Supporting Information

Single Pd Atoms Supported on Ultra-thin Bismuth Tungstate Nanosheets with Oxygen Vacancy as an Efficient Photocatalyst

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1. Experimental section

1.1 Materials and chemicals

Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, ≥ 99%), sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, ≥99%), and ethanol (≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China); K_2PdCl_4 (≥98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All chemicals used in this work are of analytical grade and used as received without further treatment. Ultrapure water with a resistivity of 18.2 $M\Omega \cdot cm^{-1}$ was produced using a Direct-Q 5 UV System (Merck Millipore, Germany). All gases were purchased from Xuzhou Special Gas Factory. The purities of O_2 and N_2 were 99.999%, and the NO cylinder contained 1001 ppm NO balanced in N_2.

1.2 Synthesis of photocatalysts

Synthesis of V_O-UBWO catalysts: The V_O-UBWO catalysts are synthesized through simple self-assembly, following the steps shown in Fig. 1a. Briefly, 0.2 g of sodium oleate is dispersed in 80 ml of ultrapure water at 50 °C by using continuous stirring magnetically for 10 min. After that, the mixed solution is cooled to room temperature. Then 0.4 g of bismuth nitrate and 0.136 g of sodium tungstate are added into the solution, followed by stirring magnetically for 30 min. This precursor solution is transferred to a 100-ml Teflon-lined stainless steel autoclave. The reactor is heated in an oven at 140 °C for 24 h, followed by natural cooling to room temperature. The obtained mixed solution is centrifuged three times with ultra-pure water at 60 °C, followed by centrifugation three more times with an organic mixture, in which the volume ratio of

cyclohexane and ethanol is 1:4. Finally, the resultant precipitation is dried in the room air to obtain V_O-UBWO samples.

Synthesis of Pd-V_O-UBWO catalysts: 0.6 g of the V_O-UBWO sample and 0.0032 g of K_2PdCl_4 are dispersed in a beaker containing 180 ml of ultra-pure water and ultrasonicated for 10 min. The mixed solution is placed in an oil bath set to 70 ℃ and stirred magnetically for 8 h. Then, the solution is centrifuged and washed using ultrapure water and absolute ethanol alternatively for three times, followed by drying in a vacuum oven at 60 ℃ for 8 h. Finally, the obtained powder is calcined in a tube furnace at 125 °C for 1 h with a heating rate of 5 °C/min in a N_2 atmosphere to obtain Pd-V_O-UBWO SACs.

Synthesis of PdNPs-V_O-UBWO catalysts: 1 g of the V_O-UBWO sample is dispersed with 100 mL of ultra-pure water, which is stirred magnetically for 30 min to prepare Solution A. 0.005g of K_2PdCl_4 is dispersed with 10 ml of ultrapure water and ultrasonated for 3 min to prepare Solution B. 0.0029 g of NaBH is then dispersed into 10 ml of ultrapure water followed by ultrasonation for 3 min to form Solution C. After that, Solutions B and C are added in sequence at an interval of 10 min to Solution A and stirred magnetically. Then the mixed solution is aged for 2 h. Finally, the resultant solution is centrifuged using ultrapure water and absolute ethanol, three times each, followed by drying in an oven at 70℃ for 8 h to obtain PdNPs-V_O-UBWO catalysts.

1.3 Characterizations

The crystal structures of the samples are characterized using X-ray diffraction (XRD, Bruker D8-Advance, Germany) with Cu Ka radiation (λ =1.5418 Å) over the 2θ range of 5°-80°. The morphologies and microstructures of the samples are examined using field emission

scanning electron microscopy (FE-SEM, Hitachi-SU8220, USA) and transmission electron microscopy (TEM, Tecnai G2-F20 FEI, USA). The thickness of the UBWO nanosheets is determined using AFM (Bruker Dimension Icon, GER). The Brunauer-Emmett-Teller (BET) specific surface areas of the samples are measured by nitrogen adsorption-desorption (Micromeritics ASAP 2460, USA). The elemental composition of the sample and the valence state of Pd are determined using XPS (Thermo ECALAB 250xi system with a monochromatic Al Kα source, USA). Optical properties are determined using UV–vis diffuse reflectance spectra (UV–vis DRS, Hitachi U-3900H, Japan). AC-HAADF-STEM images and EDS-mapping images of the samples are taken using Titan Cubed Themis G2300 (JEM-ARM200F, Japan). The amount of Pd element in the samples is determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 720ES(OES), USA). The concentrations of NO_3^- and NO_2^- in the used samples are measured using IC (Thermo Scientific Aquion, USA). Radical species are detected using ESR (Bruker EMXplus-6/1, Germany). The 5,5-dimethyl-1-pyrroline N-oxide (DMPO) is used as a trapping agent for $O_2^{\bullet-}$ and $OH^{\bullet}$.

1.4 Photoelectrochemical measurements

Photocurrent, electrochemical impedance spectra (EIS), and Mott-Schottky tests are conducted using an electrochemical workstation (CHi660E, Shanghai Chenhua, China) with a standard three-electrode system. A saturated calomel electrode (SCE) and a Pt electrode are used as the reference and counter electrodes, respectively. The electrolyte solution is 0.5M Na_2SO_4. The prepared catalysts are working electrode with an active area of *ca.*1.0×1.0 cm^2. The working electrode is prepared following this procedure: First, 5 mg of the prepared photocatalyst and 20 μL of Nafion solution (DuPont, 5 wt.%) are dispersed into 1 ml of absolute ethanol by ultrasound

for 2 min. Then 200 μL of the prepared solution is coated onto an indium-tin oxide glass (ITO 1×4 cm^2) with an effective coating area of 1×1 cm^2. Subsequently, the ITO glass is dried in an oven at 90 °C for 3 h to create the working electrode. A 300W xenon lamp with a 380 nm filter is employed as the visible light source. The photocurrent is measured for 200 s at a bias voltage of 0.5 V, and the lamp is turned on/off every 20 s. The EIS is performed at a bias voltage of 0.5 V over the frequency range from 0.01 Hz to 10000 Hz. The Mott Schottky test is performed at a frequency of 1000 Hz with voltages in the range of -0.6 -1.2 V.

1.5 Evaluation of Photocatalytic Activity for NO oxidation and RhB degradation

The photocatalytic oxidation of NO is carried out in a 5×10×0.5 cm rectangular ISO reactor. A 300W xenon lamp (DP200A PN/2123XSL, Beijing, China) with a 380 nm cut-off filter is placed vertically above the reactor as the light source. In a typical photocatalytic test, 0.08 g of the prepared catalysts is coated onto a glass slide with an area of 50 cm^2 (5×10 cm, loading capacity is 1.6 $mg \cdot cm^{-2}$). More details can be found in an earlier publication [1].

In a typical photocatalytic test, the total flow rate of the mixed gas is controlled at 200 $ml \cdot min^{-1}$ by mass flow controllers (CS200A, Zhengzhou Ketan, China). The concentration of O_2 is 5% in the simulated gas. The relative humidity (RH) of the inlet gas is maintained at 60±10% and monitored using a hygrometer (UNI-T UT333, China). RH of 0% is achieved by removing the moisture from the gas using silicone desiccants. RH of 100% is achieved by bubbling the gas into water upstream the reaction system. The reaction system reaches adsorption-desorption equilibrium after passing the gas mixture for 30 min, as indicated by the stable outlet NO concentration of 48 ppm, which is monitored every 15 s using an FTIR analyzer (MKS MultiGas 2060, USA, with an accuracy of 2%). Then the xenon lamp is turned on for photocatalysis. The

concentrations of NO_2 and HNO_2 at the outlet of the reactor are also detected simultaneously every 15s using the FTIR analyzer.

Furthermore, the photocatalytic stability of the catalyst is evaluated by cyclic tests. After each cycle, the used catalysts are regenerated by UV light irradiation for 1 h to decompose deposited nitrate. There are three cycles in total.

When light is irradiated for a duration of t s, the total moles of input NO ($n_{NO,in}$), unremoved NO ($n_{NO,un}$), removed NO ($n_{NO,rem}$), generated NO_2 ($n_{NO_2,gen}$) and generated HNO_2 ($n_{HNO_2,gen}$), conversion rate of NO (η_{NO}), removal efficiency of NO (β), the selectivity for the formation of NO_2 (S_{NO_2}), the selectivity for the formation of HNO_2 (S_{HNO_2}) in the reaction system are calculated as follows:

$$n_{NO,in} = \frac{P \times Q}{RT} \times \int_0^t C_{NO_{in}} dt \tag{S1}$$

$$n_{NO,un} = \frac{P \times Q}{RT} \times \int_0^t C_{NO_{out}} dt \tag{S2}$$

$$n_{NO,rem} = \frac{P \times Q}{RT} \times \left(\int_0^t C_{NO_{in}} . dt - \int_0^t C_{NO_{out}} . dt \right) \tag{S3}$$

$$n_{NO_2,gen} = \frac{P \times Q}{RT} \times \int_0^t C_{NO_2} \ dt \tag{S4}$$

$$n_{HNO_2,gen} = \frac{P \times Q}{RT} \times \int_0^t C_{HNO_2} \ dt \tag{S5}$$

$$\eta_{NO} = \frac{n_{NO,rem}}{n_{NO,in}} \times 100\% \tag{S6}$$

$$\beta = \frac{C_{NO,in} - C_{NO,out}}{C_{NO,in}} \times 100\% \tag{S7}$$

$$S_{NO_2} = \frac{n_{NO_2,gen}}{n_{NO,rem}} \times 100\% \tag{S8}$$

$$S_{HNO_2} = \frac{n_{HNO_2,gen}}{n_{NO,rem}} \times 100\% \tag{S9}$$

where P is the pressure in Pa; T is the temperature in the reaction system, the unit is K; R is the

molar gas constant with a value of 8.314 J•mol^{-1} • K^{-1}; and Q is the total flow rate of the gas. Its value is as follows: Q = 200 ml•min^{-1}=200×10^{-6}/60 m^3•s^{-1}=3.333×10^{-6} m^3•s^{-1}; $C_{NO,in}$ is the concentration of input NO, $C_{NO,out}$ is the concentration of NO at the outlet, C_{NO_2} is the concentration of NO_2 at the outlet, C_{HNO_2} is the concentration of HNO_2 at the outlet in the reaction system, the unit is ppm, t is the light irradiates time, the unit is s.

The moles of generated NO_3^- ($n_{NO_3^-,gen}$) and the selectivity for the formation of HNO_3 (S_{HNO_3}) are calculated as follows:

$$n_{NO_3^-,gen} = \frac{c(NO_3^{-1})V}{M_{NO_3^-}} \quad \text{(S10)}$$

$$S_{HNO_3} = \frac{n_{NO_3^-,gen}}{n_{NO,rem}} \times 100\% \quad \text{(S11)}$$

Where $c(NO_3^-)$ is the concentration of NO_3^- measured by ion chromatograph, V is the volume of NO_3^-solution in the experiment, $M_{NO_3^-}$ is the relative atomic mass of NO_3^-.

The prepared catalysts are also tested under visible light irradiation for the degradation of RhB to expand its engineering potential. The light source is another xenon lamp (Yuming YM-GHX-V, Shanghai) with a 380 nm UV-filter. The light intensity is about 29.6 mW cm^2 as measured using a radiometer (Model FZ-A from Beijing Normal University, China). In a typical test, 25 mg of catalyst is dispersed into 50 ml of solution with a RhB concentration of 10 mg·L^{-1}. Subsequently, the suspension is kept in the dark for 30 min to reach adsorption-desorption equilibrium. Then, the xenon lamp is turned on. 2-3 mL of the suspension is sampled every 10 min. The supernatant is obtained by removing the particles from the sample by centrifugation. Finally, the concentration of RhB in the supernatant is measured using a UV-visible

spectrophotometer (Hitachi U-3900H, Japan). The RhB degradation efficiency is then calculated using equation S12:

$$\eta_{RhB} = \frac{C_0 - C_t}{C_0} \times 100\% \quad \text{(S12)}$$

where η_{RhB} is the degradation efficiency of RhB in %, C_0 is the concentration of initial RhB in mg/L, and C_t is the concentration of RhB after visible-light irradiation of t min.

Active species trapping experiment: Potassium dichromate ($K_2Cr_2O_7$) is used as scavengers for e^- in the photocatalytic. The sample preparation follows a procedure that is similar to that for the photocatalytic NO test, except for the addition of 1.6 mmol of $K_2Cr_2O_7$. In addition, the photocatalytic activities of the Pd-V_O-UBWO catalysts for NO removal are tested in the absence of O_2 and moisture to investigate the effects of $O_2^{\bullet-}$ and $OH^{\bullet}$ on the photocatalytic activity.

1.6 Computational Methods

The DFT calculations are performed using the Vienna ab initio Simulation Package (VASP) software [2]. The exchange correlation function adopts the generalized gradient approximation (GGA) of Perdewe-Brukee-Ernzerhof (PBE). The energy cut-off is set to 600 eV, and the Monkhorst-Pack k-point is set to 3×3×1. Self-consistent field (SCF) convergence criterion is 1.0 × 10^{-5} eV, and the break condition for the ionic relaxation loop is 0.05 eV·$Å^{-1}$. Considering the Coulomb repulsion term (GGA+U) between electrons, the W and Pd atoms are assigned U_W of 6.2 eV and U_{Pd} of 3.6 eV, respectively[3]. The computational model of the BWO nanolayer uses two BWO (001) planes to match the thickness of the prepared V_O-UBWO, and the vacuum layer thickness is set to 20 Å. The formation energy is calculated using equation S2:

$$E_{for} = E_{Pd-V_O-UBWO} - \left(E_{Pd} + E_{V_O-UBWO}\right) \quad \text{(S13)}$$

where E_{Pd-V_O-UBWO} , E_{Pd} and E_{V_O-UBWO} are the total energies of Pd-V_O-UBWO, Pd atoms and V_O-UBWO, respectively.

Supplementary Figures

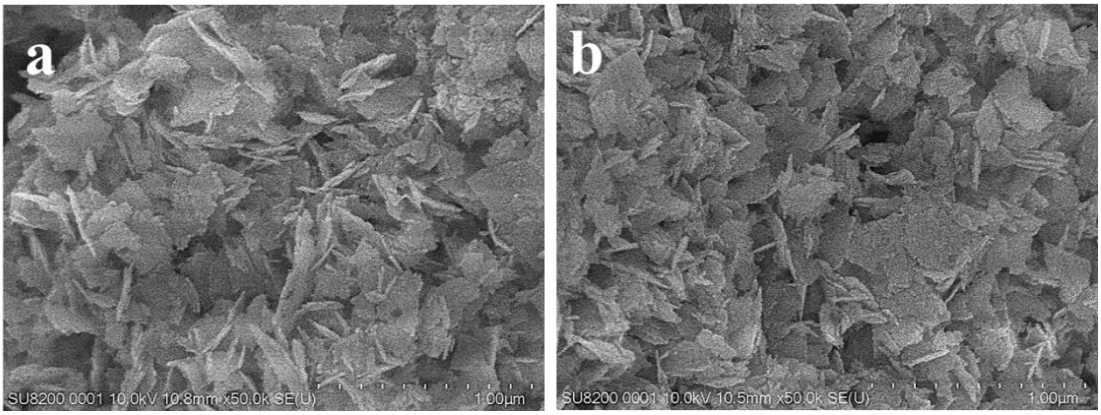


Figure S1. SEM images of (a) V_O-UBWO and (b) PdNPs-V_O-UBWO catalysts.

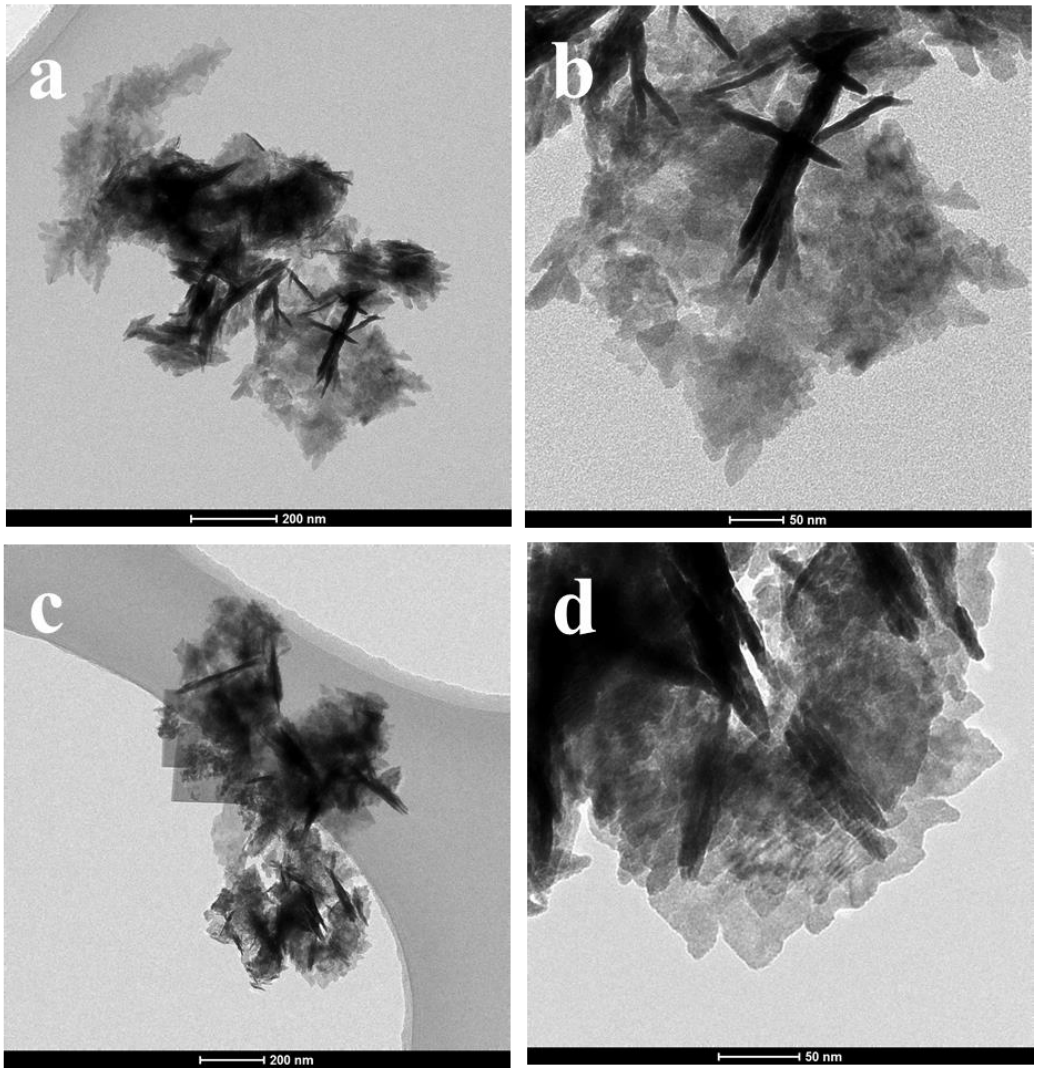


Figure S2. TEM images of (a, b) V_O-UBWO and (c, d) PdNPs-V_O-UBWO catalysts.

