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A nitrogen fixation strategy to synthesize NO via the thermallyassisted photocatalytic conversion of air

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Developing a novel strategy for energy-efficient and clean synthesis of NO at distributed sources is highly desirable. Herein, we present a facile and green way to synthesize NO through the thermal-assisted photocatalytic oxidation of N₂ using simulated air as reactant in a flow reactor. The TiO₂/WO₃ heterostructured nanorods were constructed and exhibited good activity for NO photosynthesis assisted with the heat of 200-350 °C. The yield rate of NO reached 0.16 mmol g⁻¹ h⁻¹ at 300 °C with a quantum efficiency of 0.31 % at 365 nm. ¹⁵N isotope labeling experiments proved the origin of NO from N₂ oxidation. Experimental and theoretical results revealed that the lattice oxygen in the heterostructures participated in the photooxidation reaction of N₂ and the electron transfer from WO₃ to TiO₂ at the interface of heterojunction under illumination could facilitate the adsorption of N₂ and the formation of NO^{*} intermediate and thus enhanced the photocatalytic N₂ oxidation performance. Importantly, the solar-driven generated NO can be directly used for the synthesis of fine chemicals including nitric acid and *θ*-nitrostyrolene. Our work opens a new avenue for nitrogen fixation via solar-driven N₂ oxidation at distributed source of air.

1. Introduction

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Nitrogen monoxide (NO), as one of the most important active nitrogen, has been widely used in manufacturing bulk chemical of nitric acid and various kinds of fine chemicals.¹⁻⁴ Commercial NO is produced by combining the artificial ammonia synthesis (Haber-Bosch process) and the catalytic oxidation of ammonia (Ostwald process).⁵⁻⁹ Both two highly energy-intensive processes are accompanied with the discharge of huge amounts of greenhouse gas.¹⁰⁻¹³ Moreover, centralized NO chemical plants would cause serious security risk and energy waste during transportation.¹⁴ Considering that N₂ and O₂ are the main ingredients of air, directly bonding N_2 to O_2 in air is attractive from the points of energy saving and environmental protection. But, the direct reaction of N_2 and O_2 is symmetryforbidden and thus the reaction rate is negligible even at combustion temperatures.¹ Inspired by the lightning-induced nitrogen fixation in nature, plasma-driven oxidation of N₂ with O₂ (Birkeland-Eyde process) was proposed to produce NO.¹⁵⁻¹⁷ However, the development of this technique is hindered by high energy consumption and low throughput.^{18, 19} Therefore,

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searching energy-efficient and clean solutions to directly oxidize N_2 in air to NO at distributed sources are urgently required.

Solar light provides an inexhaustible source of globally available energy, and therefore the photocatalysis conversion of solar energy into chemical energy has been recognized as a promising technology to address the global energy crisis.²⁰⁻²² Recently, photocatalytic N₂ oxidation with water to produce nitrate was presented, but, the batch reactor control accompanying the potential photoreduction of products limited the development.^{23, 24} Theoretically, solar-driven N₂ oxidation to NO requires a photocatalyst able to generate holes to oxidize N₂ (E = 1.26 V vs. normal hydrogen electrode) and many semiconductors meet this requirement.²⁵ Moreover, the standard enthalpy (ΔH) of this reaction (Eq. 1) is 90.3 kJ/mol NO, indicating it is an endothermic reaction and the equilibrium is unfavorable for NO production at ambient conditions.¹

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

(1)

Notably, the reaction entropy (ΔS) is 12.4 J/K per mol NO, suggesting that the equilibrium NO concentration would rise rapidly with temperature.^{1, 25} Thus, it is reasonable to expect that a thermal-assisted photocatalyst with suitable band structure could drive the photooxidation of N₂ to NO with a continuous reaction system.

