

RESEARCH ARTICLE Very Important Paper

Enhanced Photocatalytic Hydrogen Production Assisted by Seawater Ions

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Received: 25 June 2026 | **Revised:** 1 August 2026 | **Accepted:** 6 August 2026

Keywords: covalent organic frameworks | hydrogen production | microporous materials | photocatalysis | seawater

ABSTRACT

Photocatalytic hydrogen production from water, particularly seawater, offers a promising route for converting solar energy into storable chemical fuels. However, despite considerable efforts in photocatalyst design, the influence of seawater ions on photocatalytic processes remains poorly understood. In this study, covalent organic frameworks (COFs) are adopted as a structurally well-defined platform to investigate how representative inorganic ions present in seawater influence photocatalytic hydrogen production. Among the ionic species commonly present in seawater, sodium bromide (NaBr) is identified as the most effective promoter. Mechanistic studies reveal that Br[−] regulates the catalytic process through multiple pathways. During Pt photodeposition, Br[−] modulates the electronic structure of Pt nanoparticulate cocatalyst, promoting interfacial charge separation. During the photocatalytic reaction, Br[−] interacts with photogenerated holes and stabilizes the excited-state charge, thereby prolonging the lifetime of charge carriers. At high concentrations, Br[−] reduces the number of accessible active sites on the Pt surface, leading to catalyst poisoning. Significantly, the mechanistic insights gained from COF systems can be extended to common semiconductor photocatalysts, offering valuable guidance for ion-regulated photocatalysis under seawater-relevant conditions.

1 | Introduction

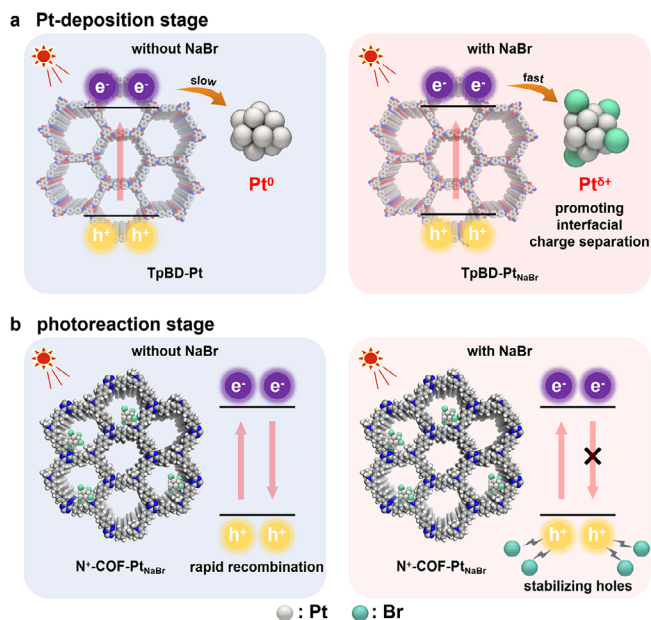
The escalating global energy crisis and increasing environmental pollution underscore the urgent need for sustainable energy solutions [1]. Photocatalytic hydrogen production, which directly converts solar energy into storable chemical fuels, is widely regarded as a promising route toward sustainable energy [2–5]. Despite significant advances in photocatalyst design, most efforts have focused on engineering the band structure of semiconductor materials to improve light absorption and charge separation

[6]. However, the overall efficiency of photocatalytic hydrogen production is increasingly recognized to be strongly influenced by interfacial processes at catalytic sites, particularly those associated with cocatalysts [7, 8]. Among various cocatalysts, Pt remains to be the most effective for hydrogen production due to its near-optimal hydrogen adsorption energy and outstanding catalytic activity. Nevertheless, its performance is highly sensitive to its electronic structure, surface chemistry, and interactions with the underlying photocatalyst, indicating that even subtle interfacial modulation can significantly influence catalytic efficiency.

Xiyuan Zhang and Yunyang Qian contributed equally to this work.

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SCHEME 1 | Schematic illustration showing the significant roles of NaBr in (a) Pt-deposition stage for TpBD COF and (b) photoreaction stage for N⁺-COF.

This sensitivity has motivated extensive efforts to optimize cocatalyst performance through strategies such as alloying, precise clustering, defect engineering, and surface modification [9–12]. While these approaches have improved catalytic activity, they predominantly focus on modifying the intrinsic properties of cocatalysts themselves. By comparison, the role of the surrounding microenvironment around Pt, especially solution-phase species, has received far less attention. Simple inorganic ions are ubiquitous in aqueous environments and can affect interfacial catalytic processes through electrostatic interactions, surface coordination, and substrate activation [13]. From a practical perspective, large-scale solar hydrogen production is unlikely to rely on highly purified water and will ultimately require the direct utilization of abundant natural water resources, particularly seawater, where complex mixtures of cations and anions are inevitably present [14, 15]. These ions may profoundly affect both cocatalyst formation and the subsequent photocatalytic reaction, yet a systematic understanding of their roles remains lacking.

A clear understanding of these effects requires model photocatalysts with structurally well-defined and chemically uniform interfaces. Covalent organic frameworks (COFs), a class of crystalline porous materials constructed from organic building blocks, provide an ideal platform [16–29]. Their periodic structures and uniform chemical environments enable homogeneous photodeposition of cocatalysts with minimized structural heterogeneity [30–38]. Moreover, the pronounced excitonic characteristics of COFs render their charge carrier dynamics highly sensitive to subtle interfacial perturbations [39]. These features make COFs particularly suitable for probing how external ionic species regulate cocatalyst electronic structures and charge transfer processes, providing insights that are often difficult to obtain in common semiconductor systems.

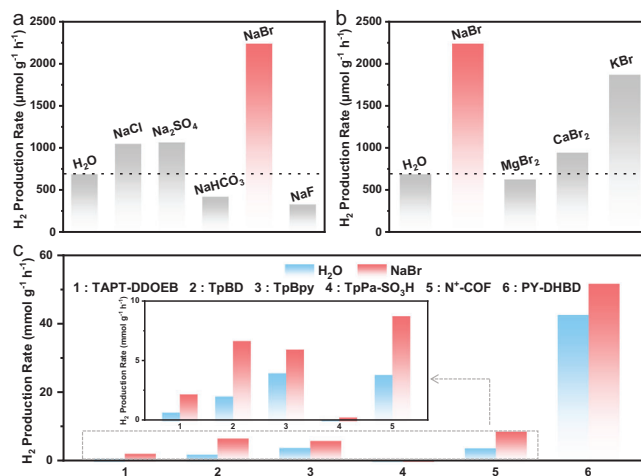


FIGURE 1 | Photocatalytic hydrogen production of TAPT-DDOEB with (a) different sodium salts and (b) different bromide salts. Reaction conditions: catalyst (5 mg), H₂O (20 mL), ascorbic acid (100 mg), metal salt (10.6 mmol), H₂PtCl₆ aqueous solution (8 μL), 300 W Xe lamp, λ ≥ 380 nm, 99.999% N₂. (c) Photocatalytic hydrogen production of different COFs in H₂O and NaBr solution.

In this study, a series of COFs with varied linkages, functional groups, and topologies are employed as model photocatalysts to systematically investigate the influence of representative inorganic ions present in seawater on photocatalytic hydrogen production. Screening of representative cations and anions identifies NaBr as the most effective promoter, achieving a 224% activity enhancement for the TAPT-DDOEB COF assembled by 1,3,5-tris-(4-aminophenyl)triazine (TAPT) and 1,4-bis(3-dimethylamino-1-oxoprop-2-en-yl)benzene (DDOEB). Further decoupling experiments reveal that NaBr regulates photocatalysis through multiple pathways. During cocatalyst photodeposition, Br⁻ modulates the electronic structure of Pt nanoparticles, favorable to interfacial charge separation (Scheme 1a). During the photocatalytic reaction, Br⁻ interacts with photogenerated holes and stabilizes excited states, thereby further boosting charge separation (Scheme 1b). Interestingly, the extent of this enhancement correlates with the intrinsic charge-separation properties of the photocatalysts. At high concentrations, Br⁻ reduces the number of accessible Pt sites at the particle surface, leading to catalyst poisoning. These findings from the COF systems can be extended to common semiconductor photocatalysts, providing key implications for ion-regulated photocatalysis.

2 | Results and Discussion

To investigate whether major seawater ions influence photocatalytic hydrogen production, a stable and highly crystalline TAPT-DDOEB COF has been first synthesized as a representative model photocatalyst (Figure S1) [40]. To compare the effects of different anions commonly present in seawater under a fixed cation background, a series of sodium salts is first employed (Figure 1a). Among the investigated anions, bromide affords the most pronounced enhancement in hydrogen production activity. Bromide is therefore selected for subsequent experiments, in which various bromide salts are examined to evaluate the influence of the accompanying cations (Figure 1b). Among these

combinations, NaBr delivers the highest photocatalytic efficiency, indicating that NaBr provides the most favorable environment for hydrogen production under the investigated conditions. The pH values of the representative salt solutions range from 5.8 to 8.2 at the concentrations used in the photocatalytic experiments, and no clear correlation is observed between solution pH and hydrogen-production activity (Table S1). The activity differences are therefore unlikely to be dominated by pH variations. To determine whether the promotional effect observed in the single-salt model systems persists in more complex media, TAPT-DDOEB is further evaluated in simulated and natural seawater (Figure S2). The hydrogen-production rates are approximately 1.5- and 1.4-fold higher than those in pure water, respectively, indicating that the ion-induced promotion remains observable in complex seawater environments. Control experiments are then performed to verify the essential components of the photocatalytic system (Figure S3). No detectable hydrogen is produced in the absence of the photocatalyst, light irradiation, or ascorbic acid, whereas omission of the Pt precursor results in only trace hydrogen production. These results confirm that efficient hydrogen production requires the photocatalyst, light, sacrificial electron donor, and Pt cocatalyst. The negligible activity without ascorbic acid further indicates that NaBr cannot serve as an effective sacrificial electron donor under the investigated conditions.

To further assess whether this effect is specific to TAPT-DDOEB or represents a more general phenomenon, a series of COF photocatalysts with diverse linkages, linkers, and topologies have been synthesized and evaluated (Figures S4–S9). Remarkably, in all cases, the introduction of NaBr leads to a significant enhancement in hydrogen production activity compared with that observed in pure water (Figure 1c). These results indicate that NaBr acts as an effective promoter for photocatalytic hydrogen production across structurally diverse COF systems.

Photocatalytic hydrogen production generally involves two key processes: the formation of cocatalysts, typically achieved through in situ photodeposition, and the subsequent photocatalytic reaction itself. Because seawater ions may influence either the cocatalyst formation process or the interfacial charge transfer dynamics during photocatalysis, distinguishing the role of NaBr in these two stages is essential for understanding its promotion effect. For decoupling these two contributions, a series of controlled experiments have been designed in which NaBr is independently introduced during either the cocatalyst-deposition stage or the photocatalytic reaction stage.

To investigate the specific role of NaBr during cocatalyst deposition, COFs with diverse structural characteristics were synthesized (Figures S4–S9), followed by in situ deposition of Pt nanoparticles in the presence or absence of NaBr, yielding COF-Pt_{NaBr} and COF-Pt, respectively. In these experiments, NaBr is present exclusively during the photodeposition process. After 2 h of Pt deposition, the resulting catalysts are thoroughly washed to remove residual NaBr and subsequently used for photocatalytic hydrogen production for 2 h in pure water. Remarkably, introducing NaBr during the Pt cocatalyst deposition consistently enhances the photocatalytic hydrogen production activity for all investigated COFs. Among them, TpBD exhibits the most pronounced improvement, showing a 160% increase in hydrogen production performance (Figure 2a). Moreover, TpBD-Pt_{NaBr}

