Light-tuned selective photosynthesis of azo- and azoxy-aromatics using graphitic C\textsubscript{3}N\textsubscript{4}

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Solar-driven photocatalysis has attracted significant attention in water splitting, CO\textsubscript{2} reduction and organic synthesis. The syntheses of valuable azo- and azoxyaromatic dyes via selective photoreduction of nitroaromatic compounds have been realised using supported plasmonic metal nanoparticles at elevated temperatures (≥90 °C); however, the high cost, low efficiency and poor selectivity of such catalyst systems at room temperature limit their application. Here we demonstrate that the inexpensive graphitic C\textsubscript{3}N\textsubscript{4} is an efficient photocatalyst for selective syntheses of a series of azo- and azoxy-aromatic compounds from their corresponding nitroaromatics under either purple (410 nm) or blue light (450 nm) excitation. The high efficiency and high selectivity towards azo- and azoxy-aromatic compounds can be attributed to the weakly bound photogenerated surface adsorbed H-atoms and a favourable N-N coupling reaction. The results reveal financial and environmental potential of photocatalysis for mass production of valuable chemicals.
Azo- and azoxyaromatic compounds are very important and precious precursors for the dye-, electronic-, pigment-, and drug industries. Traditional industrial syntheses of azo- and azoxy-aromatic compounds are realised by diazotisation (yields >70%). The process is costly and environmentally unfriendly, due to the formation of unstable intermediate diazo compounds and harsh process conditions (involving strict temperature control and the use of corrosive acids). In a more environmentally friendly approach, azo compounds can be obtained via aerobic oxidation of amines by heterogeneous catalysis, but this requires supported noble metal catalysts or expensive oxidants, which limits large-scale applications.

Heterogeneous photocatalysis shows great potential in driving several important reactions (i.e., water splitting, CO₂ reduction, and organic synthesis), and the technology has therefore attracted significant attention over the last decades. Recent development of the graphitic C₃N₄ (g-C₃N₄) has further boosted the fundamental research and industrial potential of photocatalysis, as this inexpensive, metal-free material exhibits reasonable catalytic performance and stability under visible light irradiation, both azoxybenzene and azobenzene can be synthesised by this inexpensive, metal-free material exhibits reasonable catalytic performance and stability under visible light irradiation, as this inexpensive, metal-free material exhibits reasonable catalytic performance and stability under visible light irradiation. A recent study has demonstrated that selective photosynthesis of azobenzene can also be realised at elevated temperature (90 °C), by using a cheaper metal (Cu) supported on graphene (Table 1, entry 3). However, since the nitrobenzene reduction can be initiated at 80 °C without any catalyst (poor activity and selectivity), the use of an expensive graphene support in a reaction that is inefficient at RT, affects its commercial potential negatively. In addition, the supported plasmonic metal nanoparticle based photocatalysts (i.e., Au, Ag, and Cu) show a relatively poor efficiency for light absorption compared to their semiconductor counterpart, and the particle size of the metal would have to be controlled strictly to absorb photons with the desired energies.

A number of studies have reported on the photoreduction of nitroaromatic compounds, either by inorganic semiconductor photocatalysts or by the supported plasmonic metal nanoparticles (NPs), as shown in (Table 1). The photocatalyst producing azo- or azoxy-compounds at low temperatures typically contains a precious metal. For example, a rhodium containing photo-catalyst (SiO₂/CdS/Rh) converts nitrobenzene selectively to azoxybenzene under visible light irradiation. However, in addition to the low efficiency and poor selectivity, the use of the unstable and toxic CdS photocatalyst makes this process unfavourable for industrial applications (Table 1, entry 1). Azo-benzene can be successfully synthesised at room temperature (RT) by using a Au supported TiO₂ photocatalyst (Table 1, entry 2).

A recent study has demonstrated that selective photosynthesis of azobenzene can also be realised at elevated temperature (90 °C), by using a cheaper metal (Cu) supported on graphene (Table 1, entry 3). However, since the nitrobenzene reduction can be initiated at 80 °C without any catalyst (poor activity and selectivity), the use of an expensive graphene support in a reaction that is inefficient at RT, affects its commercial potential negatively. In addition, the supported plasmonic metal nanoparticle based photocatalysts (i.e., Au, Ag, and Cu) show a relatively poor efficiency for light absorption compared to their semiconductor counterpart, and the particle size of the metal would have to be controlled strictly to absorb photons with the desired energies.

### Results

#### Lab-scale nitrobenzene conversion

As described in Table 1, the selective conversion of nitrobenzene to azobenzene and azoxybenzene can be controlled by the irradiation wavelength (450 and 410 nm, entry 7 and 8). Surprisingly, an amorphous graphitic C₃N₄ compound (A-g-C₃N₄) characterised by a larger specific surface area is suitable for this selective conversion.

### Table 1 Possible products formed by photocatalytic reduction of nitroaromatic compounds and comparison of the conversion and selectivity of different photocatalysts

| Entry | Photocatalysts | Cost (€ g⁻¹) | Radiation | Temperature (°C) | Conversion (%) | Selectivity (%) |
|-------|----------------|-------------|-----------|-----------------|---------------|----------------|
| 1     | SiO₂/CdS/Rh⁵   | 7.7         | 436 nm, 25 h | RT              | 80            | 68             |
| 2     | Au/TiO₂⁶        | 14.4        | >430 nm, 12 h | 98             | 0             | 99             |
| 4     | TiO₂/N₂/Pt⁷     | 92.2        | >400 nm, 5 h | 90              | 98            | N/A            |
| 5     | Au/TiO₂-Ag⁸     | 7.6         | >450 nm, 10 h | RT             | >99           | 0              |
| 6     | N₂O/P/CdS⁹      | 6.2         | >420 nm, 24 h | RT             | 99            | 0              |
| 7     | g-C₃N₄⁵         | 0.1         | 450 nm, 12 h | 97              | 95            | 5              |
| 8     | g-C₃N₄⁵         | 0.1         | 410 nm, 5 h  | 95              | 96            | 94             |
| 9     | A-g-C₃N₄⁸      | 0.1         | 450 nm, 12 h | 95              | 99            | 0              |

1. High-pressure Hg lamp (0.007 W cm⁻²)⁴
2. 0.01 M KOH, 300 W Xe lamp (~430 nm, 0.01 W cm⁻²)⁴
3. 0.01 M KOH, 300 W Xe lamp (400-800 nm, 0.15 W cm⁻²)⁴
4. N₂ dyes on TiO₂ with Pt: triethanolamine (TEDA) as scavenger, 3 W 530 nm LED⁴
5. 500 W Xe lamp (450-600 nm, 0.083 W cm⁻²)²¹
6. 420 nm, 500 W Xe lamp (~430 nm, 0.01 W cm⁻²)⁴
7. 0.1 M KOH, 450 nm LED (440-460 nm, 0.03 W cm⁻²)²³
8. 0.01 M KOH, 410 nm LED (420-420 nm, 0.03 W cm⁻²)²³
9. 0.01 M KOH, 450 nm LED (440-460 nm, 0.03 W cm⁻²)²³

* Entry Photocatalysts Cost (€ g⁻¹) | