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Tailoring Cu_3N_x clusters on TiO_2 nanosheets to the sub-nanometric scale for enhancing NH_3 photosynthesis

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Ammonia (NH₃) is an essential agriculture fertilizer and a promising hydrogen carrier, making its sustainable production a priority. Photocatalytic NO_3^- reduction offers an efficient, light-driven pathway towards NH_3 synthesis, addressing both energy and environmental challenges. In this study, we explore Cu_3N_x cluster incorporated TiO₂ nanosheet catalysts, where sub-nanometric Cu_3N_x clusters enhance NH_3 production by increasing active site accessibility, stabilizing Cu^+ states, and enabling efficient electron–hole separation. Consequently, the CN0.3 catalyst (Cu_3N_x size = 0.3 nm) demonstrates an NH_3 production rate 158 times higher than that of pristine TiO₂ nanosheets, with excellent stability and an apparent quantum yield of 14.2 % at 330 nm. Density functional theory calculations further reveal that Cu_3N_x stabilizes NO_3^- adsorption, lowers the energy barrier for the rate-determining deoxygenation step, and facilitates effective charge transfer. Our findings highlight the potential of Cu_3N_x/TiO_2 as a robust candidate for efficient photocatalytic NH_3 synthesis and underscore the potential of sub-nanometric metal-nitride clusters in photocatalysis.

1. Introduction

Ammonia (NH₃) is an essential fertilizer in agriculture and has gained increasing attention as a hydrogen carrier, owing to its high hydrogen content (17.6 wt%) and favorable transport and storage properties [1,2]. Beyond its agricultural significance, NH₃ can serve as a

renewable energy carrier, offering efficient hydrogen storage and enabling the integration of renewable energy sources into energy systems [3,4]. Therefore, achieving sustainable NH_3 production represents a pivotal milestone toward realizing a hydrogen-based economy [5–7].

In this context, the photocatalytic conversion of nitrate (NO $_3^-$) to NH $_3$ has garnered attention as it offers an efficient, light-driven pathway for

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NH₃ synthesis. Although NO₃-to-NH₃ conversion cannot fully replace the Haber-Bosch process due to limited feedstock availability and scalability, it holds significant potential in energy storage technologies [8]. Additionally, this approach overcomes the persistent challenges associated with N2 fixation in aqueous media-specifically the high dissociation energy, low solubility of N2 in water, and difficulty in accurately quantifying NH3 contents due to low yields and potential external contaminants [9–11]. Converting NO_3^- , a common wastewater pollutant, into a valuable resource offers a sustainable solution that addresses environmental and energy challenges simultaneously [12,13], while enabling resource recovery and integrating waste into a circular economy [8]. Despite recent progress in photocatalytic NH₃ production via NO₃⁻ reduction, the process is hindered by the sluggish kinetics of NH₃ photosynthesis and undesired side reactions (e.g., hydrogen evolution and NO₃ conversion to N₂), indicating that commercialization remains a distant goal [14,15]. These limitations highlight the need for innovative catalyst designs aimed at achieving higher NH₃ production rates.

Cu is regarded as the key element in photocatalytic NH₃ production via NO₃⁻ reduction, a process that involves a nine-proton, eight-electron transfer [16,17]. This critical role of Cu is primarily attributed to its strong binding affinity for NO₃⁻, along with its ability to facilitate the subsequent hydrogenation steps essential for NH₃ synthesis [18]. These remarkable hydrogenation properties of Cu have led to its widespread applications in diverse photo-/electrocatalytic reactions [19–21], with Cu(I) demonstrating superior activity compared to Cu(0) or Cu(II) [22–26]. However, maintaining the Cu(I) state during photo-/electrocatalytic processes, involving multiple electron transfers, is challenging due to the inherent variability in Cu's oxidation states [27,28]. Inspired by previous studies indicating that transition metal nitrides (MN_x) can stabilize metal valence states [29,30], we sought to examine Cu(I) nitride (Cu₃N) as a potential stabilizer of the Cu⁺ state and as a novel catalyst for photocatalytic NH₃ synthesis.

Furthermore, in typical photocatalytic reactions (solid-liquid heterogeneous catalysis), the particle size of the catalyst plays a notable role in determining overall photocatalytic performance [31]. Reducing the particle size of the catalyst increases its surface area, thereby creating more active sites and enhancing their accessibility, which accelerates reactant adsorption and conversion at the catalytic interface [32,33]. We selected TiO₂ in the form of nanosheets as the support to exploit their dominant exposure of (001) facets, which are known to be photochemically active and facilitate efficient charge separation and surface reactions. Consequently, optimizing the size of Cu₂N_x particles on a TiO₂ support to sub-nanometric dimensions enables effective interactions between active metal sites and NO₃⁻ ions while stabilizing the active Cu⁺ state—an essential factor for catalytic performance [22–24]. Particularly, sub-nanometric catalysts approaching the single-atom scale are anticipated to offer further advantages, as isolated metal atoms maximize active site availability and adsorption capacity [34,35].

