

Ultrasmall Ni clusters decorated In₂O₃ quantum dots on black phosphorus nanosheets for enhanced photocatalysis

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Received 1 Mar 2026, Accepted 27 Aug 2026
Available online 30 Sep 2026

ABSTRACT: A ternary heterojunction composite with ultrasmall nickel clusters anchored on In₂O₃ quantum dots decorated on few-layer black phosphorus nanosheets (Ni-In₂O₃ QDs@BP NSs) was designed to overcome non-precious metal cocatalyst aggregation and rapid charge recombination in photocatalysis. The composite was synthesized via high-temperature hydrothermal synthesis, liquid exfoliation, *in situ* deposition, and ligand-assisted loading of ultrasmall Ni clusters. Structural characterizations suggested the successful formation of ultrasmall Ni clusters and highly dispersed Ni species. Under simulated solar light, the optimized composite (3 wt% In₂O₃ QDs, 1.1 wt% Ni) exhibited a photocatalytic hydrogen evolution rate of 3265 μmol/g/h, 89.6% degradation of tetracycline within 60 min, and 93.4% degradation of Rhodamine B within 12 min. Photoelectrochemical tests and radical trapping experiments revealed significantly enhanced charge separation efficiency, with ·O₂⁻ and ·OH as the dominant active species. The synergistic effect between the In₂O₃ QDs/BP NSs heterojunction and ultrasmall Ni clusters promotes spatial separation and utilization of photogenerated carriers, offering a promising strategy for designing high-performance, non-precious metal photocatalysts.

KEYWORDS: photocatalytic hydrogen evolution, pollutant degradation, type-II heterojunction, nickel clusters catalyst, black phosphorus

INTRODUCTION

The energy crisis and environmental pollution are major challenges facing modern society. Solar photocatalysis, which can convert solar energy into clean hydrogen fuel and efficiently degrade organic pollutants, is considered a highly promising green solution [1–3]. Among numerous photocatalytic materials, two-dimensional layered black phosphorus (BP) has attracted significant attention due to its tunable direct bandgap, high carrier mobility, and broad light absorption from the visible to near-infrared regions [4–7]. Previous studies have demonstrated the potential of ultrathin BP nanosheets in applications such as reactive oxygen species generation [8] and as components in metal-free heterojunction photocatalysts for hydrogen production [9], confirming their viability in photocatalysis.

However, pristine BP suffers from rapid recombination of photogenerated electron-hole pairs and susceptibility to degradation in ambient conditions, which restricts its photocatalytic activity and stability [10]. To overcome these limitations, strategies such as heterojunction construction are employed to promote charge separation. Furthermore, loading cocatalysts onto semiconductor surfaces is a key approach to lower reaction energy barriers and accelerate surface reaction kinetics. Although noble metal cocatalysts like platinum (Pt) are highly efficient, their scarcity and high cost hinder large-scale applications [11]. Thus, developing efficient and stable non-noble metal

cocatalysts has become a critical research direction. Nickel (Ni) is abundant and possesses catalytic activity, making it a potential substitute. However, traditional Ni nanoparticles tend to aggregate and deactivate, leading to a reduction in active sites [12].

The recent emergence of single-atom catalysts (SACs) offers new possibilities for maximizing metal atom utilization and modulating local electronic structures [13–15]. Anchoring metals as single atoms on supports cannot only increase the exposure of active sites but also result in excellent catalytic activity and selectivity due to quantum size effects and metal-support interactions. This points toward a new direction for designing next-generation non-noble metal cocatalysts. However, existing research often focuses on loading single atoms onto single or conventional semiconductors. The precise and stable anchoring of non-noble metal single atoms (e.g., Ni) onto heterojunction interfaces with strong charge separation capabilities and the synergistic optimization of photocatalytic performance remain underexplored and require in-depth investigation.

To rationally design an efficient non-noble metal photocatalyst, three key factors must be considered: light absorption, charge separation, and surface reaction kinetics. BP is chosen as the primary light-harvesting component due to its tunable direct bandgap, high carrier mobility, and broad visible-to-near-infrared absorption [7,15]. However, its rapid charge recombination and susceptibility to oxidation necessitate the introduction of a second component to

form a heterojunction [15, 16]. Indium oxide (In_2O_3) quantum dots (QDs) are selected for the following reasons: (i) In_2O_3 has a suitable band alignment with BP (type-II heterojunction), which can drive spatial separation of photogenerated electrons and holes [12, 17]; (ii) the quantum dot size (2–10 nm) ensures intimate interfacial contact and provides abundant anchoring sites for cocatalysts [8]; (iii) In_2O_3 is chemically stable and compatible with BP. Nevertheless, the heterojunction alone still lacks efficient active sites for surface redox reactions. Therefore, Ni is introduced as a cocatalyst. Ni is abundant, inexpensive, and has a hydrogen adsorption free energy close to that of Pt. Moreover, dispersing Ni as ultrasmall clusters maximizes atom utilization and suppresses aggregation, which is particularly important for the thermally sensitive BP substrate. Similar Ni-based single-atom or cluster systems have been demonstrated to act as efficient cocatalysts in phosphorus-based photocatalysts, in which Ni species serve as “electron antennas” to attract photocarriers to the solid-liquid interface and activate protons for H_2 evolution [4, 11, 12]. The anticipated synergy is as follows: BP captures photons and generates electron-hole pairs; the type-II heterojunction with In_2O_3 QDs promotes charge separation; the anchored Ni clusters (likely serving as highly dispersed active sites) act as electron traps and active sites for H^+ reduction or O_2 reduction, while the holes are consumed by sacrificial agents or participate in pollutant oxidation. This ternary design thus integrates the advantages of broad light absorption (BP), efficient charge separation (In_2O_3 /BP heterojunction), and superior surface catalysis (Ni clusters), aiming to achieve enhanced photocatalytic hydrogen evolution and pollutant degradation.

