hydrogenation from N2* to NNH* with an energy of 0.810 eV is the rate-limiting step over WO3(200). While in Mn–WO3(200), the polarization effect from Mn–W dual sites greatly weaken the adsorbed N2 molecules, hence the energy barrier of subsequent hydrogenation is reduced and the rate-limiting step is changed to the hydrogenation of HNHN to H2NNH2 with an energy of 0.591 eV.

3. Conclusion

In summary, we developed a highly active and stable photocatalyst toward N2 photofixation by constructing Mn–W dual sites on WO3 semiconductor. An impressive NH3 production rate of 425 μmol gcat.−1 h−1 is achieved over the optimal 2.3% Mn–WO3 catalyst, which represents the best values among the tungsten oxide-based photocatalysts for N2 fixation. Meanwhile, nearly ≥100% of initial activity can be retained after five successive reaction rounds. Quasi in situ XPS and XANES reveal that Mn–W dual sites can highly polarize the adsorbed N2 molecules through interfacial electronic coupling. Further theoretical calculations demonstrate that the formation of Mn–W dual sites plays a pivotal role in promoting the adsorption and activation of N2 molecules. This work not only opens an avenue to develop efficient photocatalysts for N2 fixation under mild conditions via the construction of dual-metal sites, but also provides atomic-level insights into understanding the catalytic process.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Y.Z., T.H., and Q.X. contributed equally to this work. The authors appreciate the beamline BL14W1 in SSRF, BL10B, and BL07W in NSRL for synchrotron radiation measurements. The DFT calculations were conducted on the supercomputing system in the Supercomputing Center of USTC. This work was supported by National Key R&D Program of China (2017YFA0700104 and 2017YFA0403402), National Natural Science Foundation of China (Grant Nos. 11875258, 51801075, U1932213, and U1932148), the Fundamental Research Funds for the Central Universities (No. WK2060000016), Collaborative Innovation Program of Hefei Science Center, CAS (No. 2019HSC-CIP009), Users with Excellence Program of Hefei Science Center, CAS (Nos. 2018HSC-UE003 and 2019HSC-UE004), and the Youth Innovation Promotion Association, CAS (2020454).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