Building on this hypothesis, we synthesized TiO₂ nanosheets catalysts with Cu₃N_x clusters (CN) exhibiting a valence state approximating Cu⁺ for efficient NH₃ photosynthesis. Furthermore, by employing various deposition techniques, we successfully reduced the Cu₃N_x cluster size from several nanometers to the sub-nanometric scale. This optimization led to the development of CN0.3 catalyst (Cu₃N_x size = \sim 0.3 nm), which demonstrated an NH₃ production rate 158 times greater than that of pristine-TiO $_2$ nanosheets (TNS) and 6.6 times higher than that of TNS with conventional Cu nanoparticles deposited, achieving an apparent quantum yield (AQY) of 14.2 % at 330 nm. Density functional theory (DFT) calculations revealed that the subnanometric Cu₃N_x clusters stabilize NO₃⁻ adsorption configurations and reduce the energy barrier for the rate-limiting deoxygenation process (*NOH \rightarrow *N). Moreover, the Cu₃N_x clusters modulate the electronic structure of TiO₂, enhancing light absorption and promoting efficient electron-hole pair separation, thereby increasing electron availability for the photocatalytic reaction. Operando charge transfer dynamics analyses consistently confirmed the notable suppression of charge recombination in CN0.3. We believe that the CN0.3 catalyst presents a novel strategy for leveraging Cu^+ species, marking a significant advancement in the pursuit of efficient photocatalytic NH_3 synthesis.

2. Experimental section

2.1. Materials

Tetrabutyl titanate (TBOT, \geq 99.0 %), copper nitrate trihydrate (Cu (NO₃)₂·3H₂O, 99.9 %), titanium dioxide (TiO₂, anatase, 99.7 %) hydrofluoric acid (HF, 37 wt%), iodine (I₂, 99.5 %), acetone (CH₃COCH₃, 96 %), methanol (CH₃OH, \geq 99.0 %), ethanol (C₂H₆O, \geq 99.0 %), sodium borohydride (NaBH₄, 98 %), ethylene glycol (anhydrous, 99.8 %), formic acid (HCOOH, \geq 95.0 %), potassium nitrate (KNO₃, \geq 99.0 %), potassium nitrate-¹⁵N (K¹⁵NO₃, 98 atom%), and potassium sulfate (K₂SO₄, \geq 99.0 %) were purchased from Sigma Aldrich. All chemicals were obtained from commercial suppliers and used without further purification.

2.2. Catalyst synthesis

First, TNS was synthesized using a modified solvothermal method [36]. In a typical synthesis, 5 mL of TBOT was mixed with 0.6 mL of HF and stirred for 30 min to form a homogeneous solution. The mixture was then transferred into a Teflon-lined autoclave and heated at 180 °C for 4 h. The resulting product was centrifuged, washed several times with DI water, and dried overnight at 60 °C. Using the prepared TNS, CN3.0, CN1.5, and CN0.3 catalysts via distinct reduction methods (H₂ gas, aqueous NaBH₄, and photoreduction, respectively), resulting in Cu₃N_x clusters of different sizes. In all cases, excess amount of KNO₃ (e.g., 500 mg) was added as an excess nitrogen source to ensure successful Cu₃N_x formation.

For **CN3.0**, 100 mg of TNS was dispersed in ethanol (50 mL) with KNO₃. An another ethanol solution of Cu(NO₃)₂·3H₂O, adjusted to the desired *x* wt% of Cu relative to Ti contents in TNS (x = 0.5, 1, 1.5, 2 and 3, e.g., 1 wt% = 3.8 mg), was then added to the suspension and stirred for 1.5 h to achieve adsorption/desorption equilibrium. The mixture was evaporated, and the dried powder was annealed in a tube furnace under an H₂ atmosphere at 350 °C for 3 h (ramping rate = 5°C/min), resulting in the CN3.0 catalyst.

For **CN1.5**, 100 mg of TNS was dispersed in 200 mL of DI water in a three-neck flask. The aqueous solution of $Cu(NO_3)_2$ ·3H₂O and KNO₃ were added to the suspension. The solution was purged with Ar gas for 2 h to remove any residual O₂. Finally, 5 mL aqueous solution containing 50 mg of NaBH₄ was added dropwise, and the reaction proceeded under stirring for 6 h. The resulting product was washed several times with DI water and ethanol, then dried overnight at 60 °C.

For **CN0.3**, 100 mg of TNS was dispersed in 25 mL of a 20 vol% methanol aqueous solution containing the desired amount of Cu $(NO_3)_2$ ·3H₂O and KNO₃. The suspension was stirred in the dark for 1 h to achieve Cu ion adsorption. The suspension was then irradiated under vigorous stirring with a 300-W Xe lamp (Newport) for 6 h. The product was centrifuged, washed with DI water, and dried overnight at 60°C.

A **CuNP/TNS** reference photocatalyst was also prepared by the above photoreduction method without KNO_3 addition.

2.3. Characterization, calculation and experimental details

For additional details, refer to the Supporting Information.

3. Results and discussion

3.1. Characterization of Cu_3N_x clusters on TiO₂ nanosheets

First, TNS with a lateral length of ~ 20 nm was synthesized using a facile solvothermal method (Figs. S1 and S2). Following this, Cu_3N_x

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clusters were deposited onto the TNS surface through a conventional H₂ reduction process (see Experimental section for details). During the synthetic process, the presence of excess amount of N sources alongside the Cu precursor was crucial for the successful formation of Cu_3N_x clusters. Fig. 1a shows the Cu₃N_x clusters on the TNS surface using highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM), revealing that the Cu₃N_x clusters are uniformly distributed across TNS with an average size of ~ 3 nm, thus denoted as CN3.0 (Fig. S3). Further, elemental mapping of the Cu₃N_x clusters via energy-filtered (EF)-TEM confirms the presence of Cu and N species, indicating that N species are distributed around Cu in the same regions (Fig. 1b). The crystallinity of Cu₃N_x anchored onto the surface of anatase TiO₂ with the predominantly exposed 001 facets, is evident in the atomic-scale STEM image (Fig. 1c). The interatomic distance between two Cu atom columns measures 0.22 nm, corresponding to the (111) dspacing of simulated Cu₃N atomic structure. This observation confirms that the Cu_3N_x clusters are stably localized on the anatase TiO₂ (001) surface. Next, X-ray absorption spectroscopy (XAS) offers insights into the structure and chemical state of CN3.0. The Cu K-edge X-ray absorption near-edge structure (XANES) spectrum (Fig. 1d) displays the characteristic absorption edge of Cu⁺ valence state at 8994.7 eV. Moreover, a comparison between the reference configurations of Cu⁺ and Cu²⁺ reveals that Cu in the CN3.0 catalyst exists in a mixed configuration of Cu_3N and Cu_3N_2 , resulting in a valence state of + 1.3, where Cu⁺ serves as the predominant configuration. Further evidence from Fourier transformation of the extended X-ray absorption fine structure (EXAFS) of CN3.0 reveals a single characteristic peak at ~ 1.4 Å, corresponding to the Cu⁻N first shell scattering path. This indicates that the Cu atoms in the 1.3 + oxidation state are stabilized through coordination with adjacent N atoms (Fig. 1e). The absence of the peak corresponding to the Cu^Cu scattering path at ~ 2.2 Å strongly verifies that CN3.0 is free from Cu⁰ metal configurations. Moreover, the wavelet transform analysis (Fig. 1f) corroborates that Cu-N coordination is the dominant phase within the catalyst. The characteristics of the Cu_3N_x clusters were consistently demonstrated through X-ray photoelectron spectroscopy (XPS). Similarly, the Cu 2p XPS spectra (Fig. 1g) exhibit Cu⁺ characteristic peaks at 932.8 eV and 952.6 eV. Meanwhile, the N 1 s XPS spectra (Fig. 1h) present a distinct peak at 399.2 eV, corresponding



Fig. 1. (a) HAADF-STEM image of Cu_3N_x clusters on the TNS. The white box highlights the region magnified in (b) and (c). (b) Elemental maps of N, Ti, and Cu for the Cu_3N_x clusters derived from EF-TEM (c) Atomic-scale HAADF-STEM image depicting the lattice spacing of $Cu_3N (111)$. (d) Cu *K*-edge XANES spectra (inset: slope of Cu *K*-edge energies as a function of Cu valence state). (e) Fourier-transformed EXAFS in *R*-space for CN3.0 and the reference materials. (f) Wavelet-transform EXAFS plots for CN3.0 and the reference materials (Cu foil, Cu₂O and CuO). High-resolution XPS spectra of (g) Cu 2p and (h) N 1 s of CN3.0.

to N-metal coordination, further supporting the successful synthesis of Cu_3N_x clusters [37] on the TNS surface.

3.2. Size modulation of Cu_3N_x clusters

In addition to Cu_3N_x cluster decoration, we aimed to modulate the cluster size from the nanometric to the sub-nanometric scale by employing various deposition techniques. To achieve this, we utilized different reaction media (e.g., gas and liquid) and reducing agents (e.g., H₂, sodium borohydride (NaBH₄), and photogenerated electrons), thereby increasing the number of catalytic active sites and enhancing the molecular interaction and accessibility between catalytic sites and reactant molecules (Fig. 2a and see Experimental section for details). As a result, the synthesized samples exhibited different cluster sizes, which can be attributed to variations in cluster nucleation and growth kinetics influenced by the choice of reaction media and reducing agents. First, the STEM images of CN3.0 (Fig. 2b), prepared using H₂ gas reduction, revealed uniformly distributed Cu₃N_x clusters with an

average size of 3.0 nm on the TNS surface. The relatively large nm-scale clusters were clearly visible even at low magnification. Second, the sample prepared using NaBH₄ (a strong reducing agent) in an aqueous medium (Fig. 2c) exhibited uniformly distributed Cu₃N_x clusters with an average size of approximately 1.5 nm (Fig. S4), which is about 50 % smaller than that of CN3.0. Compared to the gas-phase reaction, the reduced cluster size can be attributed to the lower reaction kinetics in the liquid phase. However, the nanometer-scale clusters remained clearly visible even at low magnification. In contrast, the last sample, prepared in an aqueous medium using photogenerated electrons as a relatively mild reducing agent, exhibited the slowest nucleation and growth kinetics. As a result, sub-nanometric clusters were formed, which were not distinguishable in low-magnification images, leaving only a smooth TNS surface (Fig. 2d). However, atomic-resolution STEM images revealed bright contrasts, which were further confirmed by line scan profiling and particle size distribution analysis, demonstrating the presence of uniformly distributed sub-nanometric clusters with an average size of 0.3 nm (Fig. S5). The cluster dimensions were



