

Supplementary Material

Synthesis of a three-phase heterojunction $\text{NdVO}_4/\text{V}_2\text{O}_5/\text{BiVO}_4$ by cation-exchange method for the degradation of anionic azo dye orange II

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Note S1. Materials Characterizations

X-ray powder diffraction (XRD) analysis of all photocatalysts was performed using a BDX320 instrument, scanning in the range of 10° to 80° at a rate of 10°min^{-1} . Rietveld refinement was carried out using GSAS-II software. Surface and internal structural information of the materials were obtained through scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). On an aberration-corrected TEM operated at 300 kV, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and elemental electron energy loss spectroscopy (EELS) maps were acquired. X-ray photoelectron spectroscopy (XPS) was conducted to study the chemical states of the samples using a PHI-5000C ESCA system with a Mg/K α source. Additionally, optical properties were measured using ultraviolet-visible diffuse reflectance spectroscopy (DRS) (Shimadzu, UV-3600) and photoluminescence (PL) spectra at 371 nm were obtained using a Shimadzu RF-5301PC spectrophotometer. Time-resolved photoluminescence (TRPL) measurements were carried out at 371 nm using an Edinburgh FLS1000 spectrometer. The surface area of the samples was determined using nitrogen adsorption and the Brunauer-Emmett-Teller (BET) method with the US ASAP (Accelerated Surface Area and Porosimetry) 2020 system. Electron spin resonance (ESR) was measured on a Bruker A300 spectrometer.

Note S2. DFT Calculations

Density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP) and the Projector Augmented-Wave (PAW) method. The exchange-correlation potential was represented by the Perdew-Burke-Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA). A heterostructure consisting of 147 atoms in the Bi(002)/BiVO₄(001) interface was constructed. A vacuum layer of 15 Å thickness was included along the z-direction. The cutoff energy was set to 500 eV. The k-point sampling grids for the NdVO₄(112)/V₂O₅(200)/BiVO₄(001) heterostructure were set to 1×2×1. An effective U value of 4.5 eV was selected for the 3d orbitals of vanadium atoms. The structures were relaxed until the convergence criteria for energy and forces were below 1.0×10⁻⁵ eV/atom and 4.0×10⁻² eV/Å, respectively. A vacuum layer of 15 Å was used. The van der Waals interactions were described using the DFT-D3 method.

Note S3. Photoelectrochemical and electrochemical tests

Instantaneous photocurrent response (i-t), electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV) tests were conducted on an electrochemical analyzer equipped with a standard three-electrode system. A 0.5M Na₂SO₄ aqueous solution was used as the electrolyte in this system. Platinum foil, Ag/AgCl electrode, and ITO glass with a coated area of 2.0×2 cm² were chosen as the electrode, reference electrode, and working electrode, respectively. Visible light was simulated using a 300 W xenon lamp.

Note S4. Photocatalytic measurement

The photocatalytic activity of the prepared catalyst was assessed by degrading orange II under simulated sunlight (with a 300 W xenon lamp as the light source). A circulating cooling system was used to cool the photoreactor to reduce the impact of the heat generated by the xenon lamp. A sample of 50 mg scraped from the titanium sheet and 100 ml of orange II solution (50 mg L⁻¹) were placed into the reactor. The reaction solution was allowed to stand in the dark for 30 minutes before exposure to light to reach solid-liquid equilibrium. Subsequently,

4 ml of the reaction solution was taken every 30 min. The intensity at the maximum absorption wavelength (485 nm) of orange II was measured using a UV-1700PC spectrophotometer to analyze the concentration of the orange II solution. The degradation rate of orange II was calculated using Equation: $\eta = (C_0 - C_t) / C_0 \times 100\%$

Where:

η — Degradation rate;

C_0 — Initial concentration of the solution;

C_t — Concentration of the solution at time t under xenon lamp irradiation.