Herein, TiO₂/WO₃ nanorods with Z-scheme heterojunction were fabricated and adopted as photocatalyst for NO synthesis with the assistance of low-temperature heating (200-350 °C, Scheme 1). The TiO₂/WO₃ heterostructures showed the ability for photocatalytic NO synthesis with a yield rate of 0.16 mmol $g^{-1} h^{-1}$ at 300 °C and quantum efficiency of 0.31 % at 365 nm. ¹⁵N isotope labeling experiments proved that NO originated from N₂ oxidation in air. The lattice oxygen was confirmed as the active oxygen species for N₂ photooxidation based on the results of

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Scheme 1 Schematic illustration of the thermal-assisted photocatalytic synthesis of NO in air.

electron paramagnetic resonance (EPR). The time-resolved photoluminescence (PL) spectra, in situ X-ray photoelectron spectrum (XPS) and density functional theory (DFT) calculation were performed to probe the high activity origin of TiO_2/WO_3 heterostructures. Importantly, the external heating source could be replaced by enhanced incident light and the solardriven generated NO at the flow reactor outlet can serve as the distributed source for the direct synthesis of nitric acid and β nitrostyrolene.

2. Experimental section

2.1 Synthesis of materials

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Synthesis of WO₃ nanorods. In a typical procedure, WCl₆ (0.15 g) was dissolved in 30 mL ethanol by stirring for 20 min to form a yellow solution. Then, the yellow ethanol solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 24 h. After cooling down naturally to room temperature, blue precipitates were collected and washed in deionized water and ethanol three times, respectively, and then dried in a vacuum oven for 12 h. Finally, the blue precipitates were annealed at 500 °C for 4 h in air to produce WO₃ nanorods. Synthesis of TiO₂/WO₃ heterostructured nanorods. 0.2 g of the as-obtained WO₃ nanorods were dispersed in 30 mL isopropanol under sonication for 0.5 h. Then, 30 μL diethylenetriamine (DETA) and 0.2 mL titanium (IV) isopropoxide were successively added under strong stirring to form a homogenous suspension. The mixed suspension was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 10 h. After cooling down naturally to room temperature, blue precipitates were collected and washed in deionized water and ethanol three times, respectively, and then dried in a vacuum oven for 12 h. Finally, the blue precipitates were annealed at 500 °C for 4 h in air to produce the shallow yellow TiO₂/WO₃ heterostructured nanorods.

Synthesis of TiO₂ nanosheets. The TiO₂ nanosheets were obtained by dissolving WO₃ in the TiO₂/WO₃ heterostructured nanorods. 0.2 g of the as-obtained TiO_2/WO_3 nanorods were dispersed in 20 mL 5.0 mol L⁻¹ NaOH solution for 12 h under stirring. Then the white precipitates of TiO₂ nanosheets were collected and washed in deionized water and ethanol three times, respectively, and dried in a vacuum oven for 12 h.

2.2 Material Characterizations

a Bruker D8 Focus Diffraction System USing a CO/ CAASO 77Ce (λ =0.154178 nm). Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscope EDS (STEM-EDS) element mapping images were obtained with a Tecnai G2 F20 system equipped with EDAX. In situ and ex situ X-ray photoelectron spectroscopy (XPS) measurements were performed on a photoelectron spectrometer using Al Ka radiation as the excitation source (PHI 5000 VersaProbe). All the peaks were calibrated with C 1s spectrum at a binding energy of 284.8 eV. UV-Vis absorbance spectra were recorded on a Lambda 750S UV-vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. Photoluminescence (PL) measurements were carried out on a Jobin-Yvon-Fluorrolog 3-21 fluorescence photometer. The time-resolved PL spectra were obtained on State and Transient State Fluorescence the Steady Spectrometer (FLSP920). Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy was carried out on a Bruker ALPHA-T Fourier transform infrared spectrometer. The N₂ adsorption and desorption isotherms were measured using Autosorb-iQ2-MP instrument (Quantachrome Company, America). Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with an unfiltered He I (21.2 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV. The electron spin resonance (ESR) tests were conducted with an electron paramagnetic resonance A300 spectrometer (Bruker AXS Company, Germany). The ESR analysis was performed to detect the spin reactive O_2^- species adsorbed on the photocatalysts or dissolved in water/methanol under UV-vis light irradiation by using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX-8 spectrometer by applying an X-band (9.43 GHz, 1.5 mW) microwave and sweeping magnetic field at RT. The gas chromatograph-mass spectrometer (GC-MS) was carried out with TRACE DSQ. The liquid phase product was measured on Agilent 7890A with a thermal conductivity (TCD) and a flame ionization detector (FID). Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury Plus 400 instruments

The powder X-ray diffraction (XRD) patterns were performed on

2.3 Thermal-assisted photocatalytic N_2 oxidation

at 400 MHz (1H NMR).

The thermal-assisted photocatalytic N2 oxidation in the simulated air $(N_2:O_2 = 4:1)$ was carried out in a homemade equipment (Scheme S1). A cylindrical quartz reactor is surrounded by heating resistance wire and equipped with a top quartz window for light irradiation. The simulated solar illumination was obtained by passing light from a 300 W Xenon lamp equipped with an AM 1.5 G filter, and the power intensity of the incident light was calibrated to be 100 mW cm⁻² (1 sun). Typically, 0.1 g photocatalyst was loaded on the quartz sand breathable panel in the middle height of the reactor. The temperature of the photocatalyst was controlled by the buried

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thermocouple connecting to a heating source. In a typical measurement procedure, the photocatalyst in the reactor was firstly heated to 400 °C with Ar flow (0.8 L min⁻¹) for 2.5 h to remove the surface adsorbed impurities. Then, the temperature decreased to reaction temperature under the protection of Ar gas. Subsequently, the reaction atmosphere switched to air with a flow rate of 0.8 L min⁻¹. Finally, the NO concentration was real-time monitored by the NO_x analyzer (Thermo Fisher Scientific, Model 42i). Notably, when the thermal assisted temperature was low (≤ 200 °C), the NO concentration in the product was too low to be directly detected by the NO_x analyzer. At this time, a 50 L gas pocket was used to collect and concentrate the product with a lower flow rate of simulated air (0.2 L min⁻¹). Then, the gas pocket with concentrated production was detected through the NO_x analyzer. ¹⁵N isotope labeling experiments were conducted using the ultrapure ¹⁵N₂ as Nsource. For ¹⁵N isotope labeling experiment, ¹⁵N₂ and O₂ $(^{15}N_2:O_2 = 4:1)$ were mixed in the gas pocket and used as a reactant for photocatalytic $^{15}\mathrm{N}_2$ oxidation at 300 °C and the production was collected with a gas pocket for further GC-MS test. In this work, the related calculation of yield rate and yield were shown as follows:

Yield rate of NO (mmol g⁻¹ h⁻¹) =
$$\int_0^t C \times t \times \frac{v \times 10^{-3}}{M_{(NO)} \times m_{cat.} \times \tau}$$
 (2)
Yield of NO (mmol g⁻¹) = $\int_0^t C \times t \times \frac{v \times 10^{-3}}{M_{(NO)} \times m_{cat.}}$ (3)

where *C* is the concentration of NO detected by the NO_x analyzer (ppb), *t* is the instant time (min), *M* is the molar mass (g mol⁻¹), $m_{cat.}$ is the mass of catalyst (g), *T* is the reaction cumulative time (h), and *v* is the gas flow rate at the inlet of NO_x analyzer (0.7 L min⁻¹).

2.4 In situ synthesis of Nitric acid and 6-Nitrostyrolene

In the procedure of nitric acid synthesis, simulated air with the gas flow rate of 0.4 L min⁻¹ was used as the reactant for photocatalytic NO synthesis at 300 °C. Then, the outlet gas of the reactor was directly absorbed by 60 mL 50 mM sodium hydroxide solution under stirring, in which the generated NO would react with the excess O_2 and H_2O to produce nitric acid. The produced nitric acid reacted with sodium hydroxide to generate nitrate for further quantification. Colorimetric methods were applied to determine the concentration of nitrate.²⁶ Typically, 5 mL of the absorbing solution was successively added with 0.1 mL 1.0 M HCl and 0.01 mL 0.8 wt% sulfamic acid solution standing for 10 minutes at room temperature. The absorption spectrum was tested using an ultraviolet-visible spectrophotometer and the absorption intensities at the wavelength of 220 nm and 275 nm were recorded. The final absorbance value was calculated by the equation: $A = A_{220nm} - 2A_{275nm}$. The calibration curve was plotted using a series of concentrations of NO_3^- -N from 0 to 2.0 ppm. And the sodium nitrate applied for plotting calibration curve was pretreated by drying in the oven at 105-110 °C for 2 h in advance. In the procedure of β -nitrostyrolene synthesis, simulated air with the gas flow rate of 0.4 L min⁻¹ was used as the reactant for photocatalytic NO synthesis at 300 °C. Then, the outlet gas of the reactor was directly ventilated into 25 mL

reaction solution under stirring. And the reaction solution was composed of 1, 2-dichloroethane solven? and 2° and 2° and 2° reactant. After the reaction, the 25 mL reaction solution was steamed to remove the solvent for qualitative tests by GC-MS. And the produced θ -nitrostyrolene was further purified for the NMR test.

2.5 The measurement of Quantum Efficiency

Quantum Efficiency (QE) was tested at 300 °C under the illumination of 365 nm wavelength light, which was obtained by 300 W Xenon lamp equipped with 365 nm single-wavelength filter and the light intensity was measured to be 17.2 mW·cm⁻². 0.1 g photocatalyst was added into the quartz reactor and the irradiation region was a circular area with a diameter of 3.0 cm. The details of the QE calculation were shown as follows:²⁷ The number of absorbed photons ($N_{absorbed}$):

$$N_{absorbed} = \frac{t (s) \times P (W \cdot cm^{-2}) \times s (cm^2) \times \lambda (m)}{h (U \cdot s) \times c (m \cdot s^{-1})}$$
(4)

The QE of N₂ to NO:

$$QE = \frac{2 \times n_{NO} (mol) \times N_A (mol^{-1})}{N_{absorbed}} \times 100\%$$
 (5)

P: The optical power.

 λ : The wavenumber of the incident light.

c: The speed of light.

h: Planck constant.

t: The illumination time

2.6 Theoretical Simulation

Spin-polarized density functional theory (DFT) computations were performed as implemented in the plane wave set Vienna ab initio Simulation Package (VASP) code.^{28, 29} Projector augmented wave (PAW) potentials were used to describe the interaction between ions and valence electrons.³⁰ Generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form was adopted to describe the exchange-correlation between electrons.³¹ The DFT-D3 method was used for the vdW corrections.³² The kinetic-energy cut off was set as 500 eV. An energy convergence threshold of 10⁻⁴ eV was set in the selfconsistent field (SCF) iteration. The geometry optimization within the conjugate gradient method was performed with forces on each atom less than 0.05 eV/Å. A p (1 × 1) slab model with four W-O octahedral layers and a p (1×3) slab model with three Ti-O layers were adopted to simulate the WO₃ (001) and TiO₂ (101) surfaces, respectively. Vacuum layers larger than 15 Å were inserted along the *c* direction to eliminate the periodic image interactions. Half of the O atoms in the bottom O layer of WO₃ slab were removed to balance the W⁶⁺ valance state of the pseudo surface. The bottom W-O and Ti-O layer were fixed while other layers and the adsorbates were fully relaxed during structural optimizations. The Brillouin zone was sampled by a kpoint mesh of $4 \times 4 \times 1$. Gibbs free energies for each gaseous and adsorbed species were calculated according to the expression:

$G = E_{DFT} + E_{ZPE} - TS \qquad (6)$

where E_{DFT} and E_{ZPE} are the total energy and zero-point energy calculated with VASP, *TS* is the entropy contribution at 298.15

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K. The adsorption energy of O_2 or N_2 is calculated according to the expression:

 $E_{ads} = E_{adsorbate/slab} - (E_{slab} + E_{adsorbate})$ (7)

where $E_{adsorbate/slab}$ is the total energy of adsorbate on the surface; E_{slab} is the total energy of the surface and $E_{adsorbate}$ is the total energy of free O₂ or N₂ molecule.

3. Results and discussion

 TiO_2/WO_3 heterostructure was designed and synthesized as a model thermal-assisted photocatalyst for N_2 oxidation in air.

Fig. 1 Characterization of TiO₂/WO₃ heterostructured nanorods with a Z-scheme heterojunction. (a) HRTEM image of WO₃ nanorods (Inset: TEM image). (b) HRTEM image of the TiO₂/WO₃ heterostructured nanorods (Inset: TEM image). (c) XRD patterns of WO₃ nanorods and TiO₂/WO₃ heterostructured nanorods. (d) UV-Vis absorbance spectra and the Tauc plots (inset) of WO₃ nanorods and TiO₂ nanosheets. (e) DMPO spin-trapping ESR spectra recorded for \cdot O₂⁻ under UV-Vis light irradiation for different samples. (f) Schematic illustration for the electron transfer in TiO₂/WO₃ Z-scheme heterojunction.

First, WO₃ nanorods were synthesized through a simple solvothermal method along with thermal annealing. SEM image (Fig. S1) and TEM image (inset in Fig. 1a) showed their smooth surface and dozens of nanometer diameter. Typical HRTEM image (Fig. 1a) displayed the single-crystal structure of nanorods with the WO₃ (001) plane. XRD pattern (Fig. 1c) further proved the nanorods as pure WO₃ (JCPDS no. 43-1035). Then, WO₃ nanorods reacted with titanium (IV) isopropoxide

under solvothermal condition followed by thermal annealing to produce TiO₂/WO₃ heterostructured nanorods.19TheDsUrface of WO₃ nanorods becomes rough (Fig. S2) and a thin layer of TiO₂ nanosheets coated on the WO₃ nanorods (inset in Fig. 1b, Fig. S3). HRTEM image (Fig. 1b) displayed different lattice fringes of WO_3 (001) and TiO_2 (101) planes in core and shell, respectively. XRD pattern (Fig. 1c) confirmed the existence of WO₃ (JCPDS No. 43-1035) and TiO₂ (JCPDS No. 21-1272) in the TiO₂/WO₃ heterostructured nanorods without any peaks of other impurities. Moreover, the FTIR spectrum of TiO₂/WO₃ heterostructured nanorods was tested and shown in Fig. S4. The peaks located at 3413 and 1622 cm⁻¹ were due to the stretching and bending vibrations of the surface adsorbed water molecules. And the peaks located at 585 and 650 cm⁻¹ were attributed to the stretching vibrations of Ti-O bond in TiO₂.³³ Moreover, the W-O stretching and vibration bands in the region 960 cm⁻¹ to 800 cm⁻¹ were also detected.³³ No other absorption peaks appeared, suggesting that there were no nitrogencontaining impurities adsorbed on the surface of TiO₂/WO₃ heterostructures.³⁴ And the Brunauer-Emmett-Teller (BET) surface area of TiO₂/WO₃ heterostructured nanorods was calculated to be 72.0 m² g⁻¹ through the nitrogen adsorptiondesorption isotherm (Fig. S5). For comparison, TiO₂ nanosheets were obtained through the dissolution removal of WO₃ from

TiO₂/WO₃ heterostructures by alkali (Fig. S6). The bandgap energies (E_g) of WO₃ nanorods, TiO₂ nanosheets and TiO_2/WO_3 heterostructures were calculated to be 2.52, 3.03 and 2.76 eV, respectively, from the UV-vis absorbance spectra (Fig. 1d and Fig. S7). The valence band (VB) positions of WO₃ nanorods and TiO₂ nanosheets could be estimated at +2.88 and +2.63 V versus normal hydrogen electrode (NHE) based on the results of ultraviolet photoelectron spectroscopy (Fig. S8).³⁵ As a result, the conduction band (CB) positions of WO₃ nanorods and TiO_2 nanosheets could be deduced as +0.36 and -0.40 V versus NHE. Combining these data, the corresponding band structure diagram of WO₃ nanorods and TiO₂ nanosheets could be depicted as shown in Fig. S9. By using 5,5-dimethyl-1pyrroline N-oxide as the spin trap, ESR test exhibited that TiO₂ nanosheets and TiO₂/WO₃ heterostructures could photo-reduce O_2 into O_2^- radical,³⁶ while any signal of O_2^- could not be observed for WO₃ (Fig. 1e). Considering that the CB potential of WO_3 (+0.36 V) and TiO₂ (-0.40 V) was more positive and negative than the standard potential of O_2/O_2^- (-0.33 V vs NHE), respectively, it was reasonable to conclude a Z-scheme heterojunction mechanism (Fig. 1f) rather than the type II heterojunction mechanism (Fig. S10) in TiO₂/WO₃ heterostructure under irradiation. The photogenerated electrons in CB potential of WO₃ transferred onto TiO₂ and combined with the photogenerated holes in VB of TiO2, and thus suppressing the recombination of self-photogenerated carriers.37