Fig. 2. (a) Schematic depicting the size modulation of the Cu_3N_x clusters on the TNS. Low- and high-magnification HAADF-STEM images and the corresponding line scan profile of the circled areas, revealing the Cu_3N_x cluster size of (b) CN3.0, (c) CN1.5, and (d) CN0.3. The line scan intensity profiles were extracted from the white boxed regions indicated in each HAADF-STEM image. Cluster size was determined based on the full width at baseline. Due to the small atomic number contrast between Cu (Z = 29) and Ti (Z = 22), the intensity modulation is modest but consistent. A > 20 % intensity difference from the background was used as the threshold for defining Cu_3N_x cluster boundaries. EEL spectra of (e) Cu *L*-edge, (f) N *K*-edge, and (g) Ti L_{23} -edge for the prepared samples (CN3.0, CN1.5, and CN0.3) and the related reference materials (Cu₂O, CuO, Cu foil, commercial anatase TiO₂, and TNS).

determined from HAADF-STEM intensity profiles extracted across selected regions, with a >20% contrast threshold used to define the boundaries between $\rm Cu_3N_x$ and the $\rm TiO_2$ support. Furthermore, a variety of characterization techniques, including X-ray diffraction (XRD), XAS, and electron paramagnetic resonance analysis, confirmed that all synthesized $\rm Cu_3N_x$ clusters (CN3.0, CN1.5, CN0.3) maintained a comparable $\rm Cu^+$ valence state (estimation: 1.2–1.3). These results verify the successful synthesis and uniform distribution of $\rm Cu_3N_x$ (x = 1.2–1.3) clusters on the TNS surface with distinct sizes (Fig. S6–S9 and Table S1). Accordingly, the synthesized samples were labeled CN3.0, CN1.5, and CN0.3 based on their average cluster sizes.

The chemical properties of the Cu_3N_x clusters were further validated through electron energy loss spectroscopy (EELS) analysis. The Cu Ledge EELS spectra, obtained from the Cu₃N_x cluster regions of all three CN catalysts, CN3.0, CN1.5, and CN0.3 (Fig. 2e), exhibited Cu L₃ and L₂ peaks that closely resemble the reference spectrum of Cu₂O, confirming the spectral features of Cu(I) oxidation state. Specifically, the position of the L_3 edge and the intensity ratio between the L_3 and L_2 peaks suggest that a substantial portion of Cu species in the CN catalysts exist in the + 1 oxidation state. Furthermore, no characteristic peaks or distinct energy shifts associated with Cu(II) or Cu(0) were measured, suggesting that the presence of these configurations (Cu^{2+} or Cu^{0}) is negligible in the all CN catalysts. Additionally, the N K-edge EELS spectrum was analyzed at two distinct locations: point x, located on the Cu₃N_x clusters, and point y, located on the TNS surface (Fig. S10). Interestingly, the spectrum at point *x* displays clear N signals, while that at point *y* shows almost no detectable N signal, confirming the absence of N within the TNS itself. Moreover, the N K-edge EELS spectra obtained from all three CN catalysts (Fig. 2f) consistently exhibited π^* and σ^* peaks, characteristic of sp²- and sp³-hybridized N environments. This directly confirms the incorporation of N within the clusters, validating Cu-N coordination and providing strong evidence of the consistent formation of the Cu₃N_x phase across the different samples. The Ti L-edge EELS spectra (Fig. 2g) further demonstrated that the Ti species in all CN catalysts retained the Ti⁴⁺ oxidation state, consistent with the typical

structure of anatase TiO₂. The Ti L-edge spectra of the CN catalysts were indistinguishable from those of anatase TiO₂ and TNS, indicating that the introduction of Cu_3N_x did not alter the oxidation state of Ti. Furthermore, this suggests that TiO₂ remained structurally intact even during the Cu_3N_x cluster formation process involving various reducing agents. Additionally, Ti K-edge XAS analysis (Fig. S11) confirmed these findings again, displaying pre-edge peaks and characteristic Ti⁴⁺ peaks associated with anatase TiO₂, further supporting the results obtained from EELS analysis.