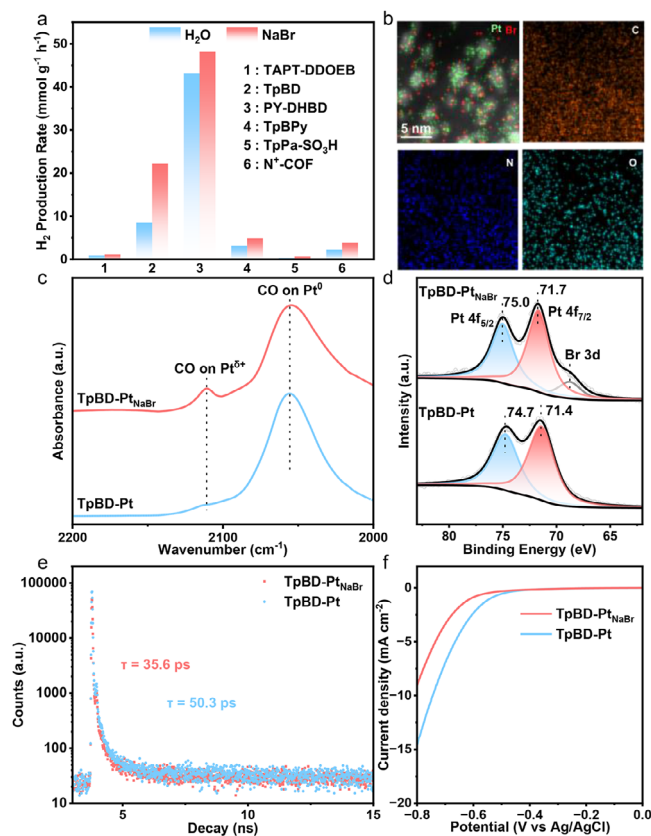


FIGURE 2 | (a) Photocatalytic hydrogen production of different COFs loaded with Pt pre-photordeposited in either H₂O or NaBr solution, followed by photocatalytic testing in pure H₂O. Reaction conditions: COF-Pt or COF-Pt_{NaBr} (5 mg), H₂O (20 mL), ascorbic acid (100 mg), time (2 h), 300 W Xe lamp, $\lambda \geq 380$ nm, 99.999% N₂. (b) High-resolution elemental mapping of TpBD-Pt_{NaBr}. (c) CO adsorption DRIFTS spectra, (d) Pt 4f XPS spectra, (e) time-resolved PL decay profiles (excitation at 373 nm, emission at 575 nm), and (f) electrochemical LSV curves for the hydrogen evolution reaction (HER) of TpBD-Pt_{NaBr} and TpBD-Pt.

maintains a stable hydrogen production rate in pure water over five consecutive photocatalytic cycles (Figure S10), while the crystallinity of TpBD remains well preserved after cocatalyst deposition and photocatalytic reactions (Figure S11), indicating the good structural stability of both the framework and the deposited cocatalyst.

Transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) reveal that the Pt particle size, morphology, lattice spacing, and loading amount in TpBD-Pt_{NaBr} are nearly identical to those in TpBD-Pt. Moreover, the measured Pt loading agrees well with the theoretical value, indicating that nearly all of the Pt precursor is deposited onto the COF (Figures S12–S15 and Table S2). Energy dispersive spectroscopy (EDS) elemental mapping and x-ray photoelectron spectroscopy (XPS) measurements confirm the presence of Br species in TpBD-Pt_{NaBr}, whereas Na is not detected (Figures S16–S18). Semiquantitative EDS analysis further estimates the Br content to be approximately 0.50 wt% in TpBD-Pt_{NaBr}. After photocatalysis, the estimated Br content of TpBD-Pt_{NaBr} remains essentially unchanged at 0.51 wt% (Table S3). In addition, ion chromatography detects no Br⁻ in the corresponding reaction

solutions either before or after photoreaction (Table S4). These results indicate that the deposited Br species remain firmly bound to the catalyst, without detectable detachment or leaching under the investigated conditions. High-resolution elemental mapping further reveals that Br species are possibly located on the surface of Pt nanoparticles (Figure 2b) [41]. Raman spectroscopy shows a characteristic peak at 222 cm^{-1} corresponding to Pt–Br bond, suggesting a strong interaction between Pt and Br (Figure S19) [42]. To probe the electronic effects of this Pt–Br interaction, CO adsorption diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and synchrotron XPS measurements are performed to probe the electronic structure of Pt. The DRIFTS spectra reveal the presence of partially positively charged Pt species ($\text{Pt}^{\delta+}$) in TpBD-Pt_{NaBr} (Figure 2c), and XPS spectra display a noticeable shift toward higher Pt binding energy compared with TpBD-Pt (Figure 2d) [43, 44]. These results collectively indicate that introducing NaBr during the Pt cocatalyst deposition facilitates the incorporation of Br species onto the Pt surface, leading to partial oxidation of Pt and modulation of its electronic structure, which aligns well with the above elemental mapping and Raman results.

Having established this electronic modulation, the influence of Pt–Br interactions on photocatalytic hydrogen production has been next evaluated by examining the three key steps: light absorption, charge separation and transfer, as well as surface reaction. In terms of light absorption, UV-vis absorption spectra show that TpBD-Pt_{NaBr} and TpBD-Pt exhibit nearly identical optical absorption profiles, indicating that the introduction of NaBr does not influence the light absorption capability of the photocatalyst (Figure S20). In contrast, clear differences emerge in the charge separation and transfer processes. Photocurrent measurements show that TpBD-Pt_{NaBr} exhibits a markedly enhanced response, suggesting more efficient charge separation (Figure S21). This interpretation is supported by electrochemical impedance spectroscopy (EIS) under visible light irradiation, which shows a smaller charge transfer resistance for TpBD-Pt_{NaBr} (Figure S22). Photoluminescence (PL) spectra further show that TpBD-Pt_{NaBr} displays a weaker intensity than TpBD-Pt (Figure S23), indicating suppressed recombination of photogenerated charge carriers. Time-resolved PL measurements confirm this comparison and reveal average lifetimes of 35.6 ps and 50.3 ps for TpBD-Pt_{NaBr} and TpBD-Pt, respectively (Figure 2e). The shorter PL lifetime of TpBD-Pt_{NaBr} suggests faster transfer of photogenerated electrons to Pt sites [10]. By contrast, linear sweep voltammetry (LSV) measurements show that TpBD-Pt_{NaBr} exhibits a smaller magnitude of current density than TpBD-Pt, indicating that the Pt–Br interaction does not provide an advantage in the surface reaction step (Figure 2f). Taken together, these results indicate that NaBr introduced during the Pt cocatalyst deposition modulates the electronic structure of Pt through Pt–Br interactions. This modification promotes interfacial charge separation and electron transfer, while slightly compromising the intrinsic surface reaction kinetics.

Beyond its effect on Pt cocatalyst photodeposition, the influence of NaBr on the subsequent photocatalytic reaction stage has been further examined. To isolate the role of NaBr during the reaction stage, Pt nanoparticles are photodeposited in the presence of NaBr, and the resulting catalysts are subsequently evaluated for photocatalytic hydrogen production either with or without NaBr

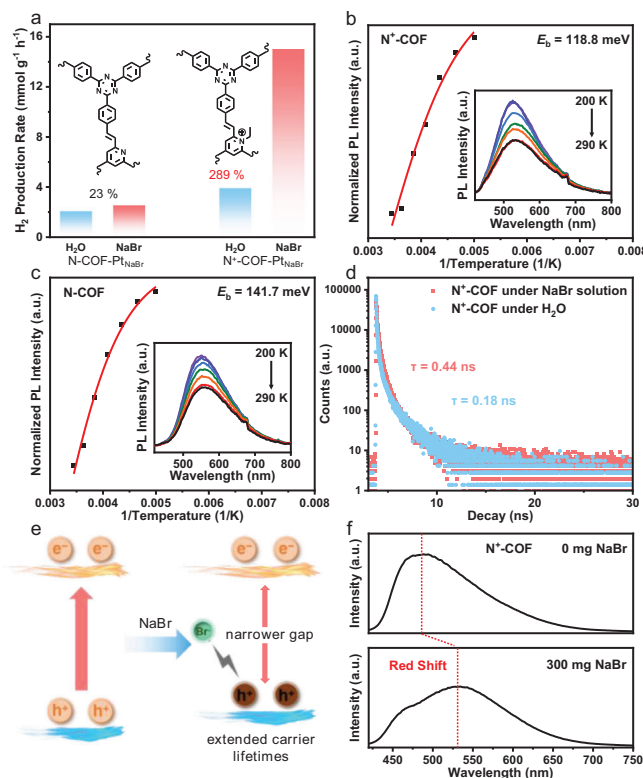


FIGURE 3 | (a) Photocatalytic hydrogen production of N-COF-Pt_{NaBr} and N⁺-COF-Pt_{NaBr} in H₂O or NaBr solution. Reaction conditions: catalyst (5 mg), H₂O (20 mL), ascorbic acid (100 mg), with or without NaBr (1090 mg), 300 W Xe lamp, $\lambda \geq 380\text{ nm}$, 99.999% N₂. The intensity of PL emission ($\lambda_{\text{ex}} = 400\text{ nm}$) as a function of temperature for (b) N⁺-COF and (c) N-COF. Inset: temperature-dependent PL spectra from 200 to 290 K in 15 K intervals. (d) Time-resolved PL decay profiles for N⁺-COF in NaBr solution and H₂O (excitation at 373 nm, emission at 530 nm for NaBr solution and 480 nm for H₂O). (e) Schematic illustration of Br-induced stabilization of photogenerated holes. (f) PL emission spectra for N⁺-COF with 0 mg NaBr (top) and 300 mg NaBr (bottom) under excitation at 400 nm, showing a 41 nm redshift of the emission peak after NaBr addition.

in the reaction solution. In contrast to the Pt cocatalyst-deposition stage, the influence of NaBr during the photocatalytic reaction stage strongly depends on the structure of the photocatalyst. For TAPB-DDOEB-Pt_{NaBr}, the hydrogen production activity decreases by 60% in the presence of NaBr, whereas TAPT-DDOEB-Pt_{NaBr} exhibits a 93% enhancement under the same conditions (Figure S24). Similarly, for N-COF-Pt_{NaBr}, the hydrogen production rate increases by 23% in the presence of NaBr, and N⁺-COF-Pt_{NaBr} exhibits a remarkable 289% increase in activity (Figure 3a). The Br-free N-COF-Pt and N⁺-COF-Pt are further evaluated in H₂O and NaBr solution, reproducing the catalyst-dependent trend observed for the corresponding Pt_{NaBr}-loaded samples (Figure S25). These results indicate that the role of NaBr during the reaction stage is highly dependent on the intrinsic properties of the photocatalyst.

To understand the origin of this catalyst-dependent behavior, density functional theory (DFT) calculations are performed to analyze the spatial distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

(LUMO) of TAPB-DDOEB, TAPT-DDOEB, N-COF, and N⁺-COF (Figures S26 and S27). The calculated results indicate that TAPT-DDOEB and N⁺-COF exhibit more favorable HOMO–LUMO separation than TAPB-DDOEB and N-COF, respectively, which correlates with their more pronounced activity response to NaBr during the photocatalytic reaction process (Figures 3a and S24). To further verify this hypothesis, the exciton binding energies (E_b) of the COFs are determined using temperature-dependent PL spectra, serving as an indicator of the intrinsic exciton dissociation ability of different COFs [39]. As the temperature decreases, the PL intensity of all COFs monotonically increases (Figure 3b,c; Figures S28 and S29). The calculated E_b values follow the order N⁺-COF (118.8 meV) < N-COF (141.7 meV), and TAPT-DDOEB (85.4 meV) < TAPB-DDOEB (93.8 meV). A smaller E_b corresponds to more efficient charge separation of photogenerated carriers [45]. These results show that NaBr-induced activity enhancement is more pronounced in COFs with stronger intrinsic charge-separation ability, indicating a close correlation between the promotional effect of Br[−] and the charge-separation characteristics of the photocatalyst.

On the basis of this correlation, further spectroscopic characterizations are carried out to probe how NaBr affects the excited-state behavior of the COFs. PL emission spectra reveal that both maximum emission wavelengths of N⁺-COF and TAPT-DDOEB, which exhibit efficient charge separation ability, undergo a distinct redshift upon the addition of NaBr (Figures S30 and S31). In contrast, N-COF and TAPB-DDOEB, which display relatively weaker charge separation ability, show no significant shift in their emission spectra (Figures S32 and S33). Ion-substitution experiments further demonstrate that the redshift originates specifically from Br[−] rather than Na⁺ in NaBr (Figures S30, S34, and S35). Moreover, UV-vis absorption spectra show no appreciable shift in the absorption profile of N⁺-COF after the addition of NaBr, indicating that NaBr does not significantly influence the ground-state electronic structure of the photocatalyst (Figure S36). This observation suggests that the interaction occurs primarily in the excited state. Time-resolved PL measurements provide further support for this assumption. The PL lifetime of N⁺-COF increases from 0.18 to 0.44 ns in the presence of NaBr (Figure 3d), consistent with stabilization of the NaBr-associated excited state [46]. Based on these results, it is proposed that, during the photocatalytic reaction stage, Br[−] interacts with photogenerated holes, stabilizing the excited state and narrowing the excited-state energy gap [13], which is verified by a redshift in the PL emission (Figure 3e). To further examine the relationship between Br[−]-hole interaction and the intrinsic charge-separation ability of the COFs, the PL responses of different COFs are compared upon addition of an identical amount of NaBr. Amongst them, N⁺-COF exhibits a pronounced 41 nm redshift in its emission maximum, whereas N-COF shows only a marginal shift of ~1 nm (Figures 3f and S37). Similarly, TAPT-DDOEB displays a 12 nm redshift, while no discernible redshift is observed for TAPB-DDOEB (Figures S38 and S39). Notably, the extent of the NaBr-induced redshift follows the same trend as the intrinsic charge-separation ability of the COFs, supporting a close correlation between charge separation and the interaction of Br[−] with photogenerated holes. As a result, the excited-state stabilization induced by Br[−] becomes more pronounced, which explains the larger activity enhancement (Figures 3a and S24).

Despite these beneficial effects, Br[−] also exerts detrimental influences under certain conditions. TAPB-DDOEB exhibits lower hydrogen production activity in NaBr solution compared to pure H₂O (Figure S24), indicating that NaBr can negatively affect the photocatalytic reaction. To better understand this unusual effect, the photocatalytic performance of TAPB-DDOEB has been further evaluated under different NaBr concentrations (Figure S40). Interestingly, a slight activity enhancement can still be observed at lower NaBr concentrations, whereas the activity gradually decreases as the NaBr concentration increases, revealing a pronounced concentration dependence. This observation suggests that the influence of Br[−] on photocatalysis is more complex than a simple promotion effect and may involve competing positive and negative contributions. However, EDS elemental mapping of TAPB-DDOEB-Pt shows that NaBr is not retained on the cocatalyst after the photocatalytic reaction process (Figure S41). This result suggests that the adverse effect is not due to persistent ion accumulation on the COF surface during the reaction stage, but is more likely associated with a transient interaction of Br[−] with the Pt surface. To directly verify the reversibility of this poisoning effect, TAPB-DDOEB-Pt_{NaBr} is sequentially evaluated in pure water, a 30 wt% NaBr solution, and pure water again after catalyst recovery and thorough washing. The hydrogen production activity is almost completely suppressed in the concentrated NaBr solution but recovers to nearly its initial level after the catalyst is returned to pure water (Figure S42). To probe whether Br species can reduce Pt-site accessibility, TpBD-Pt_{NaBr}, obtained during the deposition process, is selected as a representative model. CO pulse chemisorption measurements of TpBD-Pt_{NaBr} and TpBD-Pt show fewer accessible Pt sites for the former, consistent with partial occupation of the Pt surface by Br species (Figure 4a,b) [47]. The coexistence of these beneficial (electronic state regulation and excited state stabilization) and detrimental (Pt site blocking) effects suggests that the photocatalytic activity may follow a volcano-type dependence on Br[−] concentration (Figure 4c). This hypothesis is further supported by the photocatalytic hydrogen production performance of TpBD in NaBr solutions with different concentrations (Figure 4d). Notably, a detectable enhancement is retained at 0.04 wt% NaBr, corresponding to the NaBr concentration in the Aral Sea (Figure S43).

The mechanistic investigation based on COF photocatalysts demonstrates that introducing NaBr during the photodeposition of Pt effectively modulates the electronic state of Pt, thereby enhancing photocatalytic hydrogen production. During the photocatalytic reaction, photocatalysts with stronger directional migration of photogenerated charges are better able to stabilize photogenerated holes through interactions with Br[−] and therefore exhibit a more pronounced positive response to NaBr. However, at sufficiently high NaBr concentrations, the poisoning effect of Br species on the Pt surface becomes dominant, leading to suppressed catalytic performance.

The insights gained from COF systems also point to the broader extendability of this strategy in common semiconductor photocatalysts. To examine this possibility, SrTiO₃:Al (STO:Al), a well-known efficient water-splitting photocatalyst, has been synthesized and evaluated (Figures 4e and S44). In addition, representative semiconductor photocatalysts such as graphitic carbon nitride nanosheet (g-C₃N₄-NS) and CdS are also investi-