Therefore, this study aims to address the issues of non-noble metal cocatalyst aggregation and high photogenerated charge recombination rates in BP-based materials through rational material and structural design. The specific goal is to construct a novel ternary heterojunction photocatalyst by anchoring ultrasmall Ni clusters onto indium oxide quantum dots/black phosphorus nanosheets (In_2O_3 QDs@BP NSs) to achieve efficient and stable photocatalytic hydrogen production and pollutant degradation. These ultrasmall Ni clusters, on the one hand, exhibit atomic utilization efficiency close to that of SACs, providing atomically dispersed Ni active sites locally; on the other hand, they significantly reduce the difficulty of synthesis, enabling loading onto the thermally sensitive BP at relatively low temperatures. The novelty of this work lies in (1) the first combination of ultrasmall Ni clusters with In_2O_3 QDs and BP nanosheets in a ternary system and (2) the elucidation of the synergistic mechanism among the three components, wherein the ultrasmall Ni clusters provide active sites, In_2O_3 QDs enhance light absorption, and BP nanosheets facilitate charge transfer.

MATERIALS AND METHODS

Materials

High-purity red phosphorus (RP, 99.99%), BP crystals (99.99%), indium nitrate tetrahydrate ($\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, 99.9%), and sodium hydroxide (NaOH, 99.9%) were purchased from Macklin (Chongqing, China). Melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99.9%), sodium sulfite (Na_2SO_3 , 99.9%), and N-methylpyrrolidone (NMP, 99.9%) were purchased from Macklin (Chongqing, China). Nickel chloride (NiCl_2 , 99.9%) was purchased from Macklin (Chongqing, China). Deionized water was used in all experiments.

Preparation of crystalline BP

A special reaction kettle resistant to high temperature and pressure was independently designed and manufactured, using GH4169 alloy steel as the autoclave shell and biphenyl polyimide (UpilexS) as the inner liner. Using this reaction kettle, high-quality single-crystal BP was successfully prepared at 350 °C for 16 h.

Preparation of few-layer BP nanosheets

BP crystals (0.1 g) were dispersed in 100 ml of deoxygenated high-purity water. Under an N_2 atmosphere, 10 ml of NMP was added, and the mixture was stirred for 10 min. Subsequently, the mixture was ultrasonicated using an ultrasonic cell disruptor at 35 kHz for 1.5 h, followed by two centrifugation washes at 12,000 r/min. The precipitate was subjected to secondary ultrasonication (5 h) and washed three times by centrifugation. After freezing, few-layer BP nanosheets (BP NSs) were obtained.

Preparation of In_2O_3 quantum dots@BP NSs

For comparison, a control sample without Ni (In_2O_3 QDs@BP NSs) was synthesized under identical conditions. Indium nitrate solution (0.0042 g $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ dissolved in 100 ml of water), NaOH solution (0.0022 g dissolved in 200 ml of water), and BP NSs dispersion (50 mg dispersed in 100 ml of water) were prepared separately, and each was stirred for 30 min. The BP NSs dispersion and indium nitrate solution were transferred to a three-necked flask. Under magnetic stirring, the NaOH solution was added dropwise (approx. 3 s/drop). After the reaction, the mixture was washed three times with ethanol by centrifugation at 8,000 r/min. The precipitate was collected and freeze-dried to obtain the $\text{In}(\text{OH})_3$ @BP NSs precursor.

A series of samples with $\text{In}(\text{OH})_3$ loadings of 1 wt%, 3 wt%, and 5 wt% were prepared following the same method. The obtained $\text{In}(\text{OH})_3$ @BP NSs were re-dispersed in 100 ml of deionized water, and NaBH_4 solution (0.0016 g dissolved in 200 ml of water) was added dropwise. After completion of the reaction, the product was centrifuged, washed, and freeze-dried to obtain the In_2O_3 QDs@BP NSs composite material.

Finally, it was annealed at 300 °C for 45 min under a 2% H₂/98% N₂ atmosphere to form a stable In₂O₃ QDs-BP NSs heterojunction.

Loading of ultrasmall Ni clusters

The In₂O₃ QDs/BP NSs composite material (20 mg) was dispersed in 100 ml of anhydrous ethanol. Melamine (5 mg) was added, and the mixture was stirred in a sealed container for 40 min to allow ligand adsorption. Subsequently, a NiCl₂ precursor solution (0.5 mg NiCl₂ dissolved in a small amount of ethanol) was added dropwise, and stirring in the sealed container continued for 80 min. The product was collected by centrifugation, washed three times with anhydrous ethanol, and vacuum-dried at 60 °C for 12 h. Finally, under a high-purity N₂ (>99.999%) atmosphere, the product was heated to 180 °C at a rate of 2 °C/min and heat-treated for 50 min to obtain the ultrasmall Ni cluster-loaded composite material.

A series of samples with nominal Ni loadings of 0.8 wt%, 1.1 wt%, and 1.5 wt% was prepared using the same method. The actual loadings were determined by ICP-OES, and the results showed that the Ni loading deviation was <0.05% (absolute value) and the In₂O₃ loading deviation was <0.1% (absolute value).

Characterization

Phase analysis was performed using a D8 ADVANCE X-ray diffractometer Bruker, Karlsruhe, Germany; XRD, Cu K α radiation). Micro-morphology and lattice structure were observed using an Tecnai G2 20 transmission electron microscope (FEI, Hillsboro, OR, USA; TEM). Nanosheet thickness was measured using a Dimension 3100 atomic force microscope (Bruker; AFM). Surface elemental composition and chemical states were analyzed using an ESCALAB Xi+ X-ray photoelectron spectrometer (Thermo Scientific, Waltham, MA, USA; XPS). Photoelectrochemical tests were conducted on a CHI760E electrochemical workstation (CH Instruments, Shanghai, China).