Note S5. Photocatalytic Trapping Agent Experiment

The participation of reactive radicals in the photocatalytic degradation process was verified by conducting radical trapping experiments. 4-Hydroxy-TEMPO (nitroxyl radical piperidine), isopropanol (IPA) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were used as trapping agents for superoxide radicals ($\cdot O_2^-$), hydroxyl radicals ($\cdot OH$) and holes (h^+), respectively. The radical trapping experiments followed the same procedural steps as the photocatalytic degradation experiment. To trap $\cdot O_2^-$, 0.05 g of nitroxyl radical piperidine was added to the reaction solution; to trap h^+ , 0.11 g of ethylenediaminetetraacetic acid disodium salt was added to the reaction solution; and to trap $\cdot OH$, 2 ml of isopropanol was added to the reaction solution.

Note S5. Chemicals and materials

All reagents for the preparation of $NdVO_4$, $NdVO_4/V_2O_5$ and NVB such as ammonium metavanadate (NH_4VO_3), sodium hydroxide (NaOH), nitric acid (HNO_3), neodymium nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$) and bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) were purchased from Shanghai McLean Biochemical Technology Co. Ltd and used as received without further purification.

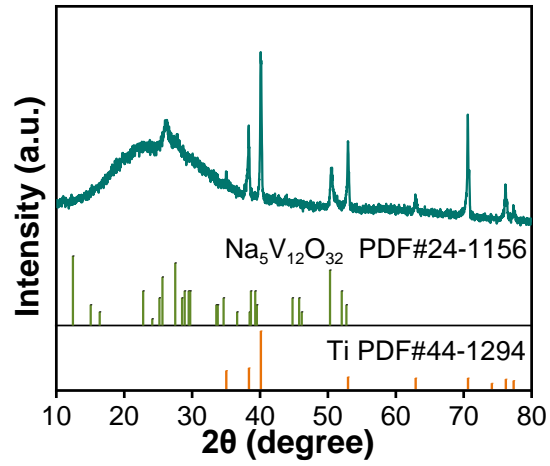


Fig. S1 The XRD spectrum of $\text{Na}_5\text{V}_{12}\text{O}_{32}$ grown on titanium foil.

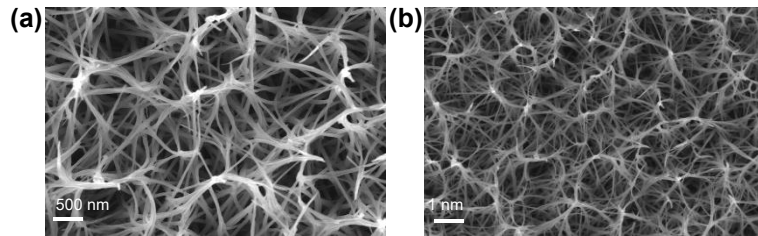


Fig. S2 The SEM spectrum of $\text{Na}_5\text{V}_{12}\text{O}_{32}$.

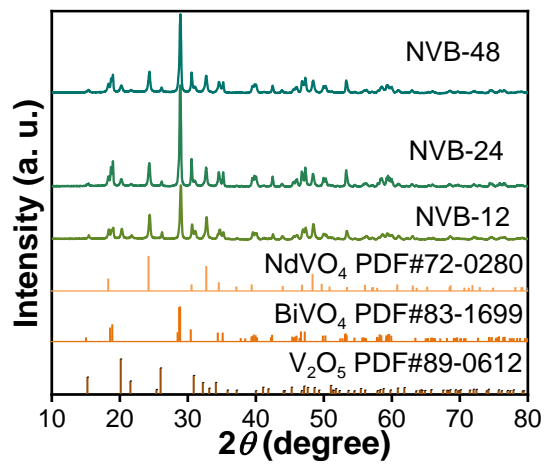


Fig. S3 The XRD spectrum of NVB-12, NVB-24 and NVB-48.

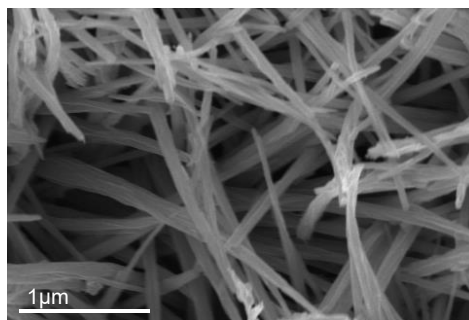


Fig. S4 The SEM spectrum of NdVO_4 .

