

Supporting Information

Revealing the primary role of V^{4+}/V^{5+} cycle in $InVO_4$ catalyst for promoting photo-Fenton reaction

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1. Materials

N-Hexadecyltrimethylammonium Chloride (CTAC), Bromohexadecyl pyridine (CPB), indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot 4.5 \text{H}_2\text{O}$), ammonium vanadate (NH_4VO_3), absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), rhodamine B (RhB), microcystin-LR (MC-LR), hydrogen peroxide (H_2O_2), isopropyl alcohol (IPA), benzoquinone (BQ), ethylenediaminetetraacetic acid (EDTA), all these reagents used in this study were analytical grade. Distilled water was used throughout the experiments.

2. Experimental

2.1 Preparation of InVO_4 in the presence of surfactant modification

InVO_4 was prepared by a hydrothermal method. Primarily, 2.5 mmol ($\text{In}(\text{NO}_3)_3 \cdot 4.5 \text{H}_2\text{O}$) had been dissolved in water (20 mL) as solution A. 2.5 mmol NH_4VO_3 had been dissolved in water (20 mL) at 60 °C as solution B, and 2.5 mmol of a surfactant (CTAC, CPB) was dissolved in 40 mL water as solution C. Then, solution A and B had been added slowly into solution C with intensively stirring, adding ammonia slowly to the mixture to tune the pH of the solution to (9 ~ 10) with yellow precipitate formed. Stir for another 60 min, the mixture had been transferred into a Teflon-lined stainless autoclave (150 mL) and heated for 24 h at 180 °C. The product was dried, and a black powder was collected. The powder was calcined at 600 °C for 10 h. The InVO_4 samples prepared with CTAC, CPB were labeled as C- InVO_4 and B- InVO_4 . For comparison, a sample, N- InVO_4 , was also prepared by the same procedures without surfactant.

2.2 Performance evaluation of InVO_4 photocatalysts

Photocatalytic degradation of RhB (1.5×10^{-5} M, 50 mL) or MC-LR (5×10^{-6} M, 4 mL) with H_2O_2 (0.045 M) under visible light was examined at room temperature in the air with an XPA-7 photocatalytic reactor. The reaction tubes were under a 400 W Xe lamp with two cutoff filters ($420 \text{ nm} < \lambda < 760 \text{ nm}$). The distance of reaction tubes and light source was 10 cm. The suspension had been stirred magnetically in the dark for 2 h before irradiation to ensure adsorption saturation in the reaction system. The reactant solution was kept at room temperature by flowing cool water. During the irradiation, the suspension was sampled and centrifuged at a regular interval. The RhB concentration was tested by UV-vis spectrophotometer (Perkin Elmer, USA).

The removal rate ($\eta\%$) of RhB was calculated as follows:

$$\eta\% = (C_0 - C_t / C_0) \times 100\% \quad (2)$$

where C_0 was the RhB adsorption equilibrium concentration, C_t was the RhB concentration at the corresponding reaction time t .

The 400 μL of the MC-LR suspension was sampled at a regular interval, centrifuged at 10000 rpm/min for 30 min, and filtered by 0.45 μm membrane to prepare the sample for HPLC analysis on Waters 600 with a C18 reverse-phase column (4.6 mm \times 250 mm, Kromasil) and 2998 photodiode array detector. The flow rate, column temperature, injection volume and detection wavelength were 0.8 mL/min, 35 $^\circ\text{C}$, 20 μL *resp.* 238 nm. The mobile phase consisted of 60% methanol, and 40% water contained 0.05% trifluoroacetic acid (TFA).

3. Characterization

The crystalline phase of the InVO_4 materials was analyzed by X-ray diffraction (XRD, Ultima IV, Rigaku Co, Japan) with $\text{CuK}\alpha$ irradiation ($\lambda = 0.15406 \text{ nm}$) using a scanning speed of $6^\circ/\text{min}$ in

the 2θ range of $10 \sim 70^\circ$, and corresponding crystal structures were drawn by Mercury software. The samples' morphology were examined by scanning electron microscopy (SEM, JSM-7500F, JEOL, Japan). The HRTEM analysis was conducted on a JEM-F200 (JEOL, Japan), and the acceleration voltage was set as 200 kV. The morphology change of the sample during the preparation process was monitored by an optical microscope (CX41, China) made by Olympus, Shanghai Lance Electronic Technology Co., Ltd. The specific surface areas and pore size distribution of the catalysts were derived from nitrogen adsorption isotherms measured on an adsorption/desorptometer (JW-BK112, JWGB, China) at 77 K using BET and BJH methods, respectively.