Photocatalytic activity tests

Photocatalytic hydrogen evolution was carried out in a closed gas circulation system with a 300 W Xe lamp as the simulated solar light source. The photocatalyst (20 mg) was dispersed in 100 ml of aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃ as hole scavengers. The amount of H₂ evolved was analyzed by gas chromatography. For pollutant degradation, 20 mg of catalyst was added to 50 ml of tetracycline (20 mg/l TC) or Rhodamine B (10 mg/l RhB) solution. The suspension was stirred in the dark for 30 min to reach adsorption equilibrium and then irradiated with simulated solar light. At given intervals, 3 ml aliquots were taken and centrifuged, and the concentration was determined by UV-Vis spectroscopy. Radical trapping experiments were performed by adding 1 mM isopropanol (IPA, $\cdot$ OH scavenger), *p*-benzoquinone (BQ,

$\cdot$ O₂⁻ scavenger), or ammonium oxalate (AO, h⁺ scavenger) prior to irradiation; radical trapping experiments: IPA, BQ, and AO were all used at 1 mM.

All photocatalytic experiments were repeated three times independently under identical conditions. Data are presented as the mean $\pm$ standard deviation (SD). The kinetic rate constants were obtained by fitting the degradation data to the pseudo-first-order model ($\ln(C_0/C) = kt$), and the coefficient of determination (R^2) was calculated for each fit.

RESULTS AND DISCUSSION

Structural and morphological characterization

XRD patterns (Fig. 1a) confirm the successful synthesis of high-purity bulk BP with characteristic peaks corresponding to (020), (021), (040), and (060) planes [17]. Due to the extremely small size of the In₂O₃ QDs and their low content (only 3 wt%), the intensity of their characteristic peaks is very low and masked by the background signal; therefore, they are not clearly detected in the XRD patterns. Similar observations have been reported for small-sized or low-loading In₂O₃ in previous studies [2, 11]. The XRD pattern of RP shows its low crystallinity and poor electrical conductivity. Using it as a comparison highlights the two-dimensional layered structure and excellent charge transport advantages of BP, thereby demonstrating that converting RP into BP is key to achieving superior photocatalytic performance in this study. After exfoliation and compositing with In₂O₃ QDs, the BP peaks become broadened and weakened, indicating the formation of few-layer nanosheets. The Raman spectrum (Fig. 1b) shows that the three characteristic peaks of BP (Ag1, B2g, and Ag2 at 358, 434, and 461 cm⁻¹, respectively) remain unchanged after modification [18], while a new peak at around 307 cm⁻¹ is observed. This peak is characteristic of cubic In₂O₃, as reported in previous Raman studies [19, 20], confirming the successful loading of In₂O₃ QDs onto the BP nanosheets. After Ni loading, the peak intensities increased, suggesting enhanced carrier concentration and improved interfacial contact [16, 21].

AFM images (Fig. 2a) reveal that the obtained BP NSs have a lateral size of $\sim$ 350 nm and a thickness of $\sim$ 8 nm. The height profiles (Fig. 2b) shows that the thickness is predominantly 8 nm, corresponding to a few-layer structure. TEM images (Fig. 2c) show In₂O₃ QDs with sizes of 2–10 nm uniformly distributed on the surface of the BP NSs. HRTEM (Fig. 2d,e) reveals lattice spacings of 0.294 nm for In₂O₃ (222) and 0.26 nm for BP (040), indicating good crystallinity [22, 23]. Elemental mapping (Fig. 2g–j) shows a uniform distribution of O, In, P, and Ni, suggesting a highly dispersed state of Ni without visible aggregation. HAADF-STEM images (Fig. 2k–m) of samples with different Ni loadings (0.8 wt%, 1.1 wt%, and 1.5 wt%) show that at 1.1 wt% Ni, highly dispersed

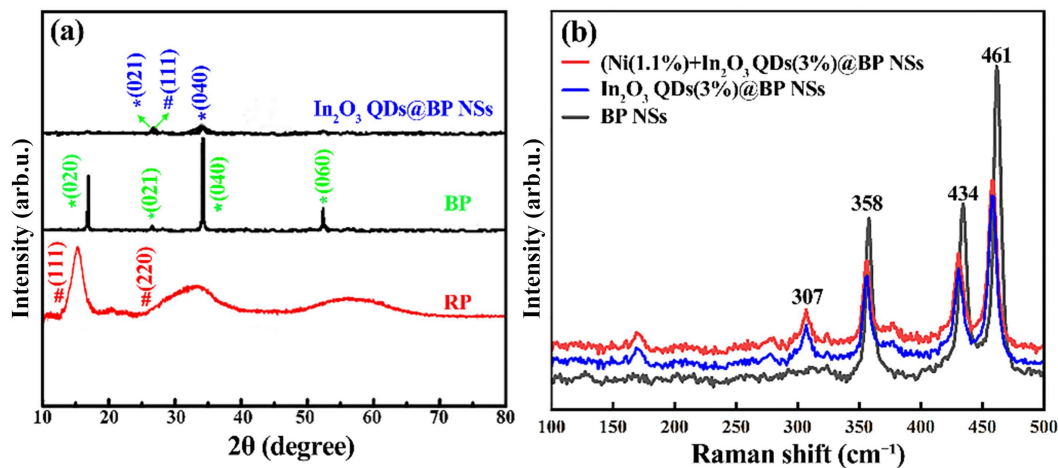


Fig. 1 (a) XRD patterns of In_2O_3 QDs, RP, bulk BP, and the 3 wt% In_2O_3 QDs@BP NSs composite. (b) Raman spectra of Ni/ In_2O_3 QDs@BP NSs with different Ni loadings.