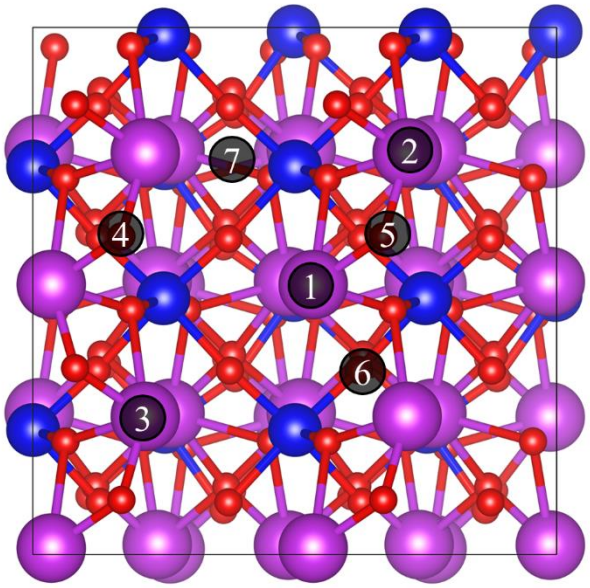


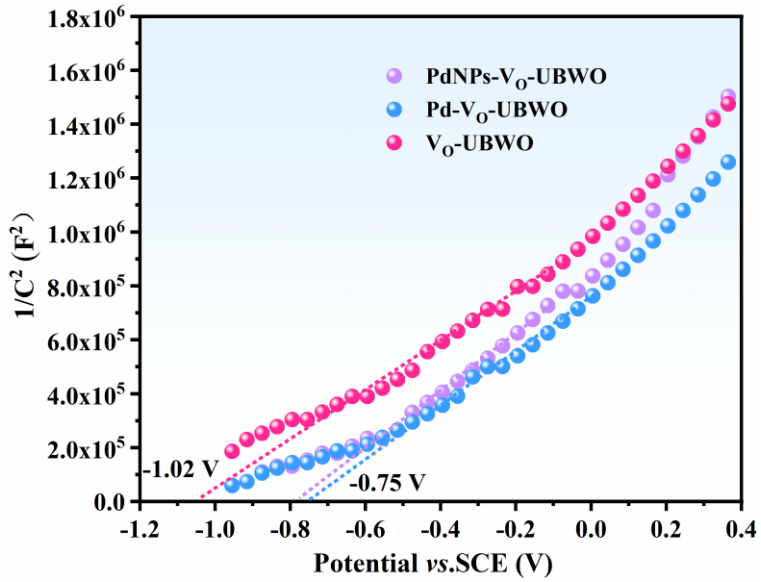
Figure S3. The 7 Possible positions of single Pd atoms on V_O-UBWO (O vacancy at position 6). Selected Pd loading positions: positions 1, 2, 3 are at the top of Bi atom at different distances from the O vacancy; positions 4, 5 are at the top of O atom at different distances from the O vacancy, positions 6 is the O vacancy on the surface of UBWO; positions 7 is the bridge between the unbonded Bi atom and O atom bit (above the midpoint of the yellow dotted line in the Figure).

Table S1. The formation energies of single Pd atoms adsorbed at different positions on the V_O-UBWO surface.

positions	formation energies（eV）
1	-1.167
2	-1.865
3	-2.105
4	-1.477
5	-1.542
6 (O vacancy)	-2.495
7	-1.931

Table S2. Pd amount of different chemical valences in Pd-BWO and PdNPs-BWO catalysts

Samples Pd species	Pd-V_O-UBWO (%)	PdNPs-V_O-UBWO (%)
Pd^{2+}	5.7	0
Pd^{+}	76.8	32.4
Pd^{0}	17.5	67.6



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173 Figure S4. The Mott Schottky curves of V_O-UBWO, Pd-V_O-UBWO, and PdNPs-V_O-UBWO

174 catalysts.

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$$E_{NHE} = E_{SCE} + 0.24\,V \quad [4] \qquad \text{(S14)}$$

for n-type semiconductors,

$$E_{CB} = E_{fb} - 0.30\,V \quad [5,6] \qquad \text{(S15)}$$

$$E_{CB} = E_g + E_{VB} \qquad \text{(S16)}$$

176 where E_{NHE} is normal hydrogen electrode potential (*NHE*);

177 E_{SCE} is *SCE* potential;

178 E_{CB} is conduction band potential;

179 E_{fB} is flat band potential; E_g is the band gap;

180 E_{VB} is valence band potential.

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Table S3. Band structures of V_O-UBWO, Pd-V_O-UBWO, and PdNPs-V_O-UBWO catalysts

