

1 **Enhancing ROS Generation and Suppressing Toxic**
2 **Intermediate Production in Photocatalytic NO Oxidation on**
3 **O/Ba Co-Functionalized Amorphous Carbon Nitride**

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1 **Abstract:** The generation of toxic intermediates during the photocatalytic reaction can
2 result in the accumulation of secondary pollutants and lead to decreased performance.
3 Here, we first designed an O/Ba co-functionalized amorphous carbon nitride (labeled
4 as O-ACN-Ba) by conducting targeted density functional theory calculations for
5 short-range and directional charge transfer in electronic transportation channels. Also,
6 the O-ACN-Ba is synthesized *via* a one-step *in situ* co-pyrolysis of urea and BaCO₃.
7 The unique electronic structure O-ACN-Ba enables highly enhanced photocatalytic
8 NO removal rate and suppresses the generation of toxic intermediate (NO₂). The O
9 and Ba are co-functionalized as a surface electronic trapping adjuster and an interlayer
10 electronic trapping mediator to induce the convergence and localization of
11 intralayer-delocalized electrons. Such internal electronic structure can facilitate the
12 adsorption and activation of NO and O₂, elongate the lifetime of photogenerated
13 carriers, and expedite the spatial charge separation to boost significantly the
14 generation of reactive oxygen species, thus suppressing toxic NO₂ generation. In
15 addition, the photocatalytic NO conversion pathway on O-ACN-Ba is characterized,
16 and an important reaction intermediate—nitrosyl species Ba-NO^{δ(+)} is discovered and
17 found to promote the selective conversion of NO to final products (nitrites or nitrates).
18 This work proposes a novel strategy to advance the application of photocatalytic
19 technology for efficient and safe air purification.
20 **Keywords:** carbon nitride; O/Ba co-functionalization; ROS; photocatalytic NO
21 oxidation; toxic intermediate.

1. Introduction

Environmental pollution and energy shortage have become global concerns that need to be solved by advances in cutting-edge science and technology [1-4]. Various renewable and sustainable technologies have been developed to address these challenges to date [5-7]. Among them, semiconductor-based photocatalysis has gained interdisciplinary attention as a result of its great potential to harness solar energy for degradation of typical pollutants [8-11].

Recently, some advances in photocatalytic air purification have garnered significant interest [12-15]. Nevertheless, most of the reported works have focused on the development of modification strategies to optimize photocatalytic performance, and the conversion pathway of photocatalytic pollutant oxidation as a key issue has not been clearly revealed [16]. Most importantly, the generation of possible toxic intermediates during photocatalytic reaction processes is typically neglected, despite the fact that it could result in the accumulation of secondary pollutants and decrease the photocatalytic performance. For instance, increased production of toxic intermediate NO_2 would probably result in its release to air during photocatalytic NO removal process. In order to promote the application of photocatalytic technology in NO purification without increasing secondary pollution, the generation of NO_2 must therefore be suppressed [17]. Thus, it is necessary to explore photocatalysts with favorable electronic structures that would enhance photocatalytic efficiency and inhibit the generation of toxic intermediates simultaneously.

Generally, a semiconductor-based photocatalysis reaction involves three steps: (1) the illumination over photocatalyst to induce the formation of electrons/holes pairs; (2) the migration and transformation of photogenerated carriers to generate the reactive oxygen species (ROS); (3) the initiation of photocatalytic redox reaction by the ROS [18-22]. As a consequence, a comprehensive atomic-level design is required to realize synergistic effects in

1 terms of visible-light utilization, charge carrier separation, and oxidation ability
2 of radicals, with the aim to attain optimized photocatalytic efficiency and
3 complete pollutant mineralization [23].

4 Graphitic carbon nitride (labelled as CN), a metal-free layered conjugated
5 semiconductor, has been extensively applied in the area of environmental
6 remediation and solar energy conversion owing to its facile synthesis, appealing
7 electronic structure, high physicochemical stability, and “earth-abundant”
8 nature [24-27]. As a result of the polymeric character of CN, its electronic
9 structure can be easily tailored by means of surface engineering at the
10 atomic-level in order to enhance its photocatalytic performance [28-30]. In
11 particular, CN is limited by the intrinsic graphitic sp^2 -hybridized array of
12 tri-s-triazine repeating units and the inert stack of layers, which enable
13 delocalized photogenerated electrons to transfer in planes randomly, leading
14 thus to a high charge-recombination rate [31-33]. Therefore, the internal
15 electronic structure of CN can be rationally designed and tailored to promote
16 the redistribution and delocalization of electrons, to achieve elongated lifetime
17 of photogenerated carriers and expedited spatial charge separation, and thus to
18 accelerate generation of abundant ROS that are capable of participating in
19 photocatalysis [34-37]. The construction of local electronic trapping/converging
20 districts and intercalating interlayer electronic mediators simultaneously is a
21 novel strategy that could allow the random migration of electrons in planes and
22 weak Coulomb interactions between layers to be modulated, realizing thus
23 efficient charge separation and localization of electrons to optimize
24 photocatalytic efficiency.

25 Here, by conducting targeted density functional theory (DFT) calculations,
26 we first propose a conceptual design for the internal electronic structure of CN.
27 Local electronic trapping segments (labeled as ETS) and surface electronic
28 trapping adjusters (labeled as ETA) are introduced into CN to induce the
29 convergence and localization of delocalized intralayer electrons.
30 Simultaneously, interlayer electronic trapping mediators (labeled as ETM) are

intercalated to bridge adjacent CN layers in order to direct the transfer of photogenerated electron. Exploiting the synergistic contributions of ETS, ETA, and ETM, an O/Ba co-functionalized amorphous carbon nitride (labeled as O-ACN-Ba) with oriented electron transportation channels is designed for the first time, resulting in an exceptionally high charge-separation rate and thus enhanced ROS generation for the photocatalytic oxidation of NO into nitrites or nitrates. Subsequently, the crafted O-ACN-Ba is synthesized *via* a facile one-step *in situ* co-pyrolysis of urea and BaCO₃. The experimental and theoretical methods are highly combined to demonstrate the successful fabrication of O-ACN-Ba, elucidate the photocatalytic NO conversion pathway, and illustrate the promotion mechanisms in terms of enhanced photoelectric properties and photocatalytic efficiency. The designed photocatalyst possesses a perfect inner electronic structure that not only facilitates the adsorption and activation of gas molecules to participate in photocatalytic NO oxidation but also expedites the spatial charge separation to optimize photocatalytic efficiency through the boosted generation of ROS. The present work represents a novel strategy for simultaneously enhanced photocatalytic efficiency and inhibited generation of toxic intermediates, and provides a new method for advancing the development of photocatalytic technology for efficient and safe air purification.

2. Experimental

2.1 DFT calculations

All spin-polarized DFT-D2 calculations were performed with the “Vienna ab initio simulation package” (VASP 5.4), utilizing a generalized gradient correlation functional [38, 39]. A plane-wave basis set with a cut-off energy at 450 eV within the framework of the projector-augmented wave method was used [40, 41]. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a $3 \times 3 \times 1$ K points. All atoms were converged to 0.01 eV/Å. The *ab initio* molecular dynamics (AIMD) calculations were carried out

to verify the CO_3^{2-} dissociation process at 823 K using *Born-Oppenheimer* approximation [42, 43]. A $2 \times 2 \times 3$ supercell of bulk CN that includes 168 atoms was first relaxed, and subsequently Ba and CO_3^{2-} were introduced into the interlayer and intralayer, respectively (Fig. S1a and S1b).

The formation energy (E_f) is defined as:

$$E_f = E_{\text{modified CN}} - (E_{\text{pure CN}} + E_{\text{species}}) \quad (1)$$

where E_{species} refers to the total energy of BaCO_3 species, which is calculated from its unit cell.

The adsorption energy (E_{ads}) is defined as:

$$E_{\text{ads}} = E_{\text{tot}} - (E_{\text{CN}} + E_{\text{mol}}) \quad (2)$$

where E_{tot} , E_{CN} , and E_{mol} represent the total energy of the adsorption complex, the pure CN, and the isolated molecule, respectively.

2.2 Sample preparation

The O-ACN-Ba-X samples were synthesized *via* co-pyrolysis of urea and BaCO_3 . At first, 10 g of urea and a known amount of BaCO_3 (0.015, 0.030, 0.060, and 0.100 g) were added to an alumina crucible (50 mL) with 20 mL distilled water. The obtained solution was dried in oven at 60°C to furnish the solid precursors. The solid precursors were placed in a semi-closed alumina crucible with a cover and calcined at 550°C for 2 h at a heating rate of 15°C/min in static air. After the thermal treatment, the obtained samples with different weight ratios of urea and BaCO_3 were collected and labeled as O-ACN-Ba-X (where X represents the amount of BaCO_3). For comparison, an *ex situ* mechanical mixture of CN and BaCO_3 was prepared and named as CN-Ba. Detailed information on characterization of the catalysts is available in Supplementary Material.

2.3 *In situ* DRIFTS investigation

In situ DRIFTS measurements were conducted using a TENSOR II FT-IR spectrometer (Bruker) equipped with an *in situ* diffuse-reflectance cell (Harrick) and a high-temperature reaction chamber (HVC), as shown in Scheme S1. Detailed descriptions of the *in situ* DRIFTS apparatus are available in the Supplementary Material.

Before measurements, the as-prepared samples were placed in a vacuum tube and pretreated 1h at 300°C. The background spectra are recorded before injecting NO into the reaction chamber. And the NO absorption bands appear once NO comes in contact with the photocatalyst at 25°C under dark conditions. Once the adsorption equilibrium is achieved, a visible-light source is applied to initiate the photocatalytic reaction. And the “baseline” spectra are the same as that of “the curve of adsorption equilibrium” in NO adsorption process. As for the temporal evolution of normalized absorbance about adsorbed species on photocatalysts surface, the integration of characteristic absorption bands of adsorbed species leads to follow their individual evolutions as a function of time. For all species, the normalized absorbance is calculated by considering their individual maximum absorbance as 1.

2.4 Visible-light photocatalytic NO removal

The photocatalytic activity was investigated by examining the removal ratio of NO at ppb levels (500 ppb) in a continuous-flow reactor (rectangular reactor, 30 cm × 15 cm × 10 cm). The concentration of NO was continuously detected by a NO_x analyzer (Thermo Environmental Instruments Inc., model 42c-TL), which can monitor the concentration of NO, NO₂, and NO_x (NO_x represents NO + NO₂). The as-prepared sample (0.20 g) of the catalyst was dispersed and coated onto two glass dishes (12.0 cm in diameter) for photocatalytic activity tests. A 150-W commercial tungsten halogen lamp (average light intensity = 0.16 W/cm²) was placed vertically outside and above the reactor. The lamp was turned on when the adsorption–desorption equilibrium was achieved. The removal ratio (η) of NO was calculated as $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet steam and the feeding stream, respectively.

3. Results and discussion

3.1 Electronic structure and microstructure

The O/Ba co-functionalized amorphous carbon nitride is composed of three

parts, namely ETS, ETA, and ETM, which function differently. Local electronic trapping/converging districts (including ETS and ETA) can be formed by the destruction of periodic arrangement of melon strands and surface O-adsorption, which facilitate the convergence and localization of intralayer-delocalized photogenerated electrons. Simultaneously, interlayer electronic delivery channels are constructed *via* intercalation of the Ba-mediator (ETM), realizing thus spatial charge separation. Detailed atomic-level O-ACN-Ba structure is simulated using DFT calculations and is illustrated in Fig. 1.

During the thermal polymerization process, CO_3^{2-} from BaCO_3 tends to attack the intralayer hydrogen bonds in CN and destroy the periodic arrangement of intralayer melon strands (hydrogen bonds) for constructing ETS. The process of hydrogen bond fracture can be simulated by CO_3^{2-} adsorption on CN. The exothermic nature of this process (-2.979 eV) indicates that the hydrogen bonds are broken easily by the introduction of CO_3^{2-} , which contributes to the formation of amorphous carbon nitride consisting of basic ETS units. The formation of ETS shortens the effective transmission distance required for carriers to arrive at the active site (i.e., fracture point of hydrogen bonds). In other words, the long-range charge transfer in CN can be transformed to short-range charge transfer in the ETS units, reducing thus the possibility of recombination during the carrier-transfer process.

Simultaneously, CO_3^{2-} as the donor of surface O species on ETS can result in the formation of ETA, inducing thus the convergence and localization of local intralayer electrons that transfer randomly. To test this reasoning, the dissociation process was simulated at atomic level by time evolution in 2 ps at 823 K in the course of *in situ* pyrolysis *via* ab initio molecular dynamics (AIMD) calculations. As shown in Fig. 1b, the C–O bond lengths of CO_3^{2-} fluctuate around 2.65 Å from the start point (<0.03 ps), and significant bond breakage of C–O is observed rapidly at <0.4 ps. After that, a dangling CO_2 molecule shifts randomly at the boundary of crystal lattice and the left O atom is gradually bonded with the C atom to form surface O species, generating the

1 basic ETA unit. In addition, the local charge distributions in the surface layer
2 are visualized by the calculation of Bader effective charge (Fig. 1c) [44]. The
3 introduction of O species gives rise to electron depletion of the adjacent C and
4 N atoms and guides these electrons to the O atom. This behavior stems from the
5 differences in electronegativity among the elements C, N, and O. According to
6 the results of the DFT calculations, the CO_3^{2-} from BaCO_3 plays a crucial role
7 not only in attacking the intralayer hydrogen bonds but also in acting as the
8 source of surface O species, resulting therefore in the effective separation of
9 local electrons and holes.

10 Differences in charge density distribution can illustrate the gain or loss of
11 electrons, and in this work these differences were used to demonstrate the
12 subtle role of Ba mediator (ETM) species sandwiched between adjacent layers.
13 As shown in Fig. 1d, the intercalation of Ba mediator bridges the contiguous
14 layers and builds an interlayer electron-delivery channel to realize interlayer
15 charge transfer and spatial charge separation. Using targeted theoretical
16 calculations, we designed the electronic structure of O-ACN-Ba to exploit the
17 synergistic contribution of ETS, ETA, and ETM units. We envisaged that the
18 designed O-ACN-Ba with localized electrons and directed charge transfer could
19 realize the elongated lifetime of photogenerated carriers and expedited spatial charge
20 separation. Subsequently, there are abundant electrons which activate the gas
21 molecules on photocatalysts and thus dramatically facilitate the conversion of
22 pollutants and the production of reactive species, enhancing the overall
23 efficiency of photocatalytic NO removal.

24 **Fig. 1.**

25 Inspired by the theoretical design, a series of samples with O-ACN-Ba
26 structure have been synthesized with different weight ratios of BaCO_3 to urea.
27 The prepared samples are labeled as O-ACN-Ba-X (where X represents the
28 content of BaCO_3). XRD analysis of CN and O-ACN-Ba-X samples (Fig. 2a)
29 reveals two characteristic diffraction peaks of CN (13.1° and 27.2°), which
30 arise respectively from the in-plane structural repeating motifs of the aromatic

1 systems and the interlayer reflection of a graphite-like structure [27, 45], and
2 indicate that the graphitic-like layered structures are maintained after
3 modification. However, two diffraction peaks characteristic of CN decreased
4 significantly following the introduction of BaCO₃ to form nearly amorphous
5 carbon nitride. These results suggest that the in-plane periodicity of the
6 aromatic systems is destroyed and, correspondingly, the periodic stacking of the
7 layers is disturbed. Subsequently, the shift of the characteristic diffraction peak
8 of CN originating from the intercalation of Ba mediator between adjacent layers
9 of CN is difficult to be observed because of the amorphous property of CN. As
10 illustrated in Fig. 1a, CO₃²⁻ arising from BaCO₃ can attack the intralayer
11 hydrogen bonds through synergic interactions between CN and BaCO₃ to form
12 amorphous carbon nitride, resulting thus in the fabrication of ETS.

13 The FT-IR spectra (Fig. 2b) were measured to further verify the basic
14 substructure units of the CN polymers (heptazine heterocyclic ring units, C₆N₇).
15 As shown in Fig. 2b, the strong adsorption bands corresponding to the
16 stretching vibration mode of the C₆N₇ units are observed in the spectrum of
17 each prepared O-ACN-Ba-X sample in the 1700–1200 and 810 cm⁻¹ range [46,
18 47], indicating thus that the O-ACN-Ba-X samples retained the basic CN
19 atomic structure. Meanwhile, the decreased absorption band (at 3500–3100
20 cm⁻¹ and 890 cm⁻¹) assigned to the N–H components stemming from
21 uncondensed amino groups are reflected, indicating the breakage of hydrogen
22 bonds [48]. In addition, the FT-IR spectra revealed the appearance of a new
23 absorption band at 2166 cm⁻¹, which can be associated with the stretching
24 vibration of N=C=N (according to the Sadtler handbook of infrared spectra).
25 These observations further demonstrate that the introduction of BaCO₃ during
26 the urea polymerization process destroys the periodic arrangement of interlayer
27 melon strands (hydrogen bonds), while simultaneously maintaining the basic
28 atomic structure of CN (C₆N₇ units) to afford unique amorphous arrangements
29 of short-range order and long-range disorder. Therefore, through a combination
30 of theoretical and experimental analysis, we can confirm that the CO₃²⁻ plays a

1 vital role in the formation of ETS for facilitating the separation of carriers and
2 exposing new active sites.

3 The chemical composition and valence states of the elements were examined
4 using XPS analysis. As shown in Fig. S2a, the N1s spectra can be deconvoluted into
5 three peaks at 398.9 eV, 400.1 eV and 401.4 eV, corresponding to the sp^2 -bonded N
6 involved in the triazine rings (C–N=C), the tertiary nitrogen N–(C)₃ groups, and the
7 amino functions (C–N–H), respectively. Besides, the corresponding binding energies
8 of C1s at 284.8 and 288.2 eV can be ascribed to the sp^2 C–C bonds and sp^2 -bonded
9 carbon in the N-containing aromatic rings (N–C=N), respectively (Fig. S2b). The
10 C–N=C, N–(C)₃, and N–C=N groups make up the basic substructure units (heptazine
11 heterocyclic ring, C₆N₇) of CN polymers. Apparently, the concentration of O
12 increased significantly from 1.22% in CN to 3.31% in O-ACN-Ba-030 (Fig. 2c).
13 When compared to pure CN, the O 1s spectrum of O-ACN-Ba-030 could be
14 deconvoluted into two peaks at 532.9 eV and 530.8 eV, which are ascribed to
15 surface adsorbed water and adsorbed O species, respectively [49, 50]. In
16 addition, Ba is detected in the high-resolution XPS spectrum (Ba 3d) of
17 O-ACN-Ba-030 (Fig. 2d) and the atomic ratio of barium to nitrogen (Ba : N)
18 for O-ACN-Ba-030 is 2.1% (Table S1), which is indicative of Ba-doping in CN.
19 Based on the results of experimental and theoretical analyses, the desired
20 O-ACN-Ba structure containing ETS, ETA, and ETM can be readily fabricated
21 using a facile co-pyrolysis method to facilitate the adsorption and activation of
22 gas molecules participating in photocatalytic NO oxidation and expediting the
23 spatial charge separation for optimized photocatalytic efficiency.

24 The morphologies and microstructures of CN and O-ACN-Ba-030 were
25 examined by TEM and SEM (Fig. 2e-h). The analysis showed that the silk-like
26 nanosheets typical of CN are well preserved after the introduction of BaCO₃. In
27 addition, the EDX elemental mapping of O-ACN-Ba-030 (Fig. S3) suggests that the
28 C, N, Ba, and O elements are distributed uniformly. Also, the increased concentration
29 of Ba can be observed in EDX elemental mapping along with the introduction of the
30 increased amount of BaCO₃. The N₂ adsorption-desorption isotherms (Fig. S4) of

CN and O-ACN-Ba-X samples displayed type IV and H3 hysteresis loops, which indicates that the introduction of BaCO₃ did not influence the pore structure of CN. All relevant parameters such as specific surface area (S_{BET}) and pore volume are listed in Table S1 for all samples. Although the specific surface area of O-ACN-Ba-X decreased following the O/Ba co-functionalization, this change had no negative effect on the photocatalytic activity of the material, as will be discussed later.

Fig. 2.

3.2 Photocatalytic mechanism and inhibition of toxic intermediates

Owing to the delicate design of the inner electronic structure, adsorption and activation of pollutants or toxic intermediates on O-ACN-Ba-based photocatalysts are expected to be elaborated. The *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to dynamically monitor the intermediates and products on the photocatalyst surface in time sequence during NO adsorption and photocatalytic NO oxidation processes.

During the NO adsorption process (the full range of *in situ* DRIFTS spectra are shown in Fig. S5a and S5b), absorption bands characteristic for NO appeared once NO was introduced onto the photocatalysts at 25 °C in dark conditions. This dark reaction arises from the reactive pyridine N atoms, which preferably donate its lone-pair electrons to O₂ molecules, producing active O-containing species as oxidants [51, 52]. Compared to the pristine CN, a clear new band at 2129 cm⁻¹ associated with nitrosyl species (Ba-NO^{δ(+)}) over O-ACN-Ba-030 was observed in Fig. 3a, and the generation of Ba-NO^{δ(+)} was significantly boosted as suggested by the evolution of the normalized absorbance of species (Fig. 3c) [53, 54]. Compared to other nitrogen-containing species, the adsorbed Ba-NO^{δ(+)}, as the main adsorption intermediate, would be preferentially oxidized to nitro compounds by ROS during the photocatalytic NO oxidation process [54, 55]. Consequently, the enhanced accumulation of Ba-NO^{δ(+)} on O-ACN-Ba could minimize the possibility of toxic intermediate (NO₂) generation in the photocatalytic oxidation process. Simultaneously, the

IR adsorption bands associated with NO_2 were observed and increased in intensity in a pattern similar to that observed for the evolution of $\text{Ba-NO}^{\delta(+)}$. Thus, the constructed O-ACN-Ba structure can facilitate the adsorption and activation of NO, giving rise to enhanced photocatalytic NO oxidation performance.

Subsequently, we recorded the time-dependent IR spectra of CN and O-ACN-Ba-030 under visible-light irradiation in time sequence once the adsorption equilibrium achieved (the full range of *in situ* DRIFTS spectra is shown in Fig. S5c and S5d). As shown in Fig. 3d, higher quantity of final products (NO_3^-) was generated on O-ACN-Ba than on pristine CN. Most importantly, comparing the normalized absorbance of NO_2 evolution (Fig. 3c, 3f), the quantity generated of NO_2 for O-ACN-Ba-030 sample was much higher than for pure CN during the NO adsorption process. However, the accumulated NO_2 was consumed noticeably during the course of the photocatalytic NO oxidation reaction, indicating that the adsorbed NO_2 can be transformed into nitrites or nitrates more effectively than that in CN. Therefore, the unique electronic structure of O-ACN-Ba can dramatically promote the adsorption and activation of pollutants, inhibit the accumulation of harmful intermediates, and enhance the photocatalytic NO removal efficiency.

The full range of *in situ* DRIFTS spectra and the corresponding discussion on the conversion pathways underlying the photocatalytic NO oxidation over CN and O-ACN-Ba-030 are provided in the Supplementary Material.

Fig. 3.

3.3 ROS generation and photocatalytic NO purification

To better understand the mechanism of NO adsorption on O-ACN-Ba, the NO activation was probed using DFT calculations. As shown in Fig. 4a, more marked electron depletion was observed for NO on the O-ACN-Ba structure than on CN, indicating that the NO adsorption on O-ACN-Ba is facilitated *via* donation of electrons to electron-deficient areas in O-ACN-Ba. This process, in turn, leads to an increase in adsorption energy (from -0.165 eV for pristine CN

1 structure to -0.719 eV for modified O-ACN-Ba structure). This outcome is also
2 consistent with the observation of $\text{Ba-NO}^{\delta(+)}$ on O-ACN-Ba (Fig. 3a). Therefore,
3 the present results indicate that the fabrication of O-ACN-Ba promotes the
4 adsorption and activation of NO and subsequently furthers photocatalytic
5 oxidation and conversion efficiency to suppress the production of the toxic
6 intermediate NO_2 , as evidenced by the *in situ* DRIFTS spectroscopy.

7 The photocatalytic NO oxidation is highly dependent on the ROS
8 (superoxide radicals $\bullet\text{O}_2^-$ and hydroxyl radicals $\bullet\text{OH}$), and thus the production
9 of $\bullet\text{O}_2^-$ was simulated using DFT by calculating the O_2 adsorption. In
10 comparison with the bare CN (Fig. 4b), the O–O bond lengths in O-ACN-Ba
11 are noticeably increased, resulting in weakened O–O Coulombic interactions.
12 The adsorption energy of the O-ACN-Ba is increased significantly *via* more
13 intense charge transfer between the O_2 and the O-ACN-Ba surface.
14 Correspondingly, the O_2 molecules adsorbed on O-ACN-Ba are activated more
15 easily and tend to receive more electrons for the production of $\bullet\text{O}_2^-$ radicals to
16 participate in the photocatalytic redox reaction—contributing to enhanced
17 photocatalytic efficiency.

18 The enhanced generation of active radicals on O-ACN-Ba was also
19 confirmed using the DMPO spin-trapping ESR experimental method. As
20 expected, much stronger DMPO- $\bullet\text{O}_2^-$ signals were detected for O-ACN-Ba-030
21 than for pure CN (Fig. 4c). The increase in the signals associated with $\bullet\text{O}_2^-$
22 radicals is linked directly to the improved adsorption and activation of O_2
23 molecules and expedited spatial charge separation, which enables O_2 molecules
24 to be activated more easily for the generation of $\bullet\text{O}_2^-$. In addition, increased
25 signals characteristic for DMPO- $\bullet\text{OH}$ was also observed (Fig. 4d). The
26 formation of $\bullet\text{OH}$ can be traced back to the reduction of $\bullet\text{O}_2^-$ in the sequence of
27 $\bullet\text{O}_2^- \rightarrow \text{H}_2\text{O}_2 \rightarrow \bullet\text{OH}$, which demonstrates that the electron excitation and
28 charge transportation on O-ACN-Ba-030 are effectively promoted.

29 The photocatalytic performance of the prepared samples towards NO
30 removal was evaluated under visible-light irradiation ($\lambda \geq 420$ nm). As shown

1 in Fig. 4e, the O-ACN-Ba-030 sample exhibits a noticeably higher NO removal
2 ratio than the pristine CN as a result of suppressed NO₂ production. The
3 maximum NO removal ratio was observed after *ca.* 5 min. The visible-light
4 irradiation could not cause the reduction of NO in the condition with no photocatalyst
5 (Fig. S6). All O-ACN-Ba-X samples exhibited superior activity when compared
6 to the pristine CN (Fig. 4e), which indicates that the photocatalytic efficiency of
7 CN within the O-ACN-Ba structure is significantly enhanced. Also, to further
8 demonstrate the interaction between CN and BaCO₃ during co-pyrolysis, the
9 mechanically mixed CN-Ba sample is also tested, and a slight decrease of
10 photocatalytic activity is observed. Thus, a facile co-pyrolysis method has been
11 developed to prepare highly efficient CN within the O-ACN-Ba structure and the
12 optimized preparation conditions are confirmed. As demonstrated by the combined
13 experimental and theoretical approach, the designed O-ACN-Ba structure can
14 boost the adsorption and activation of gas molecules (NO and O₂) participating
15 in photocatalytic NO oxidation, and also expedite the spatial charge separation
16 and thus promote the generation of ROS to optimize the photocatalytic
17 efficiency. Overall, the results demonstrate that inhibited generation of toxic
18 intermediate and accelerated transformation of NO have been realized, and then
19 facilitate optimized photocatalytic oxidation, which is in accordance with the
20 analysis of *in situ* DRIFTS.

21 **Fig. 4.**

22 **3.4 Charge separation and transfer**

23 The enhanced generation of ROS can increase the photocatalytic efficiency,
24 mostly as a result of the enhanced adsorption and activation of gas molecules
25 and efficient charge separation rate. Therefore, further experiments were carried
26 out to probe the charge separation and charge transfer processes. Based on the
27 quenching of PL peaks observed for O-ACN-Ba-030 sample (Fig. 5a) and the
28 prolonged radiative lifetime of O-ACN-Ba-030 (Fig. 5b)—which increased
29 from 2.64 ns (pristine CN) to 2.97 ns—it is apparent that the unique O-ACN-Ba
30 structure can accelerate the separation of photogenerated charge carriers.

1 Simultaneously, the stronger EPR signal intensity observed for O-ACN-Ba-030
2 reflects increased electron mobility and charge transportation (Fig. 5c).

3 In the next step, we investigated further electron transfer direction and
4 pathway using DFT calculations. Fig. 5d reveals the energy barriers associated
5 with transfer electrons between neighboring layers. The DFT calculations
6 showed that the electrostatic potential of the second layer (L2) increased
7 significantly after the introduction of O/Ba, which suggests that the barrier for
8 electron transfer from L2 to L3 decreased. In addition, the electrostatic potential
9 associated with L1 in O-ACN-Ba increased in comparison to that of pristine
10 CN, which guarantees the vertical migration of electrons in the direction
11 $L1 \rightarrow L2 \rightarrow L3$ in a one-way transmission manner, and promotes thus electron
12 transfer with low recombination rate. As a consequence, the samples with
13 O-ACN-Ba structure could extend the delocalized π bonds to deviate from the
14 planes (i.e., the X and Y directions parallel to CN planes) and induce electron
15 transfer toward the Z direction (i.e., the direction perpendicular to CN planes),
16 thus accelerating the adsorption and activation of gas molecules and boosting
17 the separation of charge carriers. In order to illustrate the gain or loss of
18 electrons between the adjacent layers, we examined the differences in charge
19 distribution of pure CN and O-ACN-Ba (Fig. 5e). The unique O-ACN-Ba
20 structure allows redistribution of inner charge *via* the synergistic effects of ETS,
21 ETA, and ETM. Specifically, intralayer-delocalized photogenerated electrons
22 are converged and localized *via* the formation of ETS and introduction of ETA.
23 Oriented interlayer-electron delivery channels are constructed by the
24 introduction of ETM to further expedite the spatial charge separation. Therefore,
25 the O-ACN-Ba structure permits increased electron localization and
26 unprecedentedly high charge separation rate to be achieved to optimize the
27 photocatalytic NO removal efficiency and suppress the production of toxic
28 intermediate.

29 **3.5 Optical properties and band structures**

The light absorption properties of the prepared samples were investigated using a combined experimental and theoretical approach. As evidenced by UV-Vis DRS spectroscopy, a red-shift in the optical absorption band edge was observed for the O-ACN-Ba-030 sample (Fig. S8a, Experiment). In addition, the promoted light harvest was certified using the calculated absorption spectra (Fig. S8a, Calculation). Overall, the results suggested that the O/Ba co-functionalized amorphous carbon nitride could increase the density and distribution of localized states, broaden the absorption range in visible-light region, and narrow the band gap of CN for enhanced photocatalysis.

Finally, we calculated the total density of states (TDOS), and the results are shown in Fig. S8b. The band energy of pure CN was calculated to be 2.44 eV. As a result of the known limitations of plain DFT method, there is a tolerable error in the calculated value in comparison with the experimental one. The narrowing of the band gap of O/Ba co-functionalized amorphous carbon nitride indicates that it possesses enhanced visible-light absorption ability in comparison with pristine CN, and this outcome is consistent with the observations shown in Fig. S7a. Additionally, the valence band (VB) and conduction band (CB) edges of O-ACN-Ba were downshifted when compared to those of bare CN. Thus, it is apparent that the band structure of CN can be successfully tailored by co-functionalization with O and Ba. Specifically, within the O-ACN-Ba structure, the extra lone-pair electrons of the two-coordinated N atoms in CN are significantly localized by the introduction of local electronic trapping/converging districts and intralayer electronic mediators (ETS, ETA, and ETM), thus facilitating electron hopping from a higher energy level to a lower one. As a consequence, dramatically enhanced electron mobility, significantly increased light absorption ability, and effectively promoted oxidization ability of VB holes can be realized under visible-light illumination, affording a material with highly enhanced photocatalytic activity for NO removal.

4. Conclusions

The present work designs and develops an O/Ba co-functionalized amorphous carbon nitride (labeled as O-ACN-Ba) for the simultaneous optimization of photocatalytic NO removal efficiency and suppression of toxic intermediate generation. Also, the successful fabrication of O-ACN-Ba, the photocatalytic NO conversion pathway underlying the reaction, and the promotion mechanisms in terms of enhanced photoelectric properties and photocatalytic efficiency are demonstrated by the highly combined experimental and theoretical methods. This research realizes the optimization photocatalytic NO removal, and provides a new method to advance the development of photocatalytic technology for efficient and safe air purification.

Supporting Information

Characterization of photocatalysts; detailed descriptions of the *in situ* DRIFTS apparatus and the specific test method; the designed reaction system for the *in situ* DRIFTS signal recording; Optimized local structures of BaCO₃ (a, b) modified CN at intercalated and in-plane sites, correspondingly; the high-resolution C 1s (a) and N 1s (b) XPS spectra of CN and O-ACN-Ba-030; N₂ adsorption-desorption isotherms curves (a) and pore-size distribution (b) of as-prepared samples; *In situ* FTIR spectra of NO adsorption (a, b) and visible-light reaction processes (c, d) on the CN and O-ACN-Ba-030 surface; photocatalytic activity comparison of CN and O-ACN-Ba-X samples toward NO removal; photoluminescence spectra of the as-obtained samples; light absorption and band structure property of the as-prepared catalysts; the information about S_{BET}, pore volume and NO removal ratio of samples; assignments of the IR bands observed during NO adsorption over photocatalyst; assignments of the IR bands observed during NO oxidation over photocatalyst under visible-light irradiation.

Acknowledgements

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Enhancing ROS Generation and Suppressing Toxic Intermediate Production in Photocatalytic NO Oxidation on O/Ba Co-Functionalized Amorphous Carbon Nitride

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Figure captions

Fig. 1. The design of the O-ACN-Ba electronic structure. Top view of the atomic structure of layered carbon nitride and amorphous carbon nitride (a); time evolution in 2 ps for CO_3^{2-} dissociation at a temperature of 823 K in the course of *in situ* pyrolysis (b); Bader effective charge of CN and O-ACN-Ba (c); charge difference distribution of O-ACN-Ba (d): charge accumulation is shown in blue and depletion in yellow; isosurfaces are set to $0.005 \text{ eV } \text{\AA}^{-3}$. All lengths are given in \AA .

Fig. 2. Chemical composition and phase structure of the as-prepared samples. XRD patterns (a) and FT-IR spectra (b) of CN and O-ACN-Ba-X; XPS spectra (O *1s*) of CN and O-ACN-Ba-030 (c); high-resolution XPS spectra (Ba *3d*) of O-ACN-Ba-030 (d); TEM images of CN (e) and O-ACN-Ba-030 (f); SEM images of CN (g) and O-ACN-Ba-030 (h).

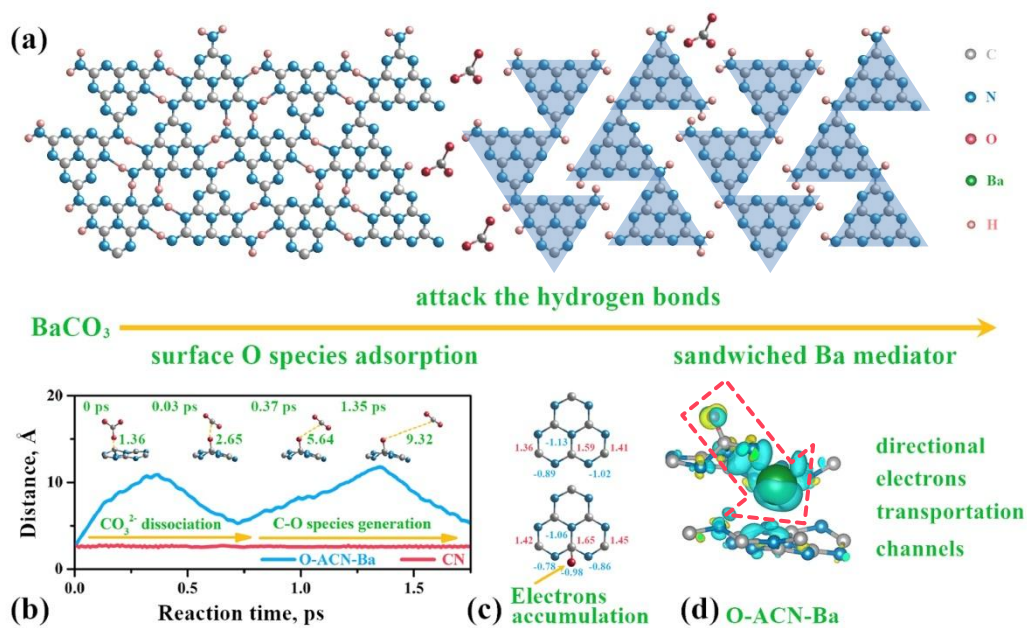
Fig. 3. *In situ* DRIFTS spectra of NO adsorption and reaction: local *in situ* DRIFTS spectra (a, b) and changes in normalized absorbance of species (c) on CN and O-ACN-Ba-030 surface during NO adsorption process ($\text{Ba-NO}^{\delta(+)}$ and NO_2); local *in situ* DRIFTS spectra (d, e) and changes in normalized absorbance of species (f) on CN and O-ACN-Ba-030 surface during visible-light photocatalytic reaction process (NO_3^- and NO_2).

