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## Alkali metal ion-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ enhances $\cdot\text{OH}$ generation *via* interfacial water activation for efficient toluene photodegradation

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The efficient removal of volatile organic compounds (VOCs) remains a significant challenge in air pollution control due to their high chemical stability and adverse health impacts. Among them, toluene is a representative aromatic VOC whose degradation requires effective generation of highly oxidative hydroxyl radicals ( $\cdot\text{OH}$ ) to achieve complete mineralization. In this study, we developed alkali metal ion-doped  $\text{Bi}_2\text{O}_2\text{CO}_3$  (BOCO) photocatalysts *via* a one-step hydrothermal method. Alkali metal ions ( $\text{Na}^+$  and  $\text{Rb}^+$ ) were successfully incorporated into BOCO *via* substitutional doping. The doping process disrupts uniform surface charge distribution, creating active sites that facilitate interfacial water adsorption and activation. This leads to markedly increased hydroxyl radical ( $\cdot\text{OH}$ ) generation in doped catalysts, essential for ring-opening degradation of aromatic intermediates. Hence,  $\text{Rb-BOCO}$  achieved a toluene degradation efficiency of 60.7% and retained a stable mineralization rate (50.1%) over prolonged illumination, compared with 25.3% for pristine BOCO. These findings provide a mechanistic framework for designing durable photocatalysts by tuning surface chemistry to boost  $\cdot\text{OH}$  radical production for efficient VOC abatement.

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### Environmental significance

The removal of volatile organic compounds (VOCs), particularly toluene, is crucial for improving air quality and mitigating environmental and health risks. Efficient photocatalytic degradation of toluene is often limited by insufficient hydroxyl radical ( $\cdot\text{OH}$ ) generation due to sluggish interfacial water activation. In this study, we demonstrate that doping with Na and Rb ions disrupts the uniform surface charge distribution of  $\text{Bi}_2\text{O}_2\text{CO}_3$ , creating active sites that significantly enhance interfacial water activation and hydroxyl radical ( $\cdot\text{OH}$ ) generation, which realizes the effective mineralization of aromatic VOCs. These insights are crucial for advancing the field of photocatalysis, particularly in environmental applications for air pollution control.

## Introduction

Volatile organic compounds (VOCs), such as toluene, benzene, and xylene, are major atmospheric pollutants that pose severe threats to human health and the environment due to their toxicity, chemical persistence, and high photochemical reactivity.<sup>1–3</sup> Among them, toluene is a representative aromatic VOC emitted extensively from industrial manufacturing, vehicular exhaust, and indoor materials. Its high chemical stability and harmful biological effects make its effective removal a persistent challenge in air pollution control.<sup>4–6</sup> Photocatalytic oxidation (PCO) has emerged as a promising green technology for VOC abatement, enabling complete

mineralization under ambient conditions using solar or artificial light as the driving force.<sup>7–11</sup> However, the practical application of photocatalysts is still hindered by limited light-harvesting ability, rapid electron–hole recombination, and insufficient reactive oxygen species (ROS) production.<sup>12–15</sup>

Bismuth-based layered photocatalysts, especially bismuth oxycarbonate ( $\text{Bi}_2\text{O}_2\text{CO}_3$ ), have attracted considerable attention due to their unique  $[\text{Bi}_2\text{O}_2]^{2+}$  layered structures, suitable valence band positions, and strong oxidative potentials.<sup>16–18</sup> These properties provide appropriate redox capacity for VOC degradation. Nevertheless, pristine  $\text{Bi}_2\text{O}_2\text{CO}_3$  often suffers from unsatisfactory performance during toluene degradation. This is mainly attributed to the poor generation of ROS, resulting in the accumulation of stable aromatic intermediates on the catalyst surface, blocking active sites and suppressing further reactions.<sup>19–21</sup> Among ROS, the hydroxyl radicals ( $\cdot\text{OH}$ ) possess high oxidation potential and are essential for breaking the benzene ring.<sup>22–25</sup> Enhancing  $\cdot\text{OH}$  generation is key to achieving efficient ring-opening reactions and complete mineralization of toluene and its intermediates.

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Surface water activation plays a decisive role in  $\cdot\text{OH}$  production.<sup>26–28</sup> For unmodified bismuth-based catalysts, surface Bi atoms exhibit weak interaction with adsorbed water molecules, leading to reversible adsorption and poor activation efficiency.<sup>29–31</sup> This phenomenon, observed in BiOCl, is also relevant to  $\text{Bi}_2\text{O}_2\text{CO}_3$  due to its similar surface coordination environments. Therefore, engineering the surface structure of  $\text{Bi}_2\text{O}_2\text{CO}_3$  to strengthen water chemisorption and lower the activation barrier for water dissociation is a promising strategy to boost  $\cdot\text{OH}$  yield and improve catalytic performance. Among various approaches, metal ion doping offers a particularly versatile route to redistribute charge density and regulate the formation of localized electrons on the catalyst surface.<sup>32,33</sup> More reactive alkali metal ions are also capable of modulating the surface electronic structure and tailoring local coordination environments. Despite its potential, alkali metal ion doping remains underexplored in  $\text{Bi}_2\text{O}_2\text{CO}_3$  systems. Targeted incorporation of such ions is anticipated to enhance interfacial water activation, increase  $\cdot\text{OH}$  generation, and ultimately achieve more efficient and durable photocatalytic degradation of toluene.

In this study, we synthesized alkali metal ion-doped  $\text{Bi}_2\text{O}_2\text{CO}_3$  *via* a facile one-step hydrothermal method. The influence of doping on the surface structure, charge distribution, water adsorption, and ROS generation was systematically investigated through experimental characterization and theoretical calculations. Furthermore, we evaluated the photocatalytic performance for toluene degradation. Our findings demonstrate that alkali metal doping significantly enhances  $\cdot\text{OH}$  generation *via* interfacial water activation, thereby improving both efficiency and stability of  $\text{Bi}_2\text{O}_2\text{CO}_3$  photocatalysts in toluene photodegradation. This work provides a rational framework for surface charge engineering *via* alkali metal doping to boost photocatalytic activity and opens a new avenue for designing robust VOC treatment technologies.

## Experimental section

### Catalyst synthesis: pure $\text{Bi}_2\text{O}_2\text{CO}_3$ preparation

The pristine  $\text{Bi}_2\text{O}_2\text{CO}_3$  (BOCO) was synthesized through a precipitation method at ambient temperature. Specifically, 4 mmol  $\text{Na}_2\text{CO}_3$  was dissolved in 60 mL of deionized water to form solution A. Under continuous magnetic stirring, 2 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was gradually added to solution A, resulting in the immediate formation of a milky suspension. After 5 h of aging under continuous stirring, the precipitate was collected by centrifugation, washed sequentially with deionized water and ethanol, and then dried at 60 °C for 10 h.

### Alkali metal ion-doped $\text{Bi}_2\text{O}_2\text{CO}_3$ synthesis

$\text{Na}^+$  and  $\text{Rb}^+$ -doped samples (denoted as Na-BOCO and Rb-BOCO) were prepared *via* hydrothermal treatment. For Na-BOCO, 2 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 4 mmol  $\text{Na}_2\text{CO}_3$  were dissolved in 60 mL deionized water under 30 min stirring. The homogeneous solution was transferred to a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. The resultant

product was subjected to identical washing/drying procedures to that of BOCO. Rb-BOCO was synthesized by substituting  $\text{Na}_2\text{CO}_3$  with equimolar  $\text{Rb}_2\text{CO}_3$ , keeping other parameters constant.

### Photocatalytic toluene degradation experiments

Photocatalytic degradation of toluene was conducted in a continuous-flow reactor to evaluate the activity and stability of the synthesized photocatalysts. For each experiment, 400 mg of photocatalyst powder was uniformly dispersed on a quartz substrate and placed at the center of the reactor. The reactant gas stream was prepared by mixing toluene with dry air to obtain an initial concentration of 40 ppm, with a total flow rate maintained at 1 L  $\text{min}^{-1}$  at ambient temperature and atmospheric pressure. A 300 W UV lamp was employed as the light source to trigger the photocatalytic reaction. The outlet gas was continuously analyzed using an online toluene analyzer (DKG-42A, Duke Technology Co. Ltd, Beijing) to monitor the concentration of toluene and carbon dioxide. The toluene degradation efficiency and mineralization rate were calculated according to the concentration change of toluene and the amount of carbon dioxide generated, respectively. The reaction stability was evaluated under continuous irradiation without catalyst regeneration.

### Characterization methods

The crystalline structures of BOCO and the doped samples were characterized using X-ray diffraction (XRD). Diffraction patterns were recorded in the  $2\theta$  range of 10–80° and compared against the standard JCPDS card PDF #41-1488 to confirm the phase purity and crystal structure. X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze surface elemental composition and chemical states. High-resolution spectra were acquired for Bi 4f, C 1s, O 1s, Na 1s, and Rb 3s. The obtained binding energies were calibrated using the C 1s peak at 284.8 eV as a reference. Reactive oxygen species, specifically superoxide ( $\cdot\text{O}_2^-$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ), were detected using Electron Paramagnetic Resonance (EPR) spectroscopy with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the spin-trapping agent. Measurements were conducted under both dark and illuminated conditions.

### Theoretical calculations

Density functional theory (DFT) calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) to investigate the electronic structures of BOCO with and without alkali metal doping. Projector augmented-wave (PAW) pseudo-potentials and a kinetic energy cutoff of 400 eV were used. Structural optimizations were carried out until the residual forces on all atoms were below 0.03 eV  $\text{Å}^{-1}$ . Charge density difference and Bader charge analysis were employed to examine the local charge distribution and changes in surface electronic properties upon doping. Water adsorption energies were calculated to evaluate the interaction strength between water molecules and catalyst surfaces.



## Results and discussion

### Crystal structure and chemical composition

The phase purity and crystal structure of all synthesized samples, including BOCO, Na-BOCO, and Rb-BOCO, were evaluated by X-ray diffraction (XRD). As shown in Fig. 1a, the diffraction patterns of all samples were consistent with the standard  $\text{Bi}_2\text{O}_2\text{CO}_3$  pattern (PDF #41-1488), confirming that the crystal structure of  $\text{Bi}_2\text{O}_2\text{CO}_3$  remained intact after alkali metal ion doping. No additional peaks corresponding to sodium (Na) or rubidium (Rb) compounds were observed, indicating that the introduction of  $\text{Na}^+$  or  $\text{Rb}^+$  ions did not form separate phases. Moreover, no evident peak shifts were detected, suggesting that only a small amount of alkali metal ions was incorporated, possibly substituting partially into lattice sites without significantly altering the lattice structure of  $\text{Bi}_2\text{O}_2\text{CO}_3$ . SEM images show that all BOCO-based samples exhibit nanosheet-like morphologies, while Na-BOCO and Rb-BOCO display a slightly increased nanosheet thickness compared with BOCO (Fig. S1).

To further investigate the surface chemical composition and electronic states of the elements, X-ray photoelectron spectroscopy (XPS) was conducted. In the high-resolution Bi 4f spectrum (Fig. S2a), two well-resolved peaks are observed at binding energies of 158.8 eV (Bi 4f<sub>7/2</sub>) and 164.0 eV (Bi 4f<sub>5/2</sub>), characteristic of  $\text{Bi}^{3+}$  species within the  $[\text{Bi}_2\text{O}_2]^{2+}$  layers.<sup>34</sup> The C 1s spectrum (Fig. S2b) displays two distinct peaks centered at 284.8 eV and 288.4 eV, which can be attributed to adventitious carbon from surface contamination and carbonate groups associated with the  $\text{Bi}_2\text{O}_2\text{CO}_3$  lattice, respectively.<sup>35</sup> In the O 1s

**Table 1** Determination of the relative content of oxygen elements in the surface composition of the sample

Sample	O-H bond	C-O bond	Bi-O bond
BOCO	0.0%	60.29%	39.71%
Na-BOCO	14.05%	61.14%	24.81%
Rb-BOCO	23.11%	53.27%	23.61%

spectrum (Fig. 1d), the peaks at 529.7 eV and 530.7 eV correspond to Bi-O bonds in the  $[\text{Bi}_2\text{O}_2]^{2+}$  layers and C-O bonds in carbonate species, respectively,<sup>36</sup> reflecting the dual oxygen environment present in the crystal structure. Additionally, the Na 1s region (Fig. S3) of pristine BOCO exhibits no detectable Na signal, further corroborating the absence of alkali metal impurities and confirming that the undoped sample is of high chemical purity. To verify successful doping, the Na 1s and Rb 3s spectra were examined for Na-BOCO and Rb-BOCO, respectively. In both the doped samples, the corresponding alkali metal signals were detected (Fig. 1b and c), confirming successful incorporation of Na and Rb ions into the  $\text{Bi}_2\text{O}_2\text{CO}_3$  lattice. The binding energies of Bi 4f, O 1s, and C 1s in both Na-BOCO (Fig. S4) and Rb-BOCO (Fig. S5) remain essentially identical to those observed in pristine BOCO, suggesting that alkali metal doping does not markedly alter the chemical state of these elements. Notably, the O 1s spectra of Na-BOCO (Fig. 1e) and Rb-BOCO (Fig. 1f) showed an additional shoulder peak at  $\sim 531.7$  eV, which can be ascribed to surface hydroxyl groups.<sup>37,38</sup> This result suggests that alkali metal ion



**Fig. 1** (a) XRD pattern of the prepared sample, (b) the high-resolution XPS spectrum (Na 1s) of sample Na-BOCO, (c) the high-resolution XPS spectrum (Rb 3s) of sample Rb-BOCO, and the high-resolution XPS spectrum (O 1s) of (d) BOCO, (e) Na-BOCO, and (f) Rb-BOCO.



doping facilitates the adsorption of water molecules, promoting the formation of hydroxyl species on the catalyst surface.

Furthermore, the relative proportions of oxygen species derived from the deconvolution of the O 1s spectra are summarized in Table 1. In BOCO, hydroxyl groups were negligible, whereas the proportion of surface hydroxyl species increased to 14.05% for Na-BOCO and further to 23.11% for Rb-BOCO. This enhancement is likely due to the lower electronegativity of  $\text{Rb}^+$  compared to  $\text{Na}^+$ ,<sup>39</sup> which enables it to donate more electronic charge to neighboring atoms, thus enhancing water adsorption and hydroxylation of the surface. Such enhanced water adsorption is expected to facilitate the photogeneration of  $\cdot\text{OH}$  under light irradiation.<sup>40,41</sup>

### Electronic structure and ROS generation

To determine the preferred doping sites of alkali metal ions within the  $\text{Bi}_2\text{O}_2\text{CO}_3$  lattice, density functional theory (DFT) calculations were conducted, with Rb chosen as a representative dopant. As shown in the top and side views of the optimized structures (Fig. S6 and S7), various potential substitutional and interstitial positions were evaluated, including an Rb atom placed in the interstitial site between surface Bi atoms, substituting a surface Bi atom, and substituting a subsurface Bi atom. Following structural optimization, it was found that Rb atoms initially positioned in interstitial voids between Bi atoms are energetically unstable, tending to migrate out of the surface (Fig. S7b). This indicates that interstitial doping is thermodynamically unfavorable for stabilizing alkali metal ions within the  $\text{Bi}_2\text{O}_2\text{CO}_3$  lattice. In contrast, substitutional doping at Bi

atom sites in either the outermost surface layer or the subsurface layer leads to stable structural configurations after optimization. In these cases, the dopant Rb atoms establish well-coordinated bonding interactions with adjacent oxygen atoms, thereby retaining lattice integrity while locally altering the electronic environment (Fig. S6 and S7). The calculated energies for Rb substitution at the surface and subsurface sites are  $-1910.74$  eV and  $-1910.75$  eV, respectively, suggesting that both configurations are equally plausible. These results confirm that Rb ions are most likely incorporated *via* substitutional doping, either at or just beneath the surface layer.

To evaluate the influence of Rb doping on surface electronic properties, we analyzed the charge density difference and Bader charge distribution. For pristine BOCO, significant charge depletion is observed around Bi atoms (yellow regions in Fig. 2a), consistent with their high oxidation state. Upon Rb substitution (Fig. 2b), the extent of charge depletion at the dopant site is markedly reduced, reflecting the altered local electron distribution. This observation was further quantitatively verified through Bader charge analysis. As shown in Fig. 2a, pristine BOCO exhibits a relatively uniform surface charge distribution, with all Bi atoms donating approximately  $1.40e$  to adjacent oxygen atoms. Upon substitution of a Bi atom with Rb (Fig. 2b), the dopant atom donates only  $0.81e$ , due to the different electronic configurations of Rb and Bi. Interestingly, the adjacent Bi atoms become slightly more positively charged ( $1.45e$ ). Notably, the total charge gain by oxygen atoms remains largely unaffected (Fig. 2b), implying that the dopant primarily modulates the cationic charge environment rather



Fig. 2 The charge gains and losses of the substitutional doping sites and the nearby atoms on the surfaces of samples (a) BOCO and (b) Rb-BOCO; the adsorption energies of  $\text{H}_2\text{O}$  molecules on the surfaces of (c) BOCO and (d) Rb-BOCO.





Fig. 3 The EPR-DMPO spectra of  $\cdot\text{O}_2^-$  in samples (a) BOCO, (b) Na-BOCO, and (c) Rb-BOCO under dark conditions and light conditions; the EPR-DMPO spectra of  $\cdot\text{OH}$  in samples (d) BOCO, (e) Na-BOCO, and (f) Rb-BOCO under dark conditions and light conditions.

than altering the anionic framework. This local perturbation in surface charge distribution disrupts the uniformity of the pristine catalyst surface, introducing new chemically active sites. These localized surface heterogeneities enhance the electrostatic attraction of polar molecules such as  $\text{H}_2\text{O}$ , potentially promoting interfacial water activation and subsequent  $\cdot\text{OH}$  formation. To substantiate this hypothesis, water adsorption calculations were performed. As shown in Fig. 2c, the adsorption energy on pristine BOCO is  $-0.50$  eV, whereas on Rb-BOCO it increases substantially to  $-0.79$  eV (Fig. 2d), indicating a stronger thermodynamic driving force for water binding.<sup>42</sup> This enhancement in water adsorption capacity can be attributed to the disruption of surface charge uniformity caused by the substitutional incorporation of Rb ions, which induces asymmetric electronic distribution and facilitates interfacial water adsorption. The enhanced water adsorption on Rb-BOCO is consistent with the increase in surface hydroxyl content observed by XPS and further supports the hypothesis that alkali metal doping facilitates interfacial water activation, a prerequisite for efficient  $\cdot\text{OH}$  generation.

The generation of reactive oxygen species (ROS), particularly superoxide ( $\cdot\text{O}_2^-$ ) and hydroxyl radicals ( $\cdot\text{OH}$ ), plays a central role in determining photocatalytic degradation efficiency.<sup>22,43</sup> To evaluate the formation of these species, electron paramagnetic resonance (EPR) spectroscopy coupled with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin-trapping was performed under both dark and illuminated conditions. The radical signals were absent in the dark, indicating that no spontaneous reactive species formation occurs in the absence of light. Upon illumination, characteristic

EPR signals corresponding to  $\cdot\text{O}_2^-$  were detected in all samples (Fig. 3a and c). The signal intensity was gradually enhanced in the Na-BOCO and Rb-BOCO samples, indicating that the doping of alkali metal ions promoted the generation of  $\cdot\text{O}_2^-$ . Notably,  $\cdot\text{OH}$  was barely detectable in BOCO under irradiation (Fig. 3d). In contrast, both Na-BOCO (Fig. 3e) and Rb-BOCO (Fig. 3f) produced strong  $\cdot\text{OH}$  signals, with Rb-BOCO showing the most intense response. The substantial increase in  $\cdot\text{OH}$  production aligns closely with the XPS results showing higher surface hydroxyl group densities in Na-BOCO and Rb-BOCO, as well as with theoretical predictions of enhanced water adsorption energies upon doping. Given that adsorbed water is the primary precursor for hydroxyl radical ( $\cdot\text{OH}$ ) formation under light irradiation, these findings underscore the role of alkali metal ion doping in modulating surface reactivity through interfacial water activation, thereby accelerating  $\cdot\text{OH}$  formation. This may contribute to the superior photocatalytic performance of alkali-metal-doped  $\text{Bi}_2\text{O}_2\text{CO}_3$  in toluene degradation.

### Photocatalytic toluene degradation

To quantify the practical impact of ROS enhancement on photocatalytic performance, toluene degradation tests were conducted in a continuous-flow reactor. After the toluene-containing reaction stream reached adsorption-desorption equilibrium under dark conditions, the light source was switched on to initiate the photocatalytic process. As depicted in Fig. 4a, following 60 min of irradiation, pristine BOCO achieved a toluene degradation efficiency of only 25.3%. In contrast, Na-BOCO exhibited a substantial enhancement, attaining a degradation



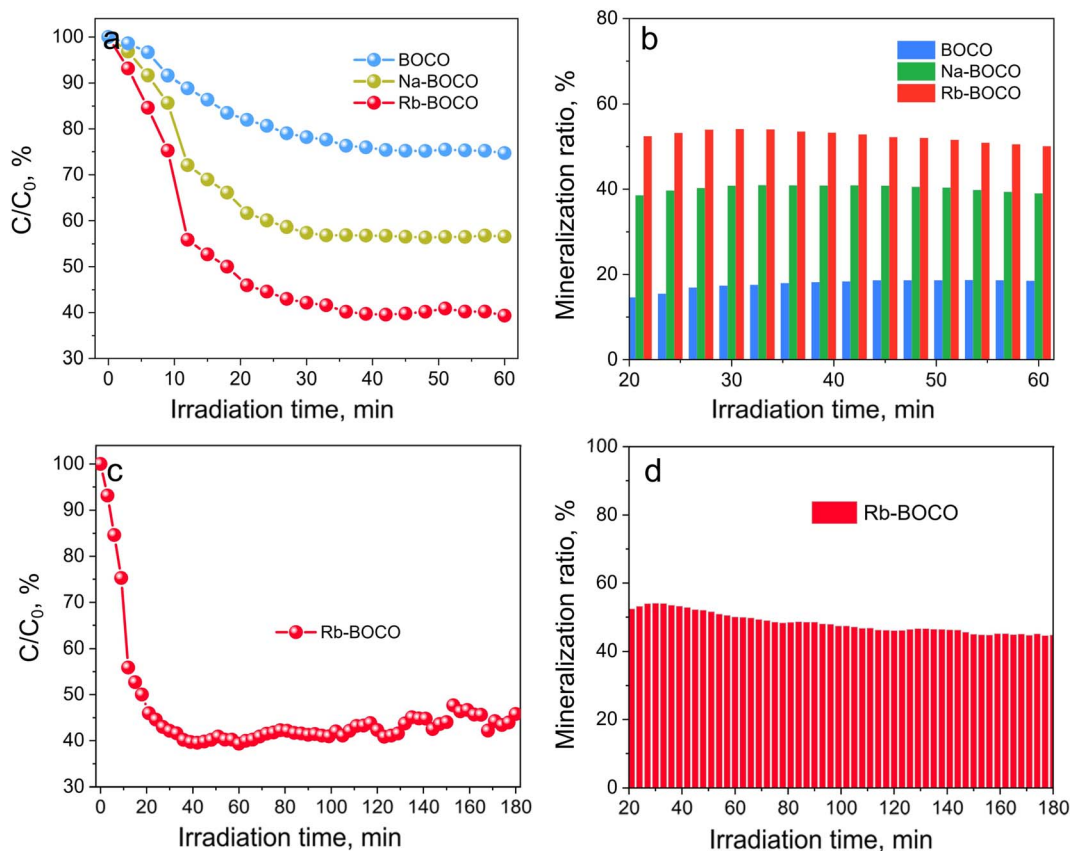


Fig. 4 (a) The efficiency of photocatalytic degradation of toluene by the prepared samples and (b) the corresponding photocatalytic toluene degradation mineralization rate; (c) the stability test of photocatalytic toluene degradation by sample Rb-BOCO and (d) the corresponding photocatalytic toluene degradation mineralization rate.

efficiency of 43.3%, corresponding to an enhancement factor of approximately 1.7 relative to BOCO. The Rb-BOCO sample demonstrated the highest activity, with a degradation efficiency of 60.7%, representing nearly a 2.4-fold improvement over the undoped catalyst. Additionally, the  $\cdot\text{OH}$  quenching experiment further confirms its dominant role in toluene degradation (Fig. S8). Upon adding *tert*-butyl alcohol, the degradation efficiency decreased drastically, indicating that  $\cdot\text{OH}$  is the primary reactive species governing the reaction. These results confirm that alkali metal ion doping substantially boosts photocatalytic activity by accelerating ROS-mediated degradation pathways. The corresponding mineralization efficiencies, evaluated *via*  $\text{CO}_2$  quantification (Fig. 4b), followed a similar trend. Notably, Rb-BOCO achieved a mineralization rate of 50.1%, indicating not only the effective removal of toluene but also its thorough conversion to benign end-products. To assess long-term stability, Rb-BOCO was subjected to continuous photocatalytic testing over 3 hours. As shown in Fig. 4c, the degradation efficiency remained stable at approximately 54.2%, and the mineralization rate also exhibited negligible decline (Fig. 4d), confirming excellent durability under dynamic reaction conditions.

To gain a deeper understanding of the photocatalytic reaction process, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is utilized to monitor the dynamic evolution process of reactant molecules on the catalyst surface

in real time. As shown in Fig. 5a and b, in the low wavenumber region ( $900\text{--}1800\text{ cm}^{-1}$ ), characteristic peaks of benzyl alcohol ( $\text{C-OH}$ ,  $926$ ,  $1051$ , and  $1161\text{ cm}^{-1}$ ), benzaldehyde ( $\text{C=O}$ ,  $1368$ ,  $1428$ ,  $1452$ , and  $1515\text{ cm}^{-1}$ ), benzene ring ( $\text{C-C}$ ,  $1645\text{ cm}^{-1}$ ), and benzoic acid ( $\text{C=O}$ ,  $1741\text{ cm}^{-1}$ ) were observed.<sup>44,45</sup> In the high wavenumber region ( $2500\text{--}4000\text{ cm}^{-1}$ ), peaks corresponding to aldehyde ( $\text{C-H}$ ,  $2598\text{ cm}^{-1}$ ), toluene methyl groups ( $\text{CH}_3$ ,  $2905$  and  $2936\text{ cm}^{-1}$ ), benzoic acid ( $\text{O-H}$ ,  $3058\text{ cm}^{-1}$ ), and the hydroxyl group of adsorbed water ( $3215\text{--}3697\text{ cm}^{-1}$ ) were detected.<sup>43</sup> These results indicate that under dark conditions, toluene undergoes partial conversion to aromatic intermediates during adsorption. Upon illumination (Fig. 5c and d), the peak intensity of toluene ( $2936\text{ cm}^{-1}$ ) decreased, while new peaks corresponding to alcohol hydroxyl groups ( $1022$ ,  $1179$ , and  $1253\text{ cm}^{-1}$ ), benzaldehyde ( $1549\text{ cm}^{-1}$ ), and benzoic acid ( $1693$ ,  $2819$ ,  $2882$ , and  $3058\text{ cm}^{-1}$ ) appeared, confirming the photocatalytic transformation of toluene into key benzene-ring-containing intermediates. Simultaneously, the peaks of benzyl alcohol ( $926$ ,  $1051$ , and  $1161\text{ cm}^{-1}$ ) and benzaldehyde ( $1368$  and  $2598\text{ cm}^{-1}$ ) were significantly depleted. Notably, the characteristic peak of the benzene ring ( $1645\text{ cm}^{-1}$ ) remained weak throughout, indicating that the intermediates were progressively degraded after radical generation.

Accordingly, such outstanding activity and stability can be attributed to the alkali-metal-ion-induced modulation of the





Fig. 5 *In situ* DRIFTS of the toluene adsorption (a and b) and degradation (c and d) process on the Rb-BOCO surface.



Fig. 6 Schematic diagram illustrating that doping with Rb ions promotes the generation of hydroxyl radicals and enhances the stability of toluene degradation.

surface electronic properties. The incorporation of Na or Rb ions enhances the adsorption and activation of interfacial water molecules, thereby facilitating the generation of hydroxyl radicals ( $\cdot\text{OH}$ ), a key oxidative species responsible for the rapid degradation of toluene and its aromatic intermediates. Overall, a comprehensive reaction mechanism is proposed and illustrated in Fig. 6. In this mechanism, alkali metal ion doping,

particularly  $\text{Rb}^+$ , modifies the local electronic environment of the BOCO surface, creating favorable sites for  $\text{H}_2\text{O}$  adsorption and activation. This process significantly enhances  $\cdot\text{OH}$  formation under light irradiation to achieve the cleavage of the aromatic ring and deep mineralization.

## Conclusion

In this study, we successfully developed alkali metal ion-doped  $\text{Bi}_2\text{O}_2\text{CO}_3$  (BOCO) photocatalysts *via* a facile hydrothermal method, with the goal of enhancing the efficiency of toluene degradation. Among the synthesized materials, Rb-doped BOCO exhibited superior photocatalytic performance and long-term stability, achieving a toluene degradation efficiency of 60.7% and a mineralization rate of 50.1% in a continuous-flow reactor. Mechanistic investigations revealed that the enhanced photocatalytic activity stems primarily from improved interfacial water activation and increased  $\cdot\text{OH}$  generation induced by alkali metal ion doping. Specifically, Rb doping significantly increased the surface hydroxyl group content, as evidenced by XPS, highlighting a stronger water adsorption capability. Theoretical simulations further demonstrated that substitutional doping at surface or subsurface Bi sites led to localized charge redistribution, breaking the uniform surface charge distribution of pristine BOCO. This perturbation enabled the formation of new active sites capable of enhancing water molecule adsorption. ROS



analysis revealed that  $\cdot\text{OH}$  radicals, critical for aromatic ring opening and complete mineralization, were significantly intensified in the doped samples, particularly Rb-BOCO. Taken together, these results provide compelling evidence that alkali metal ion doping serves as a powerful strategy to modulate the surface chemistry of BOCO photocatalysts. By enhancing interfacial water activation and radical generation, this approach enables robust photocatalytic performance for VOC removal. The mechanistic insights gained from this work offer a valuable framework for the rational design of photocatalysts with improved reactivity, stability, and environmental applicability.

## Conflicts of interest

The authors declare no competing financial interest.

## Data availability

Data available on request from the authors.

Supplementary information (SI): SEM images of the samples (Fig. S1); XPS spectrum (Bi 4f and C 1s) of BOCO (Fig. S2); XPS spectrum (Na 1s) of BOCO (Fig. S3); XPS spectrum (Bi 4f and C 1s) of Na-BOCO (Fig. S4); XPS spectrum (Bi 4f and C 1s) of Rb-BOCO (Fig. S5); top view of structure optimization (Fig. S6); side view of structure optimization (Fig. S7); quenching experiment of  $\cdot\text{OH}$  radicals (Fig. S8). See DOI: <https://doi.org/10.1039/d5va00324e>.

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