Sample / Energy band	V_O-UBWO	Pd-V_O-UBWO	PdNPs-V_O-UBWO
Eg (eV)	2.87	2.63	2.80
CB (V)	-1.08	-0.81	-0.83
VB (V)	1.79	1.82	1.97

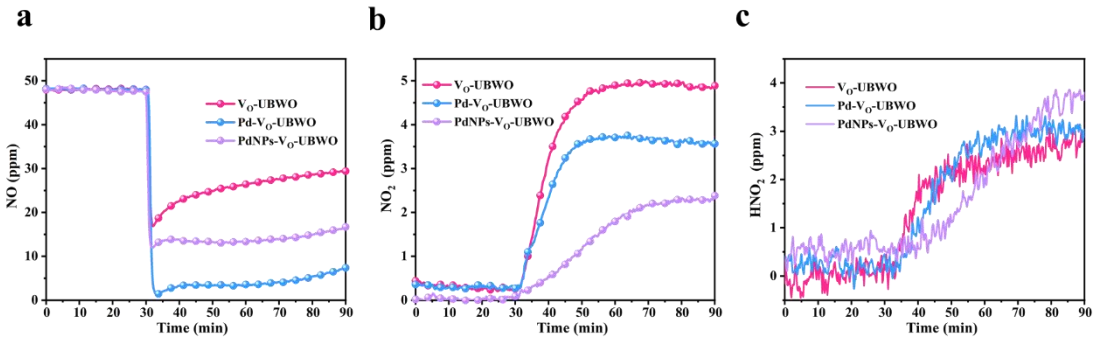

Figure S5. (a) NO removal, (b) NO_2 generation, (c) HNO_2 generation of photocatalytic NO of the V_O-UBWO, Pd-V_O-UBWO and PdNPs-V_O-UBWO catalysts under visible light irradiation for 1h at a $C_{NO,in}$ of about 48 ppm.

Pd^{2+}-V_O-UBWO catalyst was synthesized following a procedure reported earlier in the literature.[7] First, 0.6 g of V_O-UBWO catalyst was dispersed in 180 ml ultrapure water by ultrasonication for 5 min and kept magnetically stirred for 30 min, and 0.0032 g of K_2PdCI_4 was dispersed in 10 ml of ultrapure water by ultrasonication. Then, the solution was added dropwise to the V_O-UBWO solution, followed by magnetic stirring for 30 min. Then the obtained mixed solution was aged for 2 h. After that, the solution was centrifuged three times with ultrapure water and anhydrous ethanol, respectively. Finally, the obtained solid was dried in an oven at 60 °C for 8 h.

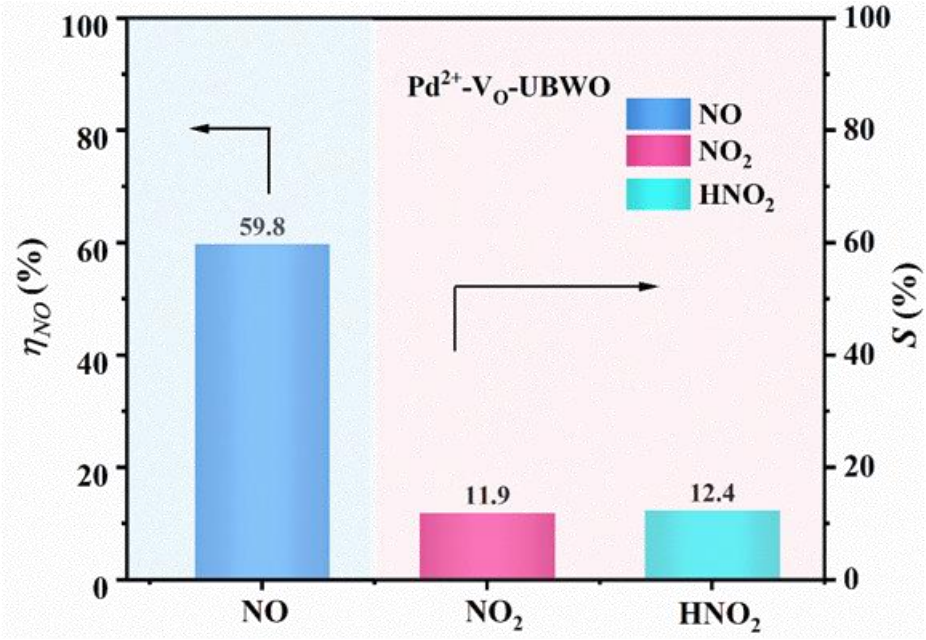

Figure. S6 The η_{NO},S_{NO_2} and S_{HNO_2} for photocatalytic NO removal of Pd^{2+}-V_O-UBWO catalyst.

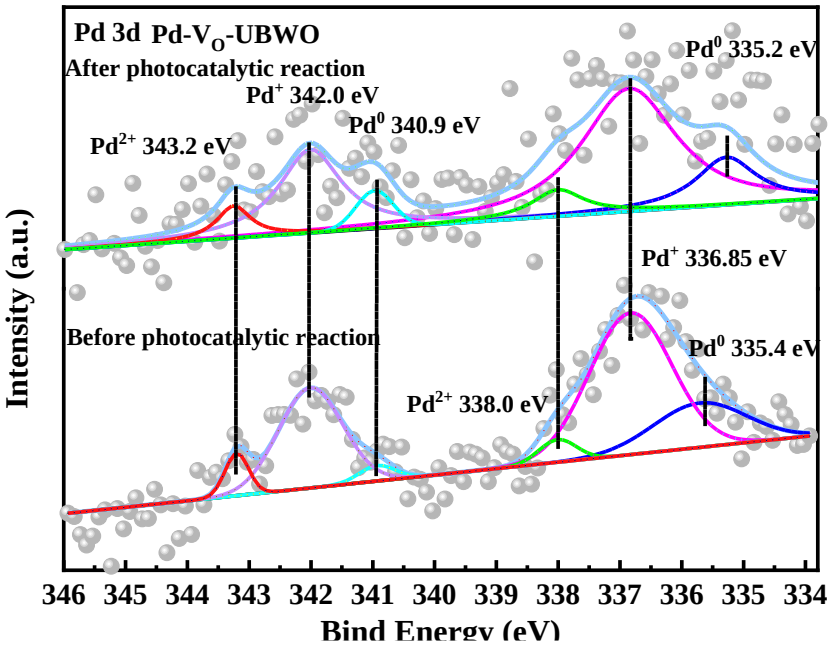

Figure.S7 Pd 3d XPS spectra of Pd-Vo-UBWO catalysts before and after irradiation under visible light for 1h with inlet NO concentration of 48 ppm.

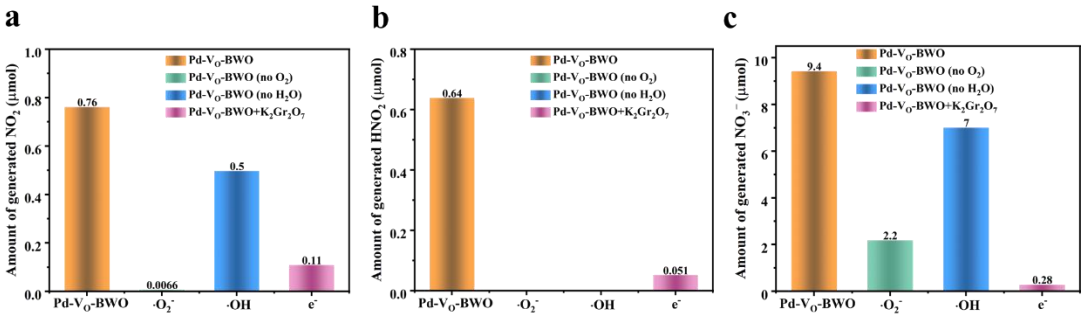

Figure S8. (a) The NO_2 generation, (b) HNO_2 generation and (c) NO_3^- generation in Pd-V_O-UBWO catalyst under the conditions of adding $K_2Gr_2O_7$ and removing O_2, moisture.

References

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