Fig. 4. Adsorption and activation of gas molecules and photocatalytic activity. Calculated differences in charge density distributions for NO (a) and O_2 (b) activation on pristine CN and O-ACN-Ba: charge accumulation is shown in blue and depletion in yellow; the isosurfaces are set to $0.005 \text{ eV } \text{\AA}^{-3}$; all lengths are given in \AA ; E_{ads} stand for the adsorption energy of adsorption molecule, negative values indicate heat release and charge obtainment; gray, blue, green, red and pink spheres stand for C, N, Ba, O and H atoms, respectively; DMPO ESR spectra in darkness and under visible-light ($\lambda \geq 420 \text{ nm}$) irradiation for 15 min, respectively in methanol dispersion for $\bullet\text{O}_2^-$ (c) and in aqueous dispersion for $\bullet\text{OH}$ (d); NO removal efficiency and NO_2 production rate of the as-prepared samples during visible-light photocatalytic reaction process (e).

1 **Fig. 5.** Analysis of charge separation and charge transfer. Photoluminescence spectra
2 (a), the ns-level time-resolved fluorescence spectra (b), and room temperature solid
3 state EPR spectra (c) of CN and O-ACN-Ba-030; calculated electrostatic potential of
4 CN and O-ACN-Ba (d); charge density difference distribution of pure CN and
5 O-ACN-Ba (e): charge accumulation is shown in blue and depletion in yellow; gray,
6 blue, green, red and pink spheres stand for C, N, Ba, O and H atoms, respectively; the
7 isosurfaces are set to $0.005 \text{ eV } \text{\AA}^{-3}$.

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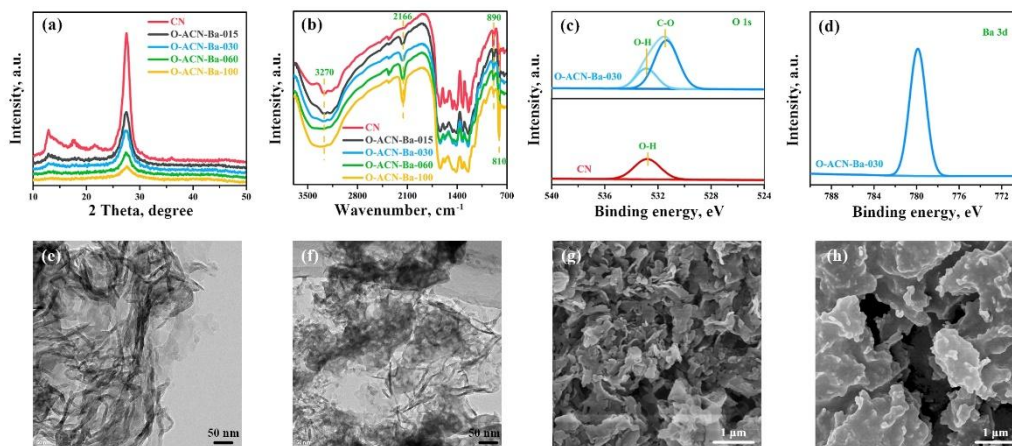
1 **Fig. 1.**



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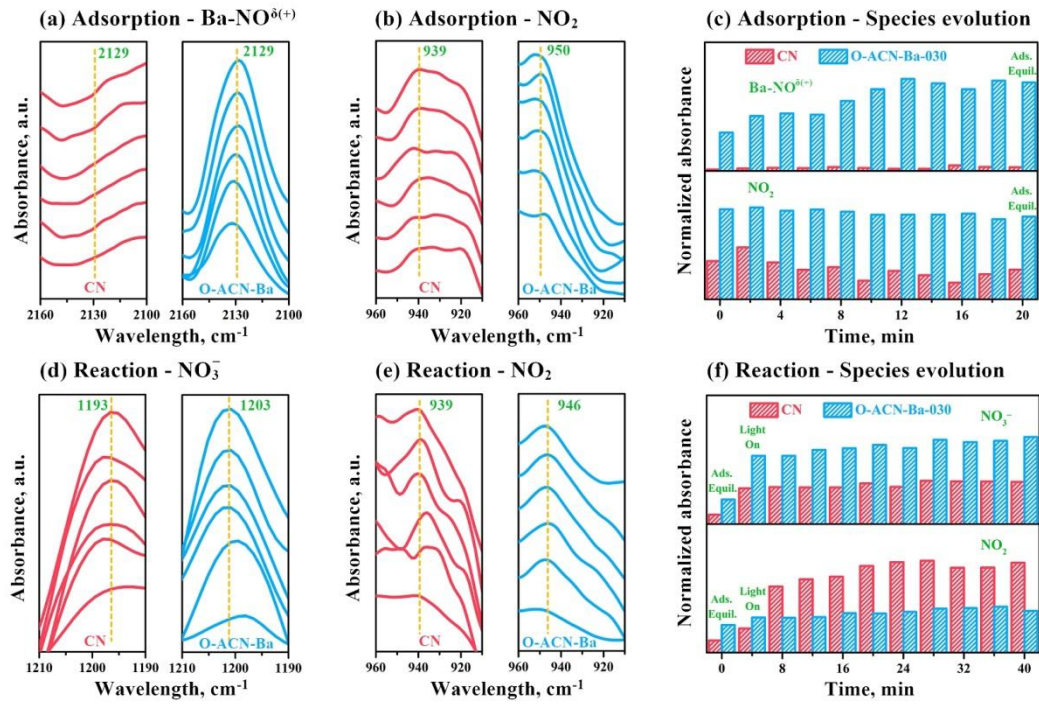
4 **Fig. 2.**



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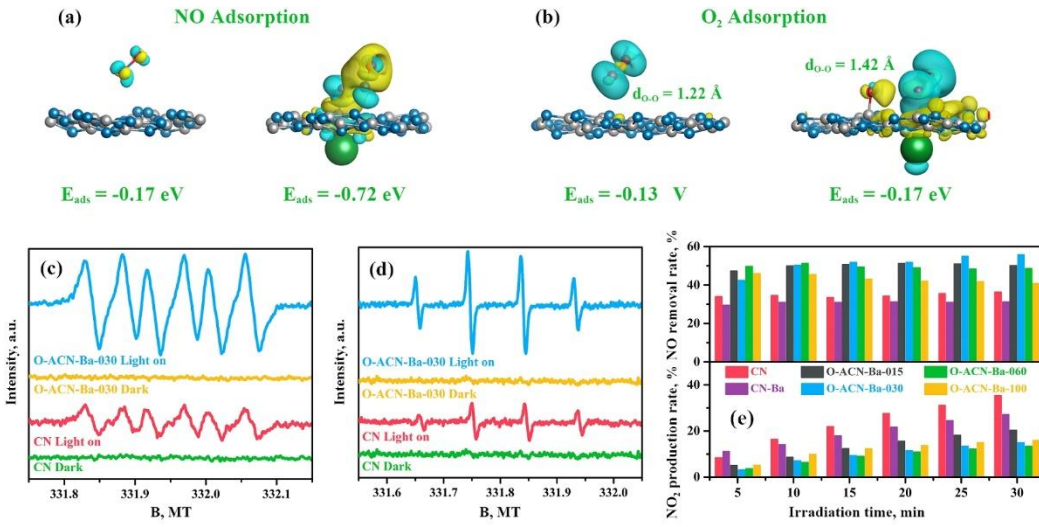
1 **Fig. 3.**



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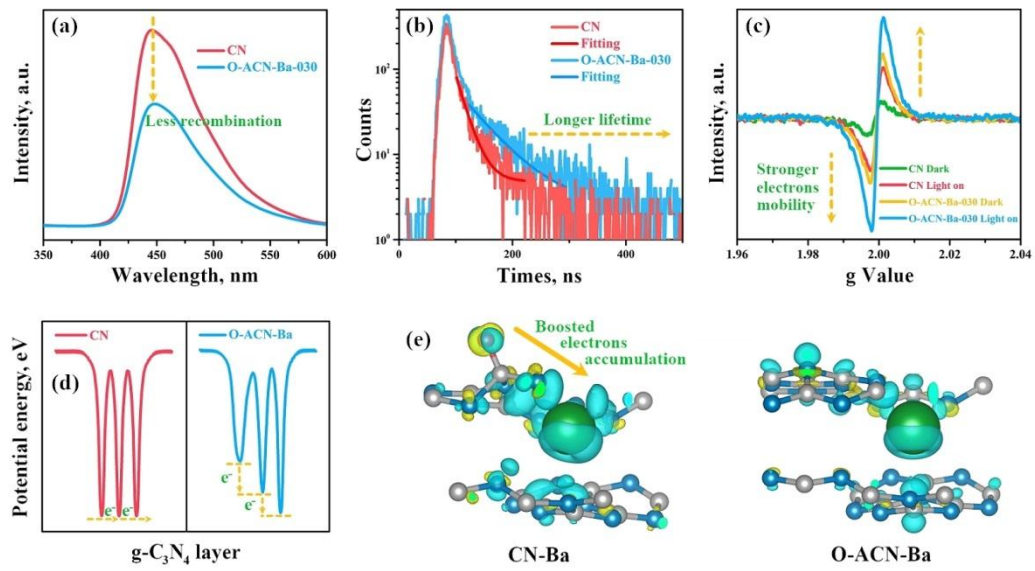
4 **Fig. 4.**



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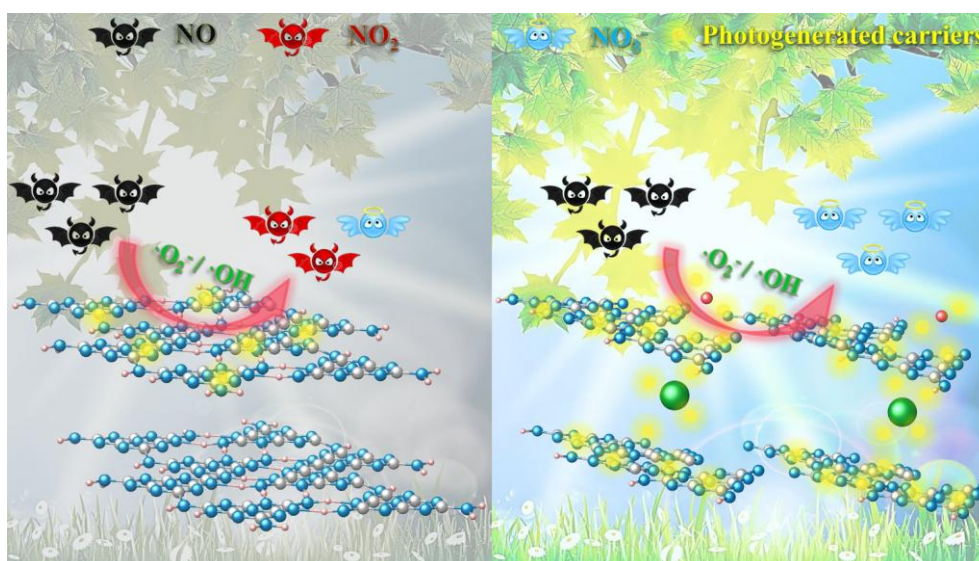
1 **Fig. 5.**



2

Graphical Abstract

TOC Art: An O/Ba co-functionalized amorphous carbon nitride (labeled as O-ACN-Ba) for short-range and directional charge transfer in electronic transportation channels has been designed, and subsequently synthesized *via* a one-step *in situ* co-pyrolysis of urea and BaCO_3 . The unique electronic structure O-ACN-Ba enable highly enhanced photocatalytic NO removal and suppressed toxic intermediate (NO_2) generation.



Research highlights

- An O/Ba co-functionalized amorphous carbon nitride was designed.
- The activation of gas molecules was facilitated with the localized electrons.
- The generation of ROS was boosted due to the optimized electronic structure.
- The promotion mechanism in enhanced photocatalysis was illustrated.
- Enhanced inhibited generation of toxic intermediates was realized.