 TiO_2/WO_3 heterostructures were applied for thermal-assisted photocatalytic N₂ oxidation using the simulated air (N₂:O₂ = 4:1) as the reactant. A homemade quartz flow reactor surrounded by heating resistance wire was used and 300 W Xenon lamp equipped with an AM 1.5 G filter (1 sun) served as the simulated solar irradiation. As shown in Fig. 2a, no NO was detected when



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no catalysts were used with air reactant and the TiO_2/WO_3 heterostructures were used as catalysts with Ar reactant under solar irradiation at 200 °C. Moreover, NO was not detected when the TiO_2/WO_3 heterostructures were used as catalysts with air reactant under dark at 200 °C, but we could detect NO production when the TiO_2/WO_3 heterostructures were used as catalysts with air reactant under solar irradiation at 200 °C. These results suggested that the production of NO derived from the photocatalytic reaction



Fig. 2 The thermal-assisted photooxidation performance of N_2 over a TiO₂/WO₃ photocatalyst. (a) NO yield rate under different conditions ("N/A" denotes "not detected"). (b) Photocatalytic yield rate of NO over TiO₂/WO₃ heterostructures at different temperatures. (c) Time-dependent yield rate curves of NO over TiO₂/WO₃ heterostructures at different temperatures. (d) Cycle tests for photocatalytic NO synthesis over TiO₂/WO₃ heterostructures (1 hour for a cycle). (e) Mass spectra of GC-MS analysis in the N₂ isotope experiment. (f) The yield rate of NO over TiO₂/WO₃ nanorods under 1 sun illumination assisted with external heating of 300 °C (up) and the yield rate of NO over TiO₂/WO₃ nanorods under 10 sun illumination without external heating (bottom).

of air reactant over TiO_2/WO_3 heterostructures assisted with 200 °C heating. And this discovery was consistent with previous works about solar-driven nitrogen oxidation by the water to produce nitrate/nitrite.^{23, 24, 38} Then the photocatalytic yield rate of NO over TiO_2/WO_3 heterostructures at different temperatures were studied. As shown in Fig. 2b, the NO yield rate improved rapidly with the increase of temperature from 200 °C to 350 °C. But, the time-dependent yield rate curves (Fig. 2c) exhibited a decline during the long-term test at 350 °C. Thus, we chose 300 °C as the operating temperature for the

subsequent study, which the yield rate of NO could reach to 0.16 mmol g⁻¹ h⁻¹. Firstly, the yield rate of NO increased from 0.16 to 0.91 mmol g⁻¹ h⁻¹ as the illumination intensity enhanced from 1 sun to 5 sun (Fig. S11), confirming the great effect of illumination intensity on the performance of photocatalytic NO synthesis. Then the 365 nm monochromatic light was chosen as the light source to evaluate the photocatalytic efficiency and the QE of 0.31% was obtained.27 Moreover, when little water vapor was introduced into the reactor, the water molecules may adsorb on the surface of TiO₂/WO₃ heterostructures and inhibit the adsorption of N₂, thus leading slight decline of NO yield rate (Fig. S12).³⁹ Finally, the NO yield showed no obvious decay after eight cycles (Fig. 2d). And there was no obvious decline of the time-dependent yield rate of NO during the continuou 8 h photocatalytic test (Fig. S13). The morphology and crystalline structure after long-term tests still maintained (Fig. S14), proving the excellent stability of TiO₂/WO₃ heterostructures.