3.3. Photocatalytic NH₃ production performance

The photocatalytic NH₃ production performance of the synthesized CN catalysts was evaluated in an aqueous NO₃ solution containing HCOOH (0.1 wt%) as the sacrificial reagent under full-spectrum irradiation (see Experimental details in the Supporting Information). During the Cu content optimization process, the CN3.0, CN1.5, and CN0.3 catalysts with a Cu loading of 1 wt% exhibited the highest NH₃ production rate, regardless of Cu₃N_x cluster size (Fig. 3a), confirming 1 wt% as the optimal loading for further studies. HAADF-STEM images (Fig. S12) further confirm that the Cu_3N_x cluster size remains largely unchanged across different Cu loadings within each synthesis condition. However, despite the size uniformity, the photocatalytic performance declines beyond 1 wt% Cu loading. This decrease is likely due to cluster agglomeration and increased surface coverage at higher loadings, which can reduce the number of accessible active sites, attenuate light absorption by the TiO₂ support (light shielding effect), and potentially promote the formation of catalytically less-active Cu⁰ species. Additionally, the actual Cu and N loadings aligned with the targeted values (Table S2). For comparison, a TNS catalyst with conventional Cu⁰ nanoparticles (CuNP), which have an average size of approximately 2-3 nm, was also prepared as a reference (Fig. S13). Regardless of particle size, the CN catalysts exhibited substantially improved NH₃ production performance compared to both TNS and CuNP catalysts. Even CN3.0 exhibited a 1.6-fold increase in NH3 production activity compared to the



Fig. 3. (a) NH₃ production rates of CN0.3, CN1.5, and CN3.0 as a function of Cu content. (b) NH₃ production rates of TNS, CuNP, CN3.0, CN1.5 and CN0.3. (c) Selectivity of N-species products for CuNP, CN3.0, CN1.5 and CN0.3. (d) ¹H NMR spectra of NH₃ produced via NO₃⁻ reduction with K¹⁵NO₃ as the reactant feedstocks. (e) Long-term stability test of CN0.3 for photocatalytic NH₃ production, where NO₃⁻ was replenished at the end of each 12-h cycle to maintain the NH₃ production rate. (f) UV-visible DRS spectra and wavelength-dependent AQY of CN3.0, CN1.5 and CN0.3. Error bars represent standard deviation (n = 3).

CuNP catalyst, highlighting the remarkable photo-conversion efficiency of MN_x cluster catalysts. The photocatalytic NH₃ production performance further improved as the CN cluster size decreased. Among the samples, CN0.3 demonstrated the highest efficiency, with an NH₃ production rate of approximately $34.9 \,\mu$ mol h⁻¹, which is 158 times higher than that of TNS and 6.6 times higher than that of CuNP (Fig. 3b). These results strongly validate the catalytic advantages conferred by Cu⁺ species and the increased availability of densely distributed active metal sites. This size-dependent performance can be attributed to both structural and electronic effects associated with nanoscale Cu_3N_x clusters. Structurally, sub-nanometric clusters such as those in CN0.3 expose a higher proportion of surface atoms, increasing active site density and enhancing NO3 adsorption. Electronically, size confinement may shift the local charge distribution and d-band center, promoting more favorable adsorption and activation of nitrate intermediates. Interestingly, particle size also had a notable impact on selectivity (Fig. 3c). In general, the primary N-species generated through photocatalytic NO3 reduction are N₂, involving a 5e⁻ transfer, and NH₃, involving an 8e⁻ transfer [38-42]. The amounts of NH₃ and N₂ produced were quantified using ion chromatography and gas chromatography, respectively. In all samples, over 95 % of the converted NO_3^- was consistently recovered as N-based products, confirming the absence of other side products. Conventional CuNP and CN3.0 catalysts, featuring nanometric-sized active metal clusters, exhibited comparable NH₃ selectivity (approximately 80-82 %). However, decreasing the Cu₃N_x cluster size correlated with an increase in NH₃ selectivity, with CN0.3 catalyst reaching approximately 93 %. This trend suggests that larger particles may facilitate N-N interactions by enabling the simultaneous adsorption of multiple reactant molecules, thus accelerating N₂ formation [43]. Conversely, subnanometric clusters are more densely and uniformly distributed, allowing for increased NO3 adsorption per unit area. Additionally, the reduction process occurring at isolated catalytic active sites promotes independent reactant molecule adsorption, minimizing N-N interactions and favoring NH₃ formation.