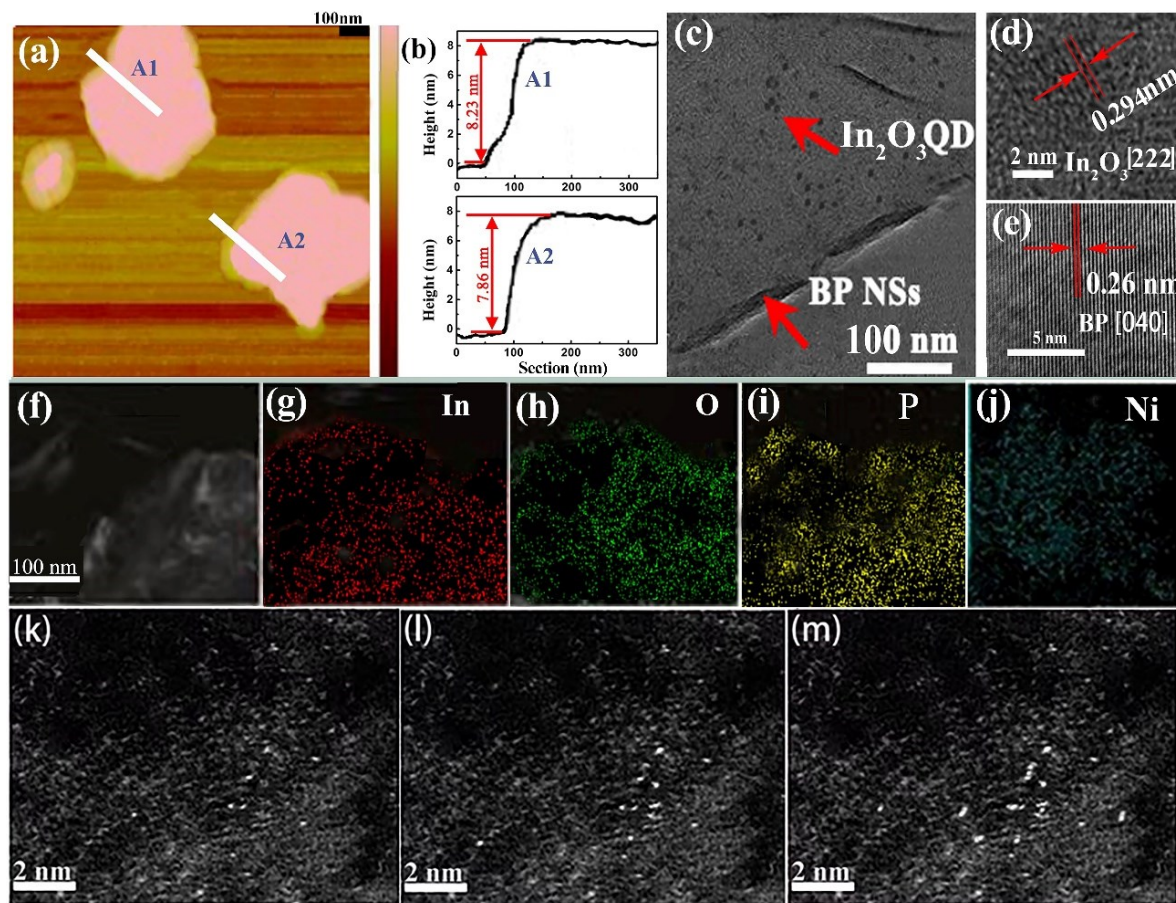


Fig. 2 (a) AFM image of few-layer BP NSs with height profiles along A1 and A2. (b) The height profiles of BP NSs. (c) TEM image of 3 wt% In_2O_3 QDs@BP NSs. (d) HRTEM image of In_2O_3 (222) lattice fringes ($d = 0.294 \text{ nm}$). (e) HRTEM image of BP (040) lattice fringes ($d = 0.26 \text{ nm}$). (f) HAADF-STEM image of $(\text{Ni}(1.1 \text{ wt\%})-\text{In}_2\text{O}_3 \text{ QDs})\text{@BP NSs}$. (g-j) EDS elemental mapping of In, O, P, and Ni, respectively. (k-m) HAADF-STEM images of Ni- In_2O_3 QDs@BP NSs with Ni loadings of 0.8 wt%, 1.1 wt%, and 1.5 wt%.

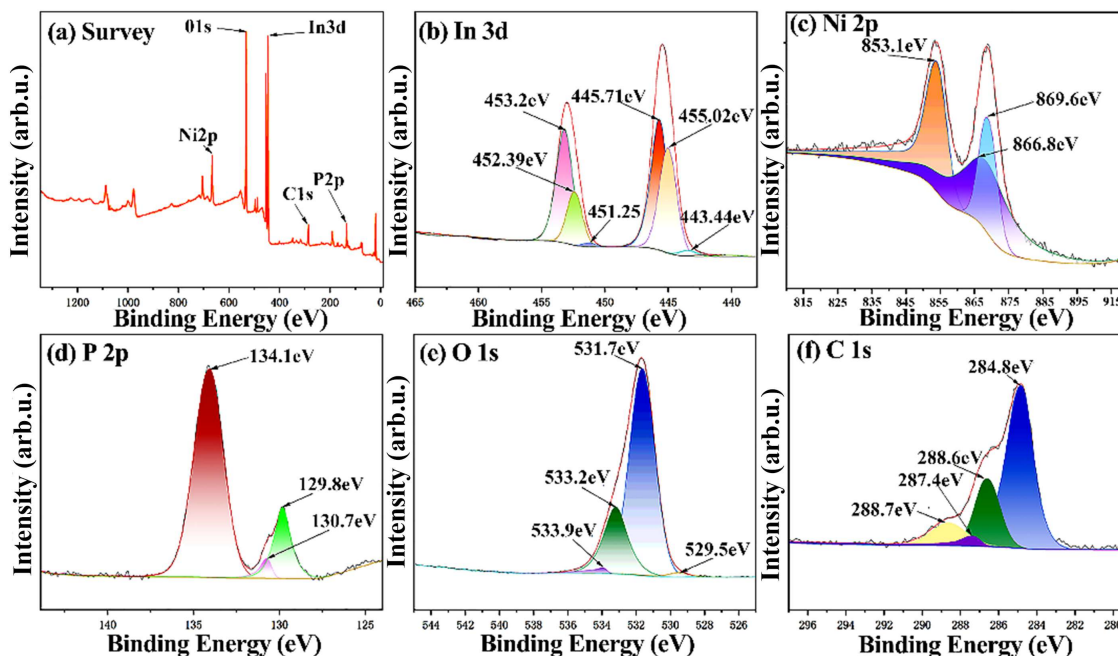


Fig. 3 XPS spectra of Ni(1.1 wt%)-In₂O₃ QDs(3 wt%)/BP NSs: (a) survey spectrum, (b) In 3d, (c) Ni 2p, (d) P 2p, (e) O 1s, and (f) C 1s.

Ni species are observed, while at 1.5 wt% some aggregation occurs. Thus, 1.1 wt% Ni loading was selected for further studies. The HAADF-STEM image of the 1.1 wt% Ni sample (Fig. 2l) shows only isolated bright spots (marked by red circles) without observable Ni aggregates, indicating that Ni is present as highly dispersed ultrafine species on the In₂O₃ QDs@BP NSs support, although direct EXAFS evidence is not available. In contrast, the 1.5 wt% sample (Fig. 2m) exhibits the appearance of small Ni aggregates, indicating that the Ni loading of 1.1 wt% is near the threshold for maintaining a highly dispersed state on the In₂O₃ QDs@BP NSs support.

The XPS spectra (Fig. 3) confirm the presence of In, Ni, P, and O elements. In the In 3d spectrum (Fig. 3b), the two peaks at 443.4 eV and 451.3 eV correspond to the In 3d_{5/2} and In 3d_{3/2} spin-orbit split components, respectively, consistent with literature reports for In³⁺ in In₂O₃ [19, 20]. The energy difference ($\Delta = 7.9$ eV) between the two spin-orbit components is in good agreement with the characteristic value for In³⁺ in cubic In₂O₃. The Ni 2p XPS spectrum (Fig. 3c) exhibits main peaks at 853.1 eV (Ni 2p_{3/2}) and 869.6 eV (Ni 2p_{1/2}), along with a satellite peak at 866.8 eV. The satellite feature is characteristic of Ni²⁺ species [24], while the binding energy of the main peak (853.1 eV) is slightly higher than that of metallic Ni⁰ (852.6 eV), suggesting a partially oxidized state or strong metal-support interaction. Given the use of melamine as a ligand and the relatively low annealing temperature (180 °C), the formation of Ni–N coordination com-

plexes is plausible. The observed Ni 2p binding energy is consistent with both Ni⁰ and Ni–N species reported for highly dispersed or atomically dispersed Ni on oxide supports [13, 14, 24]. P 2p shows a doublet at 129.8 and 130.7 eV for BP, and a peak at 134.1 eV for P–O bonds from slight surface oxidation. O 1s can be deconvoluted into lattice oxygen, –OH groups, and adsorbed water. The carbon signal originates from ambient contamination [25].

Photoelectrochemical properties

Transient photocurrent responses (Fig. 4a) show that the (Ni-In₂O₃ QDs)/BP NSs composite exhibits the highest photocurrent density, approximately 3.5 times that of pristine BP NSs, indicating efficient charge separation. Electrochemical impedance spectra (Fig. 4b) reveal the smallest arc radius for the optimal composite, suggesting reduced charge transfer resistance. Time-resolved fluorescence decay spectra (Fig. 4c) show the fastest decay for the ternary composite, indicating suppressed radiative recombination.

The enhanced photocurrent (3.5× that of pristine BP), reduced EIS arc radius, and quenched PL emission collectively indicate that the ternary composite achieves the most efficient charge separation and transfer. Specifically, the introduction of In₂O₃ QDs is proposed to form a type-II heterojunction that facilitates spatial separation of electrons and holes. This explains the 4.5-fold increase in H₂ evolution rate (3265 vs. 720 $\mu\text{mol/g/h}$) and the 1.6-fold increase in TC degradation efficiency compared with pristine BP.

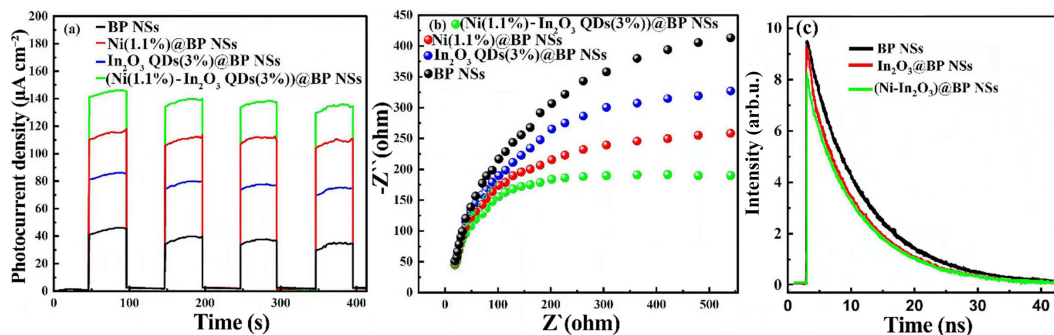


Fig. 4 (a) Transient photocurrent responses, (b) EIS Nyquist plots, and (c) Time-resolved fluorescence decay spectra of different samples under simulated solar light.