4. Photocurrent and light absorption properties of InVO₄

The photocurrent measurements were performed on an electrochemical workstation (RDE710, GAMRY) with NaSO₄ aqueous solution (0.2 M) as the electrolyte. A xenon lamp (300 W) with two filters ($\lambda < 420$ nm, $\lambda > 760$ nm) was used as the light source and the Pt foil and saturated Ag/AgCl were used as counter and reference electrode. The working electrode were prepared by 5 mg of photocatalysts, 0.05 mL of Nafion dispersion and the resulted slurry products were coated on the 1.0×1.0 cm conductive glass sheets and dried at 60°C for 2 h. The electrochemical impedance spectroscopy (EIS) measurement was used Pt foil and saturated Ag/AgCl as counter and reference electrode in 0.1 M K₄FeC₆N₆ electrolyte. For the preparation of a working electrode, 10 mg of photocatalysts were added to 1 mg carboxymethyl cellulose sodium and 2 mL ethyl alcohol and the resulted slurry products were coated on 1.0×1.0 cm conductive glass sheets and dried at 60°C for 2 h (CHI 660E, Chenhua, China). The UV-vis diffuse reflectance spectroscopy

(UV-vis DRS) was determined using Shimadzu UV-3100 spectrophotometer with BaSO₄ as a reflectance standard. The bandgap is estimated based on the Kubelka-Munk equation (Eq. (1)) as:

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (1)$$

where α , $h\nu$, A and E_g represent the absorption coefficient, photonic energy, constant, and bandgap value, respectively.

For the recycling experiments, the residual reaction was aged overnight and filtered. The filtered catalyst washed with water and absolute ethyl alcohol for three times, respectively. Then put the dried used photocatalysis into the 50 mL RhB solution (1.5×10^{-5} M) and a new H₂O₂ solution were added.

5. Identification of surface defects of InVO₄

The characteristics of surface defects were analyzed on a fluorescence spectrophotometer (HITACHI F-4500, Japan) with an excitation wavelength of 325 nm at room temperature. The analysis of valance state was carried out with X-ray photoelectron spectroscopy (XPS) conducted on a VG ESCALA-B220i-XL (Thermo Scientific, UK) with an Al K α X-ray source at a residual gas pressure below 10⁻⁸ Pa. All binding energies of the elements examined were calibrated according to the C1s peak at 284.6 eV, which was assigned to the adventitious carbon.

6. H₂O₂ activation by InVO₄ photocatalysts

6.1 Decomposition rate of H₂O₂

The concentration of H₂O₂ was analyzed using the titanium (IV) sulphate method: to the filtered sample (60 μ L), a mixture (1 mL) of sulfuric acid (H₂SO₄, 3 M) and titanium sulphate (Ti(SO₄)₂,

0.05 M) was added, and the absorbance at 405 nm was determined using a UV-vis spectrometer (Perkin Elmer, USA).

6.2 Measurement of reactive species

Firstly, the radical trapping experiment was conducted to identify the active species in the photodegradation over a photocatalyst. Isopropanol (IPA, 1 M), p-benzoquinone (1 M) and ethylenediaminetetraacetic acid (EDTA) was added as a scavenger for $\bullet\text{OH}$, $\text{O}_2\bullet^-$ and metal ions, respectively. The electron spin resonance (ESR) was obtained on a Bruker ER200-SRC spectrometer (Bruker, Germany). DMPO was used as a trapping agent for $\bullet\text{OH}$ in water and $\text{O}_2\bullet^-$ in methanol. The laser was Nd:YAG with 532 nm. The intensity of the central magnetic field was 3486.7 G.

7. Adjusted surface defects by surfactants

7.1 In situ observation of the preparation process

An optical microscope (CX41, China, manufactured by Olympus, Shanghai Lance Electronic Technology Co., Ltd.) was used to monitor the morphology changes during the preparation process.