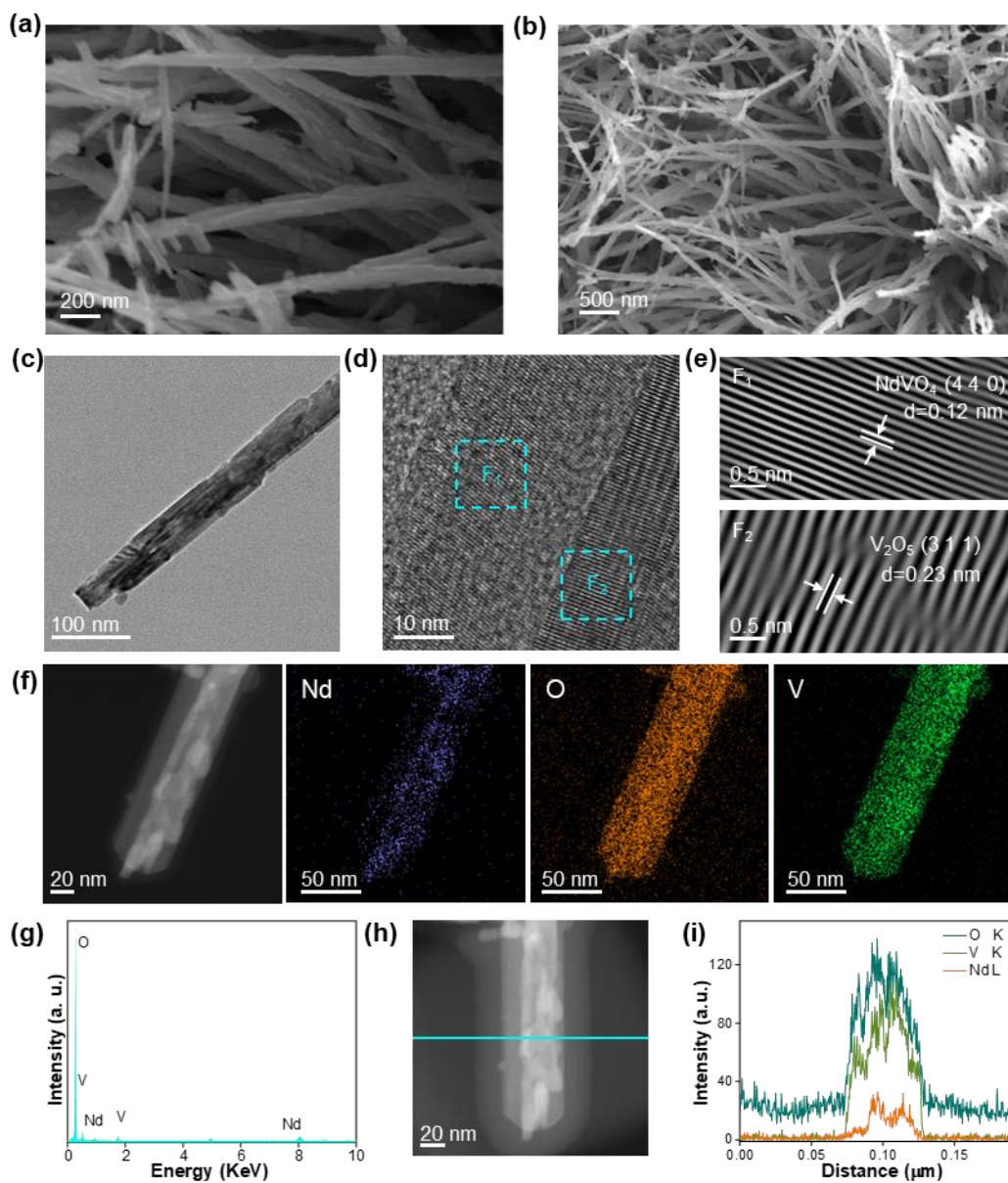


Fig. S5 (a-b) The SEM, (c-e) TEM images and corresponding FFT and IFFT images in the region of $\text{NdVO}_4/\text{V}_2\text{O}_5$. (f) EDS mapping images and (g) EELS spectra of $\text{NdVO}_4/\text{V}_2\text{O}_5$. (h) The TEM image of the $\text{NdVO}_4/\text{V}_2\text{O}_5$ and (i) the corresponding EDS line scan.

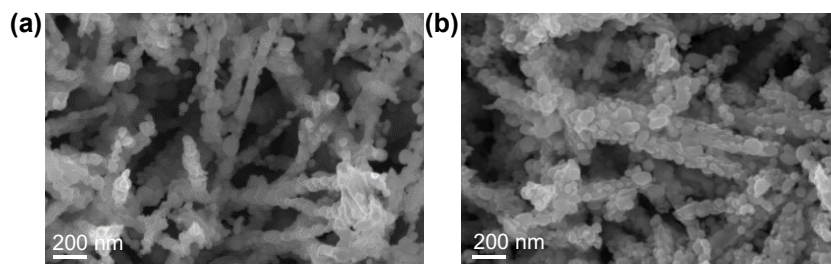


Fig. S6 The SEM images of (a) NVB-12 and (b) NVB-48.

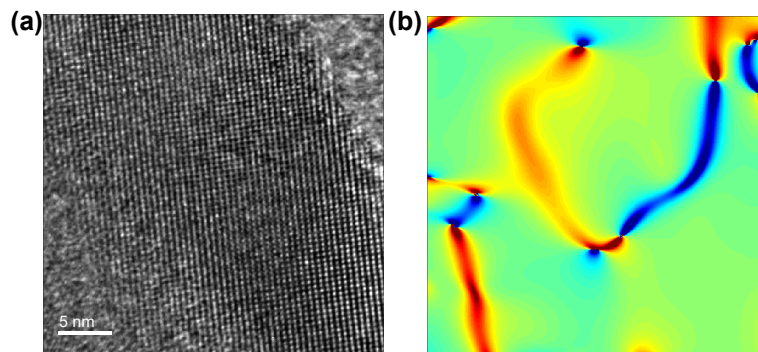


Fig. S7 The GPA strain map of $\text{NdVO}_4/\text{V}_2\text{O}_5$, showing ϵ_{xy} component.

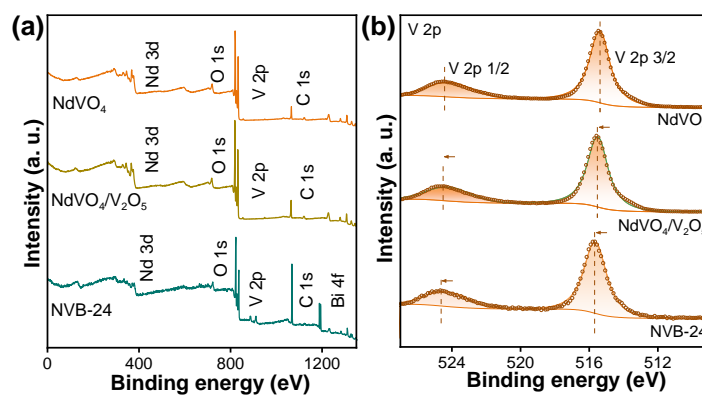


Fig. S8 The full XPS spectra of NdVO_4 , $\text{NdVO}_4/\text{V}_2\text{O}_5$ and NVB-24. (b) The XPS spectra of V2p for the NdVO_4 ,

$\text{NdVO}_4/\text{V}_2\text{O}_5$ and NVB-24.