Photocatalytic degradation performance

The degradation data in Fig. 5a are presented as the mean $\pm$ SD ($n = 3$). Under simulated solar light, the degradation of TC (Fig. 5a) by pristine BP NSs reaches $57.6 \pm 0.9\%$ in 60 min. After loading 3 wt% In₂O₃ QDs, the degradation rate increases to $77.7 \pm 0.7\%$. The optimal composite with 1.1 wt% ultrasmall Ni clusters achieves a degradation efficiency of $89.6 \pm 1.1\%$ after 60 min (mean $\pm$ SD, $n = 3$) [26], which is mainly attributed to the ability of the ultrasmall Ni clusters to both enhance charge separation efficiency and increase effective active sites. The pseudo-first-order kinetic fitting (Fig. 5b) yields rate constants (k) of 0.023 min^{-1} for Ni/In₂O₃/BP, 0.015 min^{-1} for In₂O₃/BP, and 0.009 min^{-1} for pristine BP, with corresponding R^2 values of 0.991, 0.982, and 0.976, respectively. All data points represent the mean $\pm$ SD from three independent experiments. Cycling tests (Fig. 5c) show only slight activity loss after five cycles, indicating good stability. For RhB degradation (Fig. 5d), the optimal composite achieves $93.4 \pm 1.3\%$ removal within 12 min [27], with a rate constant of 0.154 min^{-1} , with a corresponding R^2 value of 0.995, significantly higher than those of the other samples (Fig. 5e). Cycling tests (Fig. 5f) also demonstrate excellent reusability.

To identify the dominant reactive species, radical trapping experiments were conducted on the optimal composite (Fig. 6). For TC degradation (Fig. 6a), the addition of BQ ($\cdot\text{O}_2^-$ scavenger) drastically reduces the degradation efficiency to 45.7%, indicating that $\cdot\text{O}_2^-$ is the dominant species. For RhB degradation (Fig. 6b), IPA ($\cdot\text{OH}$ scavenger) causes the greatest inhibition (degradation efficiency drops to 53.0%), suggesting that $\cdot\text{OH}$ plays a major role. Thus, both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are involved, with pollutant-dependent dominance [28].

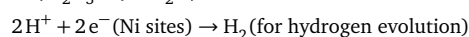
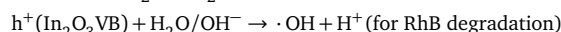
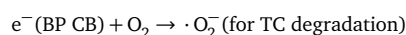
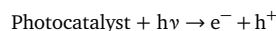
Photocatalytic hydrogen evolution

The hydrogen evolution rate (Fig. 7a) of pristine BP NSs is $720 \pm 56 \mu\text{mol/g/h}$. After the loading of 3 wt% In₂O₃ QDs, the rate increases to $2620 \pm 97 \mu\text{mol/g/h}$. The optimal Ni(1.1 wt%)-In₂O₃ QDs(3 wt%)@BP NSs composite achieves $3265 \pm 131 \mu\text{mol/g/h}$, out-

performing many noble-metal-based catalysts. For example, the BP/Au/CN heterojunction achieved a H₂ evolution rate of $1400.8 \mu\text{mol/g/h}$ under UV-Vis irradiation [29], while our Ni/In₂O₃/BP ternary composite exhibits a rate of $3265 \pm 131 \mu\text{mol/g/h}$ under similar conditions, demonstrating the great potential of non-noble metal catalysts in BP-based systems and competitive performance compared with many reported noble-metal-based photocatalysts. Notably, previous studies have demonstrated that non-noble metal cocatalysts in BP-based systems can even outperform Pt/BP benchmarks [30]. This value ($3265 \mu\text{mol/g/h}$) is competitive with, and even surpasses, recently reported non-noble metal single-atom photocatalysts [31], Ni single atoms on RP QDs [32], and Ni-P₄ single atoms on violet phosphorene ($377.8 \mu\text{mol/g/h}$) [33]. Time-dependent H₂ production (Fig. 7b) shows a linear increase, indicating a stable reaction. Cycling tests (Fig. 7c) demonstrate that the Ni-modified composite retains higher activity than the unmodified one after five cycles, confirming enhanced stability [34, 35]. The Ni-In₂O₃ QDs@BP NSs catalyst after five cycles was characterized by XRD and XPS (Fig. 7d,e). The XRD patterns showed no significant change in the BP peaks, and the P 2p XPS spectrum revealed a slight increase in the P-O peak (from 134.1 eV to 134.4 eV), indicating minor surface oxidation. This limited oxidation is attributed to the protective effect of In₂O₃ QDs covering the BP surface, which suppresses direct contact with water and oxygen. Similar protection strategies, such as encapsulating BP nanosheets in a protective shell to enhance ambient stability, have been reported for BP-based photocatalysts [23].

Proposed photocatalytic mechanism

The proposed reactions are as follows:



Based on the results, a possible mechanism is

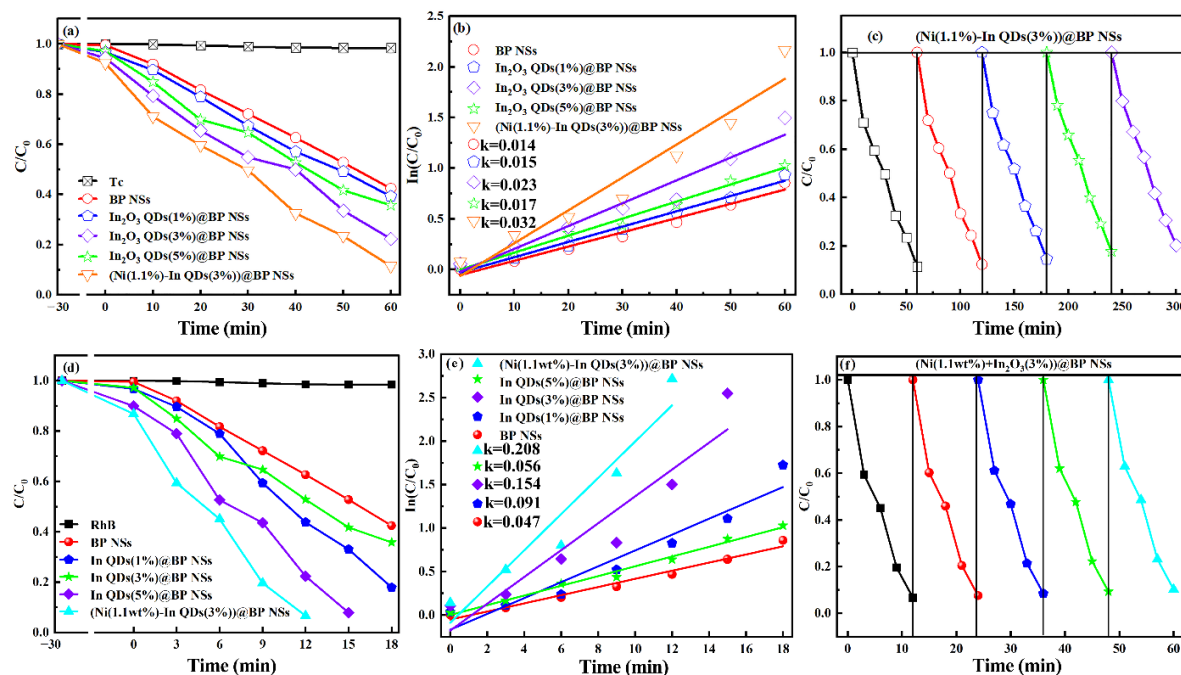


Fig. 5 Photocatalytic degradation: (a) TC degradation over time (mean $\pm$ SD, $n = 3$); (b) corresponding pseudo-first-order kinetics (R^2 values are given in the text); (c) cycling stability for TC; (d) RhB degradation over time (mean $\pm$ SD, $n = 3$); (e) corresponding kinetics (R^2 values are given in text); and (f) cycling stability for RhB.

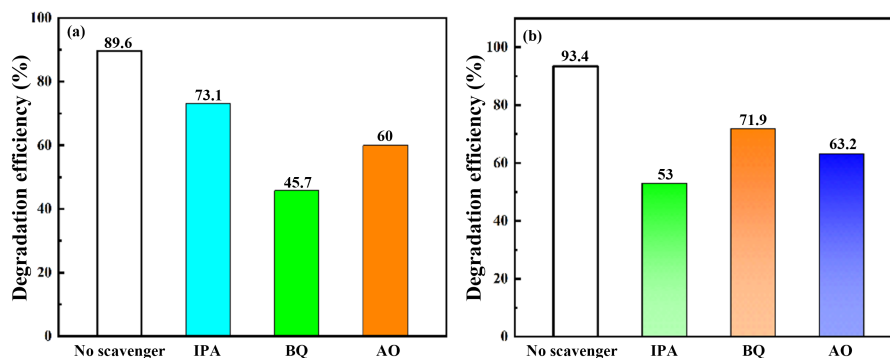


Fig. 6 Effects of different active species scavengers on the photocatalytic degradation efficiency of (a) tetracycline and (b) Rhodamine B by the optimal (Ni(1.1 wt%)- In_2O_3 QDs(3 wt%))@BP NSs composite.

proposed (Fig. 8). Under illumination, both In_2O_3 QDs and BP NSs generate electron-hole pairs. According to previous reports [12, 27], the CB/VB levels of In_2O_3 and BP are $-0.8/2.4$ eV and $-0.2/1.5$ eV (vs. NHE), respectively, which suggests a plausible type-II band alignment. Thus, photogenerated electrons are likely to transfer from the CB of In_2O_3 to that of BP while holes transfer from the VB of BP to that of In_2O_3 , leading to efficient spatial charge separation and suppressed recombination. The ultrasmall Ni clusters anchored at the interface act as electron traps, further accumulating electrons. These electrons reduce O_2 to $\cdot\text{O}_2^-$, which is mainly responsible for TC degradation. Holes accumulated on the In_2O_3 VB oxidize

$\text{H}_2\text{O}/\text{OH}^-$ to $\cdot\text{OH}$, the key species for RhB degradation. For hydrogen evolution, electrons at Ni sites directly reduce H^+ to H_2 , while holes are consumed by the sacrificial agent ($\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$). The synergistic effect of the heterojunction and ultrasmall Ni clusters leads to enhanced charge separation and surface reaction kinetics [36–38].