To confirm the origin of NO, nitrogen isotope labeling experiments were conducted using the ${\rm ^{15}N_2}$ and ${\rm ^{14}N_2}$ as the Nsource, respectively. The gas-phase products were analyzed by gas chromatograph-mass spectrometry (GC-MS). ¹⁵NO (m/z = 31) can only be detected when ${}^{15}N_2$ was used as the reactant (Fig. 2e) and no ^{15}NO (m/z = 31) was detected in the feed $^{15}N_2$ gas (Fig. S15), suggesting that NO originated from the oxidation of N₂. Furthermore, no nitrous oxides were detected after replacing air with Ar, further confirming that the source of NO lied in N₂ oxidation rather than impurities in the reaction system (Fig. S16). Finally, the performance of WO₃ nanorods and the physically mixed TiO₂+WO₃ was studied for comparison. As shown in Fig. 2f, the NO yield rate of TiO₂/WO₃ heterostructures was distinctly higher than those of WO₃ nanorods and TiO₂+WO₃ mixtures, proving that the Z-scheme heterojunction in TiO_2/WO_3 heterostructure could enhance the performance. Notably, when the incident light source switched to 10 suns, the solar-driven surface temperature of photocatalysts increased to 200 °C (Fig. S17). At this time, the NO yield rate was even higher than that under 1 sun illumination with 300 °C external heating owing to more photogenerated carriers (the bottom in Fig. 2f). Thus, the external heating source is expected to be replaced by the adoption of a stronger incident light derived from a condenser, indicating the promising application potential of this technique in the future.

To further probe the origin of high performance of TiO₂/WO₃ heterostructures, temperature-programmed desorption (TPD) of NO, EPR, time-resolved PL spectra, *in situ*

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Fig. 3 Experimental characterization and theoretical calculation of the photooxidation performance of N₂ over TiO_2/WO_3 heterostructures. (a) EPR spectra of untested TiO_2/WO_3 heterostructures and tested TiO_2/WO_3 heterostructures under different atmospheres. (b) Time-resolved PL spectra of different samples. (c) W 4f and (d) Ti 2p XPS spectra of TiO_2/WO_3 heterostructures with and without light irradiation. (e) Reaction free energy diagram of N₂ oxidation over different samples.

XPS and DFT calculations were performed (Fig. 3). First, the NO-TPD profile showed that chemisorbed NO on TiO₂/WO₃ heterostructures desorbed at 296 °C (Fig. S18), indicating external heating can not only increase the NO equilibrium concentration but also promote the desorption of NO. Then, as shown in Fig. 3a, no EPR signals were detected for untested TiO₂/WO₃ heterostructures, suggesting no immanent oxygen vacancies in TiO₂/WO₃ heterostructures. There were also no EPR signals for TiO₂/WO₃ heterostructures after the photocatalytic test using air as the reactant. Interestingly, when the TiO_2/WO_3 heterostructures were tested using pure N₂ as the reactant, an obvious EPR signal of oxygen vacancies at g factor of ~2.002 appeared, indicating that the lattice oxygen in the heterostructures participated TiO₂/WO₂ in the N_2 photooxidation reaction.¹⁷ As shown in Fig. 3b, the TiO_2/WO_3 heterostructures possessed an extended PL lifetime compared to WO₃, indicating an enhanced separation efficiency of photogenerated charge carriers.⁴⁰ The intrinsic activity of photocatalysts was closely related to their electronic structure, and thus the electronic structure of TiO₂/WO₃ heterostructure was investigated. Under irradiation, the XPS peak of W 4f shifted to higher binding energy by 0.2 eV (Fig. 3c). On the contrary, the XPS peak of Ti 2p shifted to lower binding energy by 0.2 eV compared to that under darkness (Fig. 3d). The in situ XPS results indicated the electron transfer from WO₃ to TiO₂ at Page 6 of 9

the interface of TiO₂/WO₃ heterostructure under irradiation, which was consistent with the previous of the deduced 21 section heterojunction mechanism in TiO₂/WO₃ heterostructure (Fig. 1f).

The reaction Gibbs free energies (ΔG) of N₂ photooxidation were simulated to unveil the reaction path (Fig. 3e). Based on the results of the aforementioned in situ and ex situ characterizations, the WO₃ surface was positively charged by removing two electrons from the pure surface to reflect the interfacial charge transfer.^{41, 42} First, the N₂ adsorption energies on different samples were calculated (Fig. S19). Pure WO₃ (-1.69 eV) and interfacial WO₃ in TiO₂/WO₃ heterostructures (-2.48 eV) showed more negative adsorption energies than those of pure TiO₂ (-0.37 eV) and interfacial TiO₂ in TiO₂/WO₃ heterostructure (-0.22 eV). This result revealed that N₂ photooxidation proceeded on the surface of WO3 in the TiO2/WO3 heterostructure and interfacial charge transfer facilitated N₂ adsorption. Then, the N≡N bond was broken and one of the N atoms would take one surface lattice O atom away to form the first NO molecule, leaving the other N atom combining with the lattice O on WO₃ surface. The free energy increase for the first NO formation over pure WO_3 was as high as 3.59 eV. Interestingly, the free energy on the interfacial WO_3 surface was only 1.52 eV. The as-formed NO* easily released with ΔG value of -0.11 eV and 0.21 eV over pure and interfacial WO₃ surfaces, respectively, to form the second NO, leaving two surface oxygen vacancies in WO₃. Because the O₂ adsorption energy on the interfacial TiO₂ (-1.12 eV) was more negative than that of interfacial WO_3 (-0.36 eV) (Fig. S20) and the surface of interfacial TiO₂ was negatively charged (Fig. 1f), O₂ in air were absorbed on the interfacial TiO₂ and reduced by photoelectrons, and then transferred to interfacial WO₃ to fill back the surface oxygen vacancies. The interfacial WO₃ could promote the adsorption of N2 and the formation of NO* intermediate compared with pure WO₃, and thus the reaction was facilitated over TiO_2/WO_3 heterostructures.

To further excavate the application value of this solar-driven N₂ oxidation strategy, the generated NO was directly used to synthesize the value-added products. 0.64 µmol nitrate generated during 8 h accumulation time when the air flow at the outlet of the reactor was absorbed by alkaline solution (Fig. 4a and Fig. S21). β -nitrostyrolene played an important role in the pharmaceutical industry and can be produced by the reaction of styrene and NO.^{43, 44} As shown in Fig. 4b, β -



Fig. 4 The direct use of the as-produced NO. Synthesis of (a) nitric acid and (b) β -nitrostyrolene using photocatalytic generated NO.

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nitrostyrolene with 100% selectivity (Fig. S22) was obtained when the solar-driven NO production reacted with styrene. Notably, no products were detected in the control experiment using Ar gas as the feed gas (Fig. 4 and Fig. S23). This further demonstrated that the generated NO originated from N₂ photooxidation and it can be directly used to synthesize nitric acid and fine chemicals. Moreover, NO and the nitrate has also been proved as the raw materials for ammonia synthesis.⁴⁵⁻⁴⁸

4. Conclusions

In summary, TiO₂/WO₃ nanorods with Z-scheme heterojunction were successfully synthesized and adopted as thermal-assisted photocatalyst for solar-driven NO synthesis from air in a flow reactor. The as-obtained TiO₂/WO₃ heterostructures could efficiently photo-oxidize N_2 in air into NO with a yield rate of 0.16 mmol g $^{\rm -1}$ h $^{\rm -1}$ at 300 °C and a quantum efficiency of 0.31 % at 365 nm. ¹⁵N isotope labeling and blank experiments proved NO originating from N₂ oxidation. EPR revealed the critical role of lattice oxygen in N₂ activation. Combining time-resolved PL spectra and in situ XPS, DFT calculation revealed that the electron transfer at the interface of Z-scheme TiO₂/WO₃ heterojunction could not only facilitate the photo-charges separation but also promote the adsorption of N_2 and the formation of NO* intermediate, and thus enhanced the reaction. Moreover, the external heating source could be replaced by stronger incident light and the solar-driven generated NO can serve as the distributed source for the direct synthesis of nitric acid and fine chemical of β -nitrostyrolene, indicating the promising application potential of this technique. This work offers a new avenue for energy-efficient and green synthesis of NO from the air.

Conflicts of interest

There are no conflicts to declare

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A thermally-assisted photocatalytic conversion of air as an alternative nitrogen fixation strategy is reported to synthesize NO, which can be directly used for the synthesis of fine chemicals including nitric acid and β -nitrostyrolene.