7.2 Exposed crystal plane analysis

An optical microscope (CX41, China, manufactured by Olympus, Shanghai Lance Electronic Technology Co., Ltd.) was used to monitor the morphology changes during the preparation process.

8. Physical characterization of nanocatalysts (Fig S1-S11 and Table S1-S4)

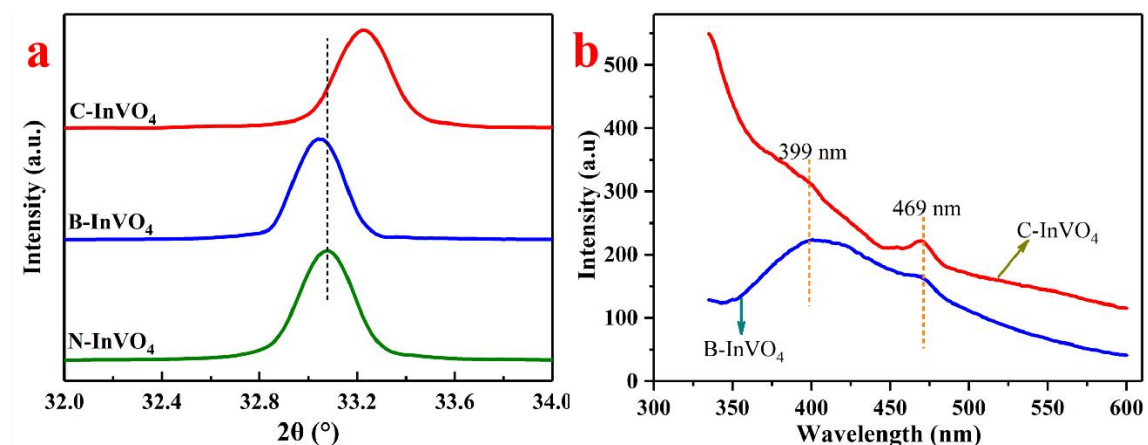


Fig. S1. (a) Enlarged XRD patterns of InVO₄ at the diffraction peaks of 33.05° and (b) PL spectra of as-prepared C-InVO₄ and B-InVO₄ samples with excitation at 315 nm.

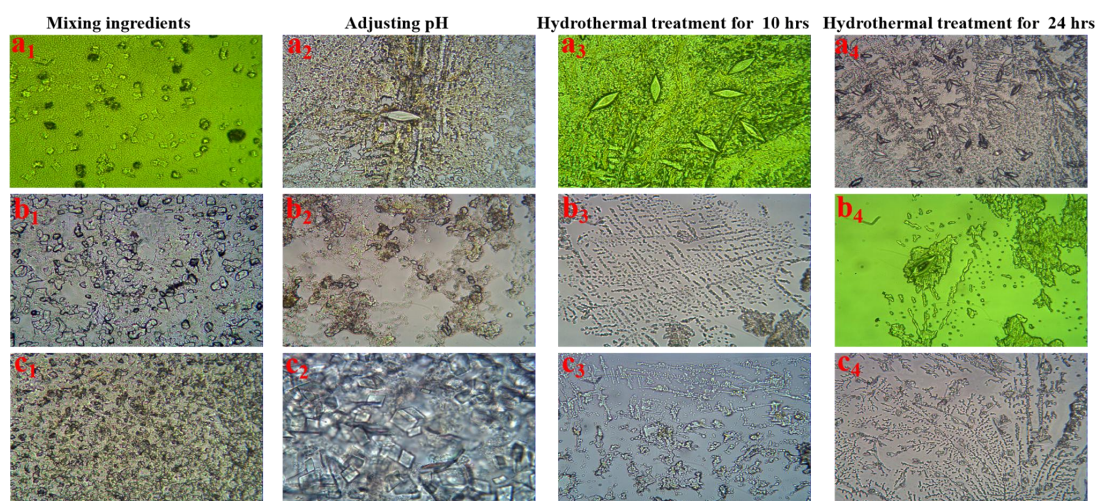


Fig. S2. Optical microscope map of the process preparation of InVO₄: (a₁-a₄) N-InVO₄, (b₁-b₄) C-InVO₄, (c₁-c₄) B-InVO₄. [four preparing process: mixing ingredients (1), adjusting pH (2), hydrothermal treatment for 10 hrs (3) and 24 hrs (4), respectively].