Furthermore, all CN samples displayed a distinct doublet ¹H nuclear magnetic resonance (NMR) peak indicative of ¹⁵NH⁺₄, thereby dispelling concerns regarding the source of N in the produced NH_3 (Fig. 3d). The NH₃ quantities measured via ion chromatography and NMR were in strong agreement, with both methods yielding similar concentrations (~8.2 ppm) for the CN0.3 sample (Fig. S14). This consistency was further confirmed in isotopic labeling tests using ¹⁵NO₃, where the quantification results again matched closely across both methods. These cross-validated results confirm the accuracy of the quantification process and verify that the observed NH₃ originated from the photocatalytic reduction of the supplied NO₃, effectively ruling out external contamination. CN0.3 demonstrated excellent stability, exhibiting < 10 % decline in its NH₃ production rate over a 48-h extended stability test, ultimately yielding 1.1 mmol of NH₃ (Fig. 3e). Post-characterization analyses, including XRD, XPS, ICP-AES, and EELS, confirmed that CN0.3 maintained its structural integrity and \mbox{Cu}^+ valence state even after prolonged reaction cycles (Fig. S15). In particular, Cu L-edge EELS spectra collected before and after the stability test retained identical L₃/ L₂ edge positions and intensity ratios, indicating that Cu⁺ remained the dominant oxidation state. The Cu and N contents measured by ICP-AES were also nearly unchanged, suggesting compositional retention of the Cu₃N_x phase. Although Cu 2p XPS spectra showed slight broadening after testing, no satellite peaks indicative of Cu²⁺ were detected. Given the low Cu loading (~1 wt%) and the known limitations of Cu 2p XPS in distinguishing between Cu⁺ and Cu²⁺, we consider EELS to provide more definitive evidence of Cu⁺ stability. These results collectively validate the structural and electronic robustness of CN0.3 during longterm photocatalysis. Moreover, the Cu and N wt% remained unchanged before and after the reaction, confirming that the N species within the catalyst did not participate in the reaction. The enhanced NH₃ production rate was further supported by AQY measurements, which followed trends consistent with their UV-visible diffuse reflectance

spectra (DRS), particularly in the UV region. Among the samples, CN0.3 achieved the highest photon energy conversion efficiency of 14.2 % at 330 nm (Fig. 3f). The photocatalytic performance of CN0.3 was further compared with representative catalysts reported in literature (Table S3), confirming its superior NH3 yield and AQY among state-of-the-art photocatalysts for nitrate reduction. Furthermore, due to Cu's intrinsic visible-light absorption capability, the catalysts exhibited AOY values of 1-3 % in the sub-500 nm region, demonstrating improved light absorption. However, due to the inherent bandgap limitation of TiO₂, the photocatalytic performance enhancement in wavelengths beyond 500 nm was relatively minimal. The exceptional photocatalytic performance was also demonstrated through additional photocatalytic hydrogen evolution reaction (HER) tests conducted without NO₃ supply (Fig. S16). DFT calculations revealed that the CN0.3 sample provides more HER active sites than the TNS by enabling both O and N atoms to serve as active sites, achieving a 202-fold enhancement in H₂ production performance relative to that of the TNS (Fig. S17). These findings highlight the versatility of Cu₃N_x clusters across diverse photocatalytic reactions.

3.4. Charge-transfer dynamics

To explore the origin of the exceptional performance of CN0.3, we conducted a detailed analysis of its interfacial charge dynamics. To examine the charge-transfer dynamics within the bulk of the catalyst, we initially used steady-state photoluminescence (PL) emission and timeresolved photoluminescence (TRPL) spectroscopy. The quenched PL emission upon Cu₃N_x decoration suggests the introduction of nonradiative recombination pathways within TNS [44], indicating that photogenerated charges within TNS migrate toward Cu₃N_x clusters (Fig. 4a). This non-radiative recombination effect is more pronounced in sub-nanometric clusters, where more densely distributed active sites provide more electron transfer channels, effectively enhancing charge carrier separation. This hypothesis was further supported by the accelerated PL decay kinetics (i.e., reduced average carrier lifetime) observed in the presence of Cu_3N_x clusters (Fig. 4b), indicating that chargetransfer dynamics within TNS are further expedited through an additional pathway toward Cu₃Nx clusters. The CN0.3 catalyst, with a charge-transfer constant of 0.79 s^{-1} (vs. TNS), demonstrating superior charge-transfer efficiency, which explains its outstanding photocatalytic performance (Table S4).

Operando Cu K-edge XANES spectra revealed that the Cu valence state remains stable after light irradiation across all catalysts, underscoring the role of nitrides as valence state stabilizers (Fig. 4c). A downward shift in peak intensity was also observed for all samples upon light exposure, suggesting that accelerated charge separation allows electrons localized on Cu₃Nx to populate unoccupied orbitals. This electron localization effect becomes more pronounced as Cu₃N_x cluster size decreases. Accordingly, the CN0.3 catalyst exhibits the most pronounced shift, indicating the highest level of electron accumulation within the more densely distributed sub-nanometric Cu₃N_x clusters. Further insights into surface charge dynamics of the catalysts were provided by operando Kelvin probe force microscopy (KPFM) analysis. The topography mappings of each catalyst are illustrated in Fig. S18. Fig. 4d displays the calculated surface potential differences (Δ SP) for each catalyst with and without UV-B irradiation, with insets depicting surface topography mapping. Typically, an increase in SP following illumination indicates charge accumulation on the photocatalyst surface, specifically on the Cu₃N_x clusters in our case. Notably, this increase in Δ SP intensifies as cluster size decreases to the sub-nanometric scale, reflecting enhanced charge localization. Consequently, the CN0.3 catalyst shows a Δ SP value of approximately 62 mV, representing a 60-fold enhancement in charge accumulation compared to TNS and more than a 10-fold improvement over CN3.0. This enhancement reflects the highest photogenerated electron density in sub-nanometric Cu₃N_x clusters, which directly contributes to its superior photocatalytic NH₃ production performance. The exceptional photogenerated charge transfer