CONCLUSION

A novel ternary photocatalyst comprising ultrasmall Ni clusters anchored on In_2O_3 QDs-decorated few-layer BP NSs was successfully synthesized. The optimal composite (1.1 wt% Ni and 3 wt% In_2O_3) exhibits outstanding photocatalytic activity for both hydrogen

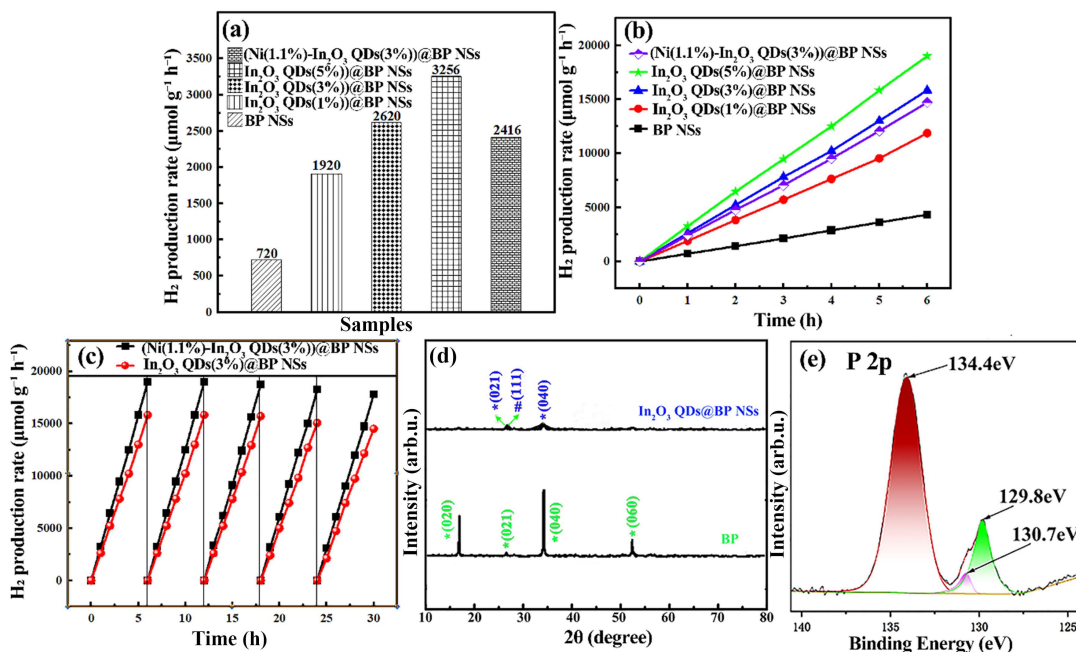


Fig. 7 (a) Photocatalytic H_2 evolution rates of different samples, (b) time-dependent H_2 evolution curves, and (c) cycling stability of In_2O_3 QDs(3 wt%)@BP NSs and $(\text{Ni}(1.1 \text{ wt}\%)-\text{In}_2\text{O}_3 \text{ QDs}(3 \text{ wt}\%))@BP \text{ NSs}$. (d) XRD patterns and (e) P 2p XPS spectra of the fresh and used catalyst.

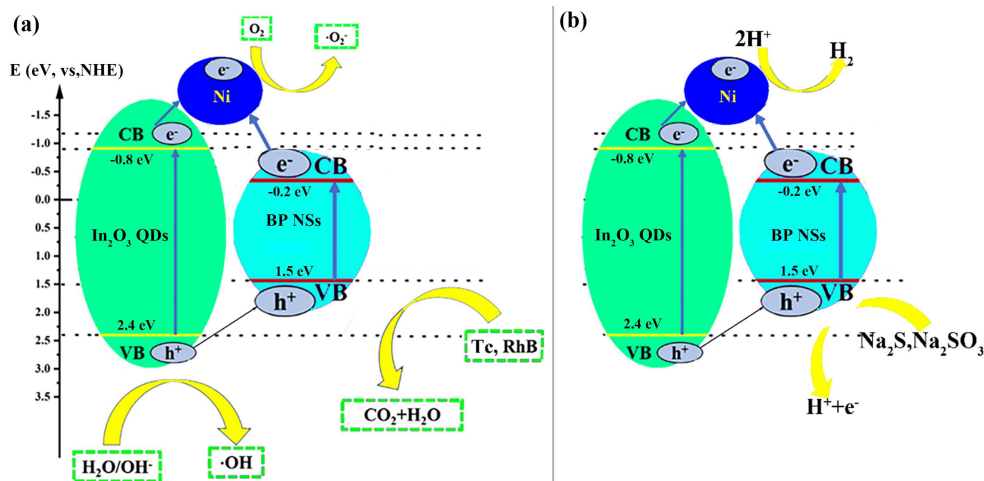


Fig. 8 Schematic of the proposed photocatalytic mechanism for (a) pollutant degradation and (b) hydrogen evolution over the $\text{Ni}-\text{In}_2\text{O}_3$ QDs@BP NSs composite.

evolution ($3265 \mu\text{mol/g/h}$) and the degradation of TC (89.6% in 60 min) and RhB (93.4% in 12 min) under simulated solar light. The enhanced performance is attributed to the proposed type-II heterojunction between In_2O_3 QDs and BP NSs, which is believed to promote spatial charge separation, and to the ultrasmall Ni clusters that act as electron traps and active sites. Radical trapping experiments identified $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ as the dominant reactive species. This work provides a promising strategy for designing efficient and stable non-noble metal photocatalysts through multi-scale

structural engineering.

Acknowledgements: This work was supported by the Higher Education Research Project of the Guizhou Provincial Department of Education (Youth Project) (Approval No. Qian Jiao Ji [2022] No. 319), the Doctoral Research Start-up Fund Project (Approval No. Zunshi BS [2022] No. 09), the Zunyi Municipal Joint Fund Project (Approval No. Zunyi Kehe HZ Zi [2024] No. 152), and the Zunyi Normal University Special Project for Serving the Local Industrial Revolution (Approval No. Zunyi XY [2024] No. 06).

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