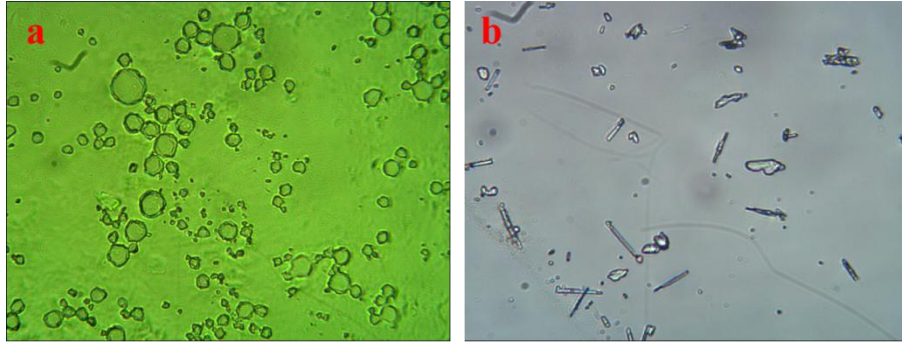


Fig. S3. (a) Optical microscope map of the suspension of CTAC and (b) CPB.

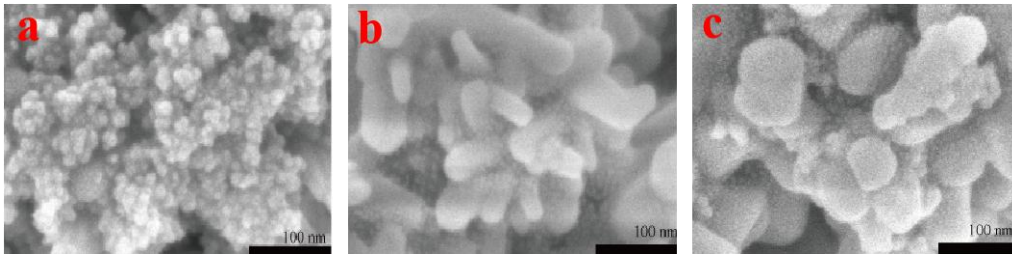


Fig. S4. SEM images of (a) C-InVO₄, (b) B-InVO₄, (c) N-InVO₄

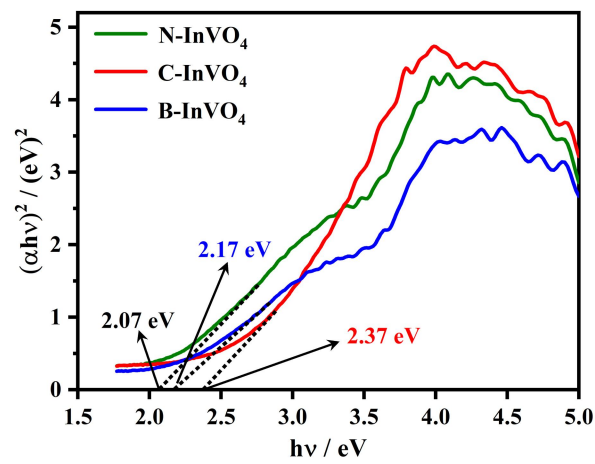


Fig. S5. The relationship of $(\alpha h\nu)^{n/2}$ and $h\nu$.

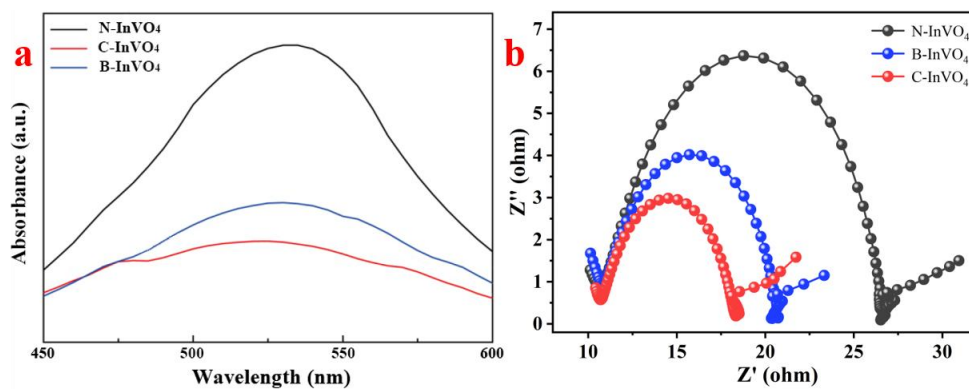


Fig. S6. (a) PL spectra and (b) EIS Nyquist plots of different InVO₄ samples.