Fig. 4. (a) Steady-state PL emission spectra and (b) TRPL decay spectra of the TNS, CN3.0, CN1.5 and CN0.3, recorded under ambient conditions ($\lambda_{Ext} = 375$ nm). (c) Operando Cu *K*-edge XANES spectra of CN3.0, CN1.5 and CN0.3 before and after irradiation. (d) Calculated surface potential difference of TNS, CN3.0, CN1.5 and CN0.3 with and without UV-B irradiation (inset: KPFM topography mapping of each catalyst in the dark (top) and under light irradiation (bottom). Scale bars, 500 nm). (e) EIS Nyquist plots of TNS, CN3.0, CN1.5 and CN0.3 under continuous irradiation (inset: an equivalent circuit for catalyst/electrolyte interfaces, where R_s = electrolyte resistance, R_{ct} = charge-transfer resistance of photocatalyst, and CPE = constant phase element).

properties of CN0.3 were further validated through electrochemical impedance spectroscopy (EIS) under simulated light irradiation. The Nyquist plot revealed that CN0.3 exhibited the smallest semi-circle radius and the lowest charge-transfer resistance ($R_{ct} = 12 \ \Omega$) (Fig. 4e and Table S5). This represents at least a 4.5-fold reduction in charge-transfer resistance compared to its counterparts, further confirming that CN0.3 enables the most efficient separation of photogenerated charge carriers under irradiation. Such an efficient charge-transfer capability consistently demonstrated across multiple assessments highlights CN0.3 as a key factor in achieving impressive photocatalytic NH₃ synthesis activity.

3.5. DFT calculations

Beyond efficient charge separation and transfer, DFT calculations were further conducted to gain deeper mechanistic insights into the impact of Cu₃N_x decoration on photocatalytic NH₃ production. The optimized structures of pristine TiO2 and the Cu3N/TiO2 composite (Fig. S19) confirm the thermodynamic feasibility of Cu₃N cluster decoration ($E_{form} = -9.76 \text{ meV atom}^{-1}$). Additionally, the band structure calculations revealed that incorporating Cu₃N clusters transforms the indirect bandgap of TiO₂ into a direct bandgap, enhancing photon absorption and emission and thereby improving photocatalytic activity (Fig. 5a and Fig. S20). This improvement in light absorption was corroborated by experimental DRS absorption data (Fig. S21). Notably, the projected density of states (PDOS) reveals each atom's contribution to the electronic states in a given catalyst (Fig. 5b and Fig. S22). In pristine TiO₂, the valence band (VB) typically consists of O(2p) orbitals, while the conduction band (CB) is mainly composed of Ti(3d) orbitals. However, the introduction of Cu₃N cluster forms mid-gap states derived from Cu(3d) orbitals, facilitating charge separation. Additionally, a

band-decomposed charge density analysis provides more detailed, bandspecific insights crucial for understanding and optimizing the electronic properties of semiconductors. Fig. 5c displays the band-decomposed charge density at the VB maximum (VBM) and CB minimum (CBM) energy levels. These results clearly show that electrons are localized around Ti atoms, while holes are localized in the Cu₃N region, providing further evidence of effective electron–hole separation. The combination of direct optical transition and efficient electron–hole separation into different layers makes the Cu₃N/TiO₂ composite significantly more advantageous for solar energy harvesting than either material alone.

The deposition of Cu₃N clusters influences the NH₃ photosynthesis reaction mechanism, beginning with NO_3^- adsorption on the catalyst surface—crucial to the overall reaction. Given that NO_3^- can adsorb to various sites, multiple adsorption configurations were explored on both TiO2 and Cu3N/TiO2 surfaces. Overall, two configurations were considered: the 1-O pattern, where one oxygen atom bonds to the surface, and the 2-O pattern, where two oxygen atoms bond to the surface. On pristine TiO₂, NO₃⁻ adsorbed most stably on the Ti atom in the 2-O configuration, whereas on the Cu₃N/TiO₂ surface, NO₃⁻ stabilized in the 1-O configuration, bonding simultaneously with both Ti and Cu atoms. These stable NO3 adsorption configurations are illustrated in Fig. S23. Furthermore, NO₃⁻ adsorption onto Cu₃N/TiO₂ (ΔG_{*NO3} = –0.29 eV) was more favorable than on pristine TiO₂ ($\Delta G_{*NO3} = -0.03$ eV). The subsequent reaction can proceed via either a direct associative or a dissociative-associative mechanism, with the dissociativeassociative pathway confirmed as viable for both TiO₂ and Cu₃N/TiO₂ in our system. Along this pathway, the adsorbed NO₃ first dissociates into *O and *NO2, which then adsorb onto separate active sites. *O and *NO2 subsequently undergo protonation to yield the intermediate NO, which further accepts H successively to produce *NH, then *NH₂, and finally NH₃ (Fig. 5d and Fig. S24). From a thermodynamic perspective,