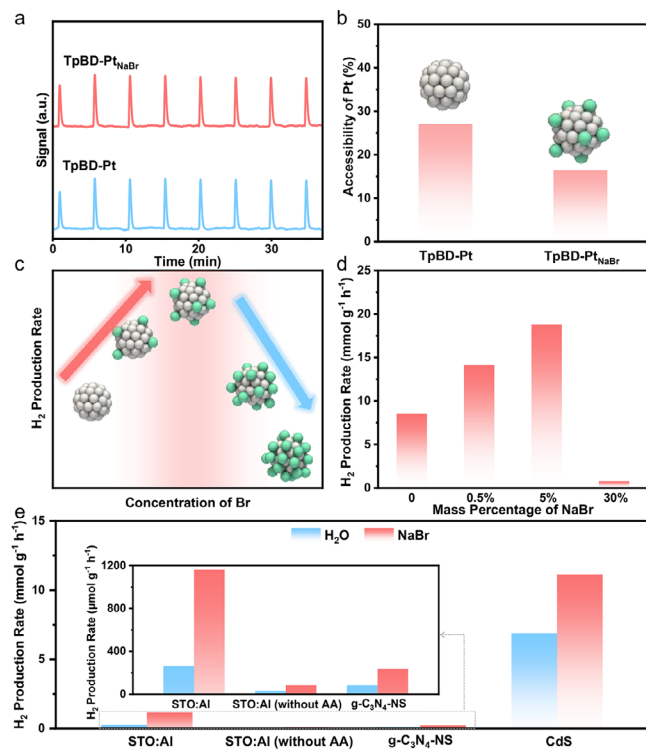


FIGURE 4 | (a) CO pulse chemisorption profiles at 308 K, and (b) accessible Pt sites of TpBD-Pt and TpBD-PtNaBr determined by CO pulse chemisorption. (c) Schematic illustration of the volcano-type dependence of the hydrogen production rate on Br[−] concentration. (d) Photocatalytic hydrogen production performance of TpBD with different NaBr mass percentages. (e) Photocatalytic hydrogen production of conventional semiconductor photocatalysts. Reaction conditions: catalyst (5 mg), H₂O (20 mL), ascorbic acid (AA, 100 mg), NaBr (1090 mg), H₂PtCl₆ aqueous solution (8 μL), 300 W Xe lamp, 99.999% N₂.

gated (Figure 4e). Among these systems, STO:Al exhibits the most pronounced improvement in hydrogen production performance upon NaBr addition. This behavior can be attributed to the intrinsic ability of STO:Al to direct photogenerated electrons and holes toward different crystal facets, enabling efficient spatial charge separation [48]. Such directional charge migration facilitates the interaction between Br[−] and photogenerated holes, which is consistent with the mechanism revealed in the above COF systems.

3 | Conclusion

In summary, this work provides a comprehensive mechanistic picture of how NaBr regulates photocatalytic hydrogen production. Using COFs as a structurally well-defined model system, NaBr is shown to play dual roles in both the Pt cocatalyst deposition and photocatalytic reaction stages. During the Pt photodeposition, NaBr modulates the electronic structure of Pt nanoparticles, promoting interfacial charge separation and enhancing hydrogen production activity. During the photocatalytic reaction, Br[−] ions interact with photogenerated holes, stabilize the excited state, and prolong the lifetime of charge carriers. At high concentrations, however, Br[−] blocks accessible Pt surface sites, reducing the Pt site accessibility and leading

to a volcano-type dependence of activity along with Br[−] concentration. The magnitude of this promotional effect is closely associated with the intrinsic charge-transport properties of the photocatalyst, and COFs with more efficient directional charge migration exhibit a more pronounced response. The extension of these mechanistic insights to common semiconductor photocatalysts further demonstrates the broader relevance of ion-mediated interfacial regulation. These results clarify how representative inorganic ions present in seawater affect photocatalytic processes and provide mechanistic guidance for photocatalysis in ion-containing aqueous media.

Author Contributions

Xiyuan Zhang: data curation, investigation, formal analysis, writing – original draft, writing – review and editing. **Yunyang Qian:** data curation, investigation, formal analysis, writing – review and editing. **Lanqing Xiao:** validation, investigation. **Meng-Fan Wang:** visualization, writing – review and editing. **Kang Sun:** formal analysis, data curation, writing – review and editing, investigation. **Jinxun Liu:** writing – review and editing, formal analysis. **Teng-Teng Chen:** formal analysis, writing – review and editing. **Hai-Long Jiang:** conceptualization, writing – review and editing, formal analysis, supervision, resources, project administration, funding acquisition.

Acknowledgments

This work is supported by the National Key Research and Development Program of China (2021YFA1500400), the NSFC (22331009, 22405258 and 22405262), the Key Project of Natural Science Foundation of Anhui Province (2508085ZD002), the Strategic Priority Research Program of the Chinese Academy of Sciences (Category B, 2026-IMR), the Natural Science Foundation Youth Project of Anhui Province (2408085QB070), and the Fundamental Research Funds for the Central Universities (WK9990250187 and WK9990000148). The authors thank BL10B at NSRL for XPS measurements. This work was partially carried out at the Instruments Center for Physical Science, USTC.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: anie74259-sup-0001-SupMat.doc.