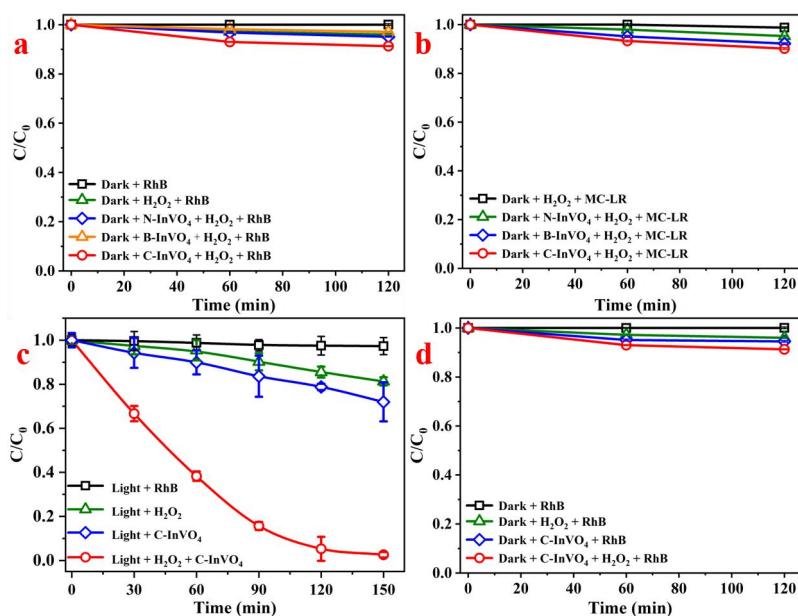


Fig. S7. The degradation curve of (a) RhB (1.5×10^{-5} M) and (b) MC-LR (5×10^{-6} M) using different InVO₄/H₂O₂ systems in dark; The degradation curve of RhB (1.5×10^{-5} M) using C-InVO₄/ H₂O₂ (c) under visible and (d) in dark. Both conditions: [catal]=0.4 g/L, [H₂O₂] = 0.045 M, T= 35.5°C, pH = 5.93

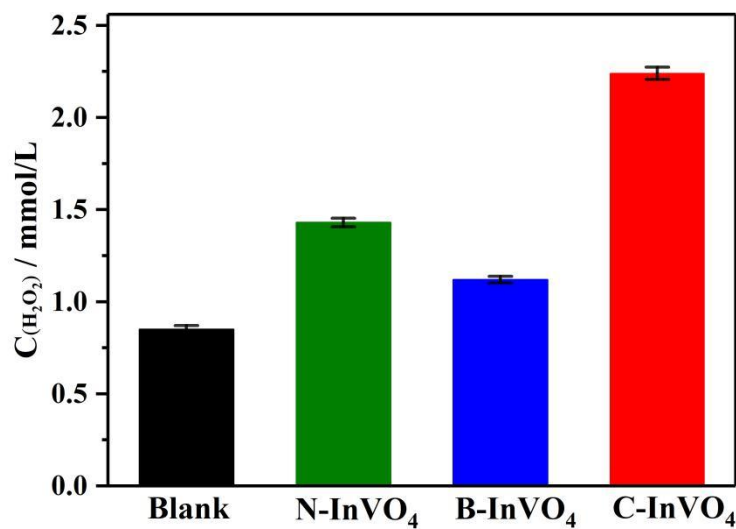


Fig. S8. The total quantity of H₂O₂ decomposed in the 150-minute degradation process

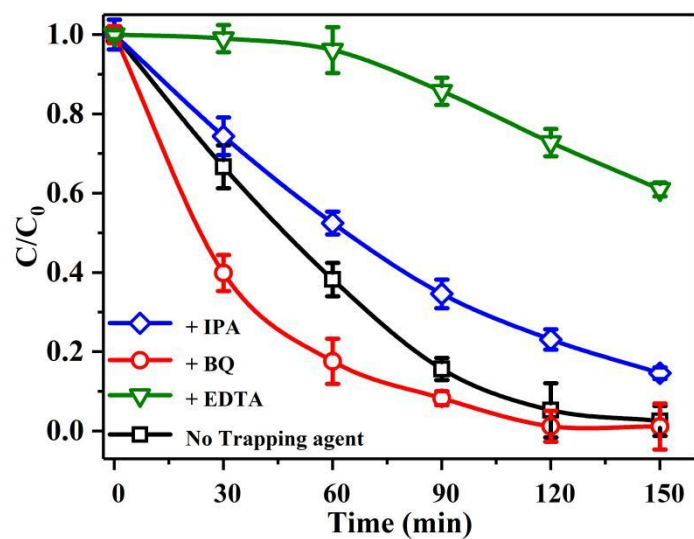


Fig. S9. The radical trapping experiments for RhB solution photocdegradation by C-InVO₄/H₂O₂.

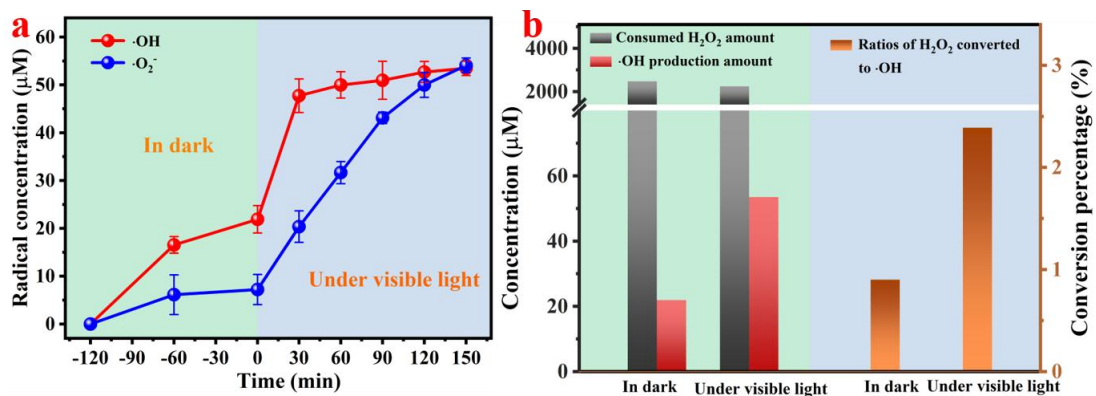


Fig. S10. (a) $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ production and (b) the conversion percentage of H_2O_2 to $\cdot\text{OH}$ in the C-InVO₄ photo-Fenton reaction.

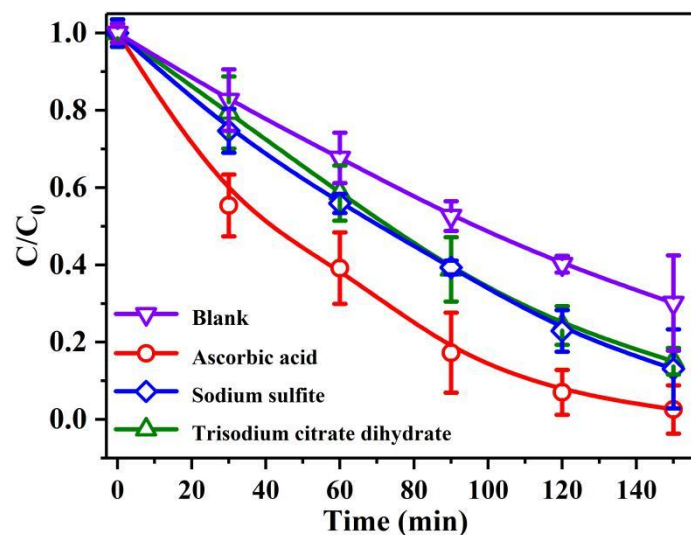


Fig. S11. The photodegradation of RhB solutions with the addition of different reductant by C-InVO₄ [catal]=0.4 g/L, [RhB]= 1.5×10^{-5} M, T=35.5 °C; [H_2O_2] = 0.045 M