Fig. 5. (a) Band structure of Cu_3N/TiO_2 . (b) PDOS of Cu_3N/TiO_2 . (c) Band-decomposed charge density at the Γ point of the VBM (left) and CBM (right) for Cu_3N/TiO_2 . (d) Optimized structures of NO_3 reduction reaction intermediates, depicting the minimum energy pathway for NH_3 production on the Cu_3N/TiO_2 (001) surface. Free energy diagrams of photocatalytic NH_3 production via NO_3 reduction on (e) TiO₂ and (f) Cu_3N/TiO_2 . Cu, N, Ti, and O atoms are denoted with blue, green, cyan, and red balls respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

free energy changes for each reaction step were calculated to assess reaction feasibility and mechanism. The calculated reaction free energy values along the pathway reveal that transitions involving *OH–*NO₂, *OH–*NO, *NOH, and *N are uphill processes with positive free energy changes, while the formation of other intermediates corresponds to downhill processes with negative free energy changes (Fig. 5e and f). For both TiO₂ and Cu₃N/TiO₂ catalysts, the *NOH-to-*N transition exhibits the highest ΔG value (ΔG_{max}) as the rate-determining step, with values of 2.83 eV for TiO₂ and 1.89 eV for Cu₃N/TiO₂. These results demonstrate that the Cu₃N/TiO₂ catalyst outperforms pristine TiO₂, owing to its reduced rate-determining step energy barrier, direct bandgap, and efficient charge transfer facilitated by effective electronhole separation. These findings indicate that Cu₃N/TiO₂ emerges as a promising candidate for efficient NH₃ photosynthesis.

To further elucidate the enhanced photocatalytic performance of Cu_3N/TiO_2 , we performed charge density difference and Bader charge analyses, which provided insights into the interfacial electron migration and charge stabilization mechanisms. The charge density difference analysis (Fig. S25) reveals distinct electron depletion around Cu atoms and electron accumulation around O atoms in TiO₂, indicating effective interfacial electron migration. This redistribution of charge demonstrates that Cu_3N clusters serve as electron donors, transferring electrons to the TiO₂ support, which facilitates enhanced charge separation and minimizes recombination during photocatalysis. These observations are further validated by Bader charge analysis, which quantifies the charge states of the involved atoms: Cu atoms exhibit a partial positive charge

(+0.4 e), reflecting electron donation while maintaining the Cu⁺ oxidation state; N atoms are electron-rich (-0.97 e), acting as stabilizing centers; Ti atoms hold a charge of + 2.02 e, consistent with their oxidized state; and O atoms possess a charge of -1.02 e, indicating substantial electron acceptance. This charge redistribution not only stabilizes the Cu⁺ oxidation state but also promotes efficient charge transfer to TiO₂, reinforcing the electron flow required for the photocatalytic reduction of NO₃ to NH₃. Overall, these findings indicate that the Cu₃N/TiO₂ interface facilitates effective charge separation, reduces recombination losses, and enhances the overall photocatalytic conversion efficiency.

4. Conclusion

In summary, this study demonstrates that CN catalysts, particularly the CN0.3 variant, exhibit exceptional photocatalytic NH₃ production capacity via NO₃⁻ reduction under ambient conditions. The subnanometric Cu₃N_x clusters increase active site accessibility owing to their small size, stabilize the Cu⁺ configuration, and facilitate effective charge transfer, resulting in a substantial boost in the NH₃ photosynthesis yield (AQY = 14.2 % at 330 nm). DFT calculations further indicate that Cu₃N/TiO₂ lowers the energy barrier for the rate-determining process (*NOH \rightarrow *N) in NO₃⁻ reduction, enables direct bandgap transitions and efficient electron-hole separation, all of which contribute to its superior NH₃ photosynthesis performance compared to pristine TiO₂. The stability, facile synthesis, and versatility of Cu across various

photocatalytic reactions suggest broader applicability of CN catalysts, underscoring the potential of Cu_3N -based catalysts as sustainable solutions for NH₃ synthesis and other environmental and energy applications. Moreover, the use of earth-abundant materials and mild synthesis conditions highlights the environmental compatibility and practical scalability of this photocatalytic platform.

CRediT authorship contribution statement

Hyun Sik Moon: Writing - original draft, Investigation, Formal analysis, Data curation, Conceptualization. Yu-Jeong Yang: Writing original draft, Investigation, Formal analysis, Data curation. Getasew Mulualem Zewdie: Writing - original draft, Investigation, Data curation. Geon Youn: Investigation, Formal analysis. Yi-An Chen: Writing original draft, Investigation, Formal analysis. Yu-Peng Chang: Investigation, Formal analysis. Kai-Chi Hsiao: Formal analysis, Data curation. Ting-Han Lin: Investigation, Data curation. Yi-Dong Lin: Investigation, Data curation. Jun Kue Park: Investigation, Data curation. Jucheol Park: Investigation, Formal analysis, Data curation. Yan-Gu Lin: Validation, Supervision. Ming-Chung Wu: Validation, Supervision, Resources. Yung-Jung Hsu: Validation, Supervision, Resources. Hyevoung Shin: Validation, Supervision, Software. Si-Young Choi: Validation, Supervision, Resources. Kijung Yong: Writing - original draft, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2025.163915.

Data availability

Data will be made available on request.

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