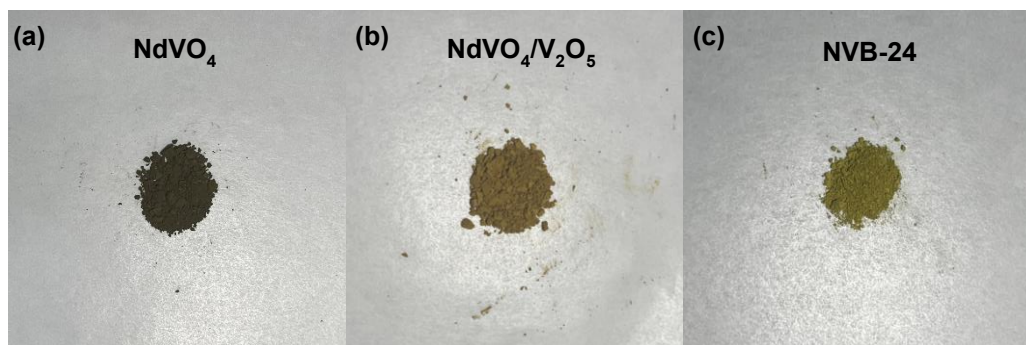


Fig. S9 Digital photos of three products.

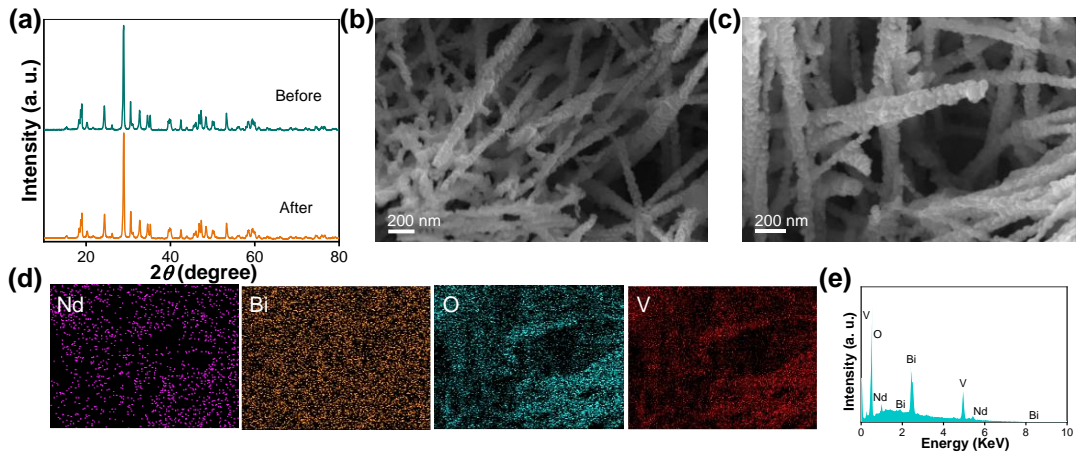


Fig. S10 (a) The XRD images before and after cyclic test of NVB-24.

(b, c) The SEM images and (d, e) EDS mapping images after cyclic test of NVB-24.

Tab. S1 The cell parameters of NVB-24 after XRD refinement.

	NVB-24		
	NdVO ₄	V ₂ O ₅	BiVO ₄
a (Å)	7.3113	11.4993	5.1892
b (Å)	7.3113	3.5665	5.0960
c (Å)	6.4530	4.3889	11.6953
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90.3327
V(A ³)	344.9430	180	309.2700

Tab. S2 The ratios of O_v for the NdVO₄ and NVB-24.

samples	O _v (%)
NdVO ₄	17
NVB-24	26

Tab. S3 The degradation rate of orange II by NVB-24 is compared with that of photocatalysts reported in previous literature.

Photocatalysts	Light source	Degradation rate (%)	Refs.
NVB-24	50 mg/L	96.15	This work
ZOFA-20	100 mg/L	77.27	1
BiOI/HKUST-1	200 mg/L	94.70	2
Zn _{0.9} Co _{0.1} O	10 mg/L	80.00	3
Montmorillonite KSF	12 mg/L	76.40	4
Trace Cu(II)	20 mg/L	95.52	5
Fe ³⁺ /H ₂ O ₂	1.0 × 10 ⁻⁴ M	81.40	6
FeOCl/WS ₂	60 mg/L	93.40	7

References

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