Table S1 The percentage of V 2p_{3/2} and O1s of the fresh InVO₄ photocatalysts

Sample	V ⁴⁺ /V 2p _{3/2}	O1/O1s	O2 /O1s	O3 /O1s
C-InVO ₄	18.3%	38.53%	36.0%	25.47%
B-InVO ₄	12.57%	14.56%	45.0%	40.44%
N-InVO ₄	9.49%	88.55%	7.54%	3.91%

Table S2. Surface areas, pore diameters, pore volumes and particle size of InVO₄ samples.

Sample	Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)
C-InVO ₄	23.08	14.59	0.084
B-InVO ₄	10.95	7.02	0.019
N-InVO ₄	3.91	8.40	0.008

Table S3. Comparison of the catalytic activity of InVO₄ with other reported catalysts for photo-Fenton reaction.

No.	Targeted pollutant	Catalyst	Oxidant	Degradation efficiency	Time (min)	Ref.
1	RhB (5×10 ⁻⁵ M)	InVO ₄ (0.4 g/L)	H ₂ O ₂ (0.045 mM)	100%	150 min (Visible light)	This work
2	Methylene blue (20 mg/L)	Zn _{1-x} Dy _x Fe ₂ O ₄ (1.0 g/L)	H ₂ O ₂ (2 M)	97.5%	45 min (Visible light)	Vinoshia et al., 2022
3	Methylene blue (20 mg/L)	α-Fe ₂ O ₃ @diatomite (0.1 g/L)	H ₂ O ₂ (90 mM)	98.0%	4 h (UV irradiation)	He et al., 2018
4	Acetaminophen (5 mg/L)	CuS/MIL-Fe (0.2 g/L)	H ₂ O ₂ (15 mM)	100%	30 min (Simulated solar irradiation)	Fang et al., 2023

5	2, 4-dimethyl phenol (5×10^{-5} M)	CuO/g-C ₃ N ₄ (0.5 g/L)	H ₂ O ₂ (0.1 mM)	99.0%	160 min (Visible light)	Sharma et al., 2020
6	Benzoic acid 12 mg/L	Fe ^{III} Cu ^I @SiO ₂ (2 g/L)	H ₂ O ₂ (0.17 M)	89.0 %	180 min (Blue light)	Pratiwi et al., 2021
7	RhB 15 mg/L	Fe ₂ O ₃ /reduced graphene oxide aerogel (0.08 g/L)	H ₂ O ₂ (1.0mM)	100%	120 min (UV irradiation)	Feng et al., 2018
8	Methylene blue (20 mg/L)	CuS-functionalized cellulose based aerogel (0.75 g/L)	H ₂ O ₂ (/)	97.6%	90 min (Visible light)	Saeed et al., 2019
9	Antibiotic cefotaxime (0.4 mM)	Ferrihydrite/TiO ₂ (0.2 g/L)	H ₂ O ₂ (10 mM)	99.2%	30 min (UV irradiation)	Jiang et al., 2021
10	Crystal violet dye 10 mg/L	Gd ₂ Zr ₂ O ₇ (0.5 g/L)	H ₂ O ₂ (0.2 M)	90.0%	60 min (UV irradiation)	Abdelbaky et al., 2023
11	Methylene blue (10 mg/L)	Fe ₂ O ₃ ·CuO·MnO _x ·MCM-41 mesoporous silica (1.0 g/L)	H ₂ O ₂ (0.045 mM)	99.6%	45 min (UV irradiation)	Sun et al., 2020
12	Dye RB19 0.075 g/L	Magnetite (1.0 g/L)	H ₂ O ₂ (100 mM)	78.0%	60 min	Tavares et al., 2022

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Table S4 The percentage of V 2p_{3/2} for the samples of C-InVO₄ , B-InVO₄ and N-InVO₄ after degradation.

Sample	V ⁴⁺ /V 2p _{3/2}	V ⁵⁺ /V 2p _{3/2}
C-InVO ₄	5.7%	94.3%
B-InVO ₄	8.19%	91.81%
N-InVO ₄	7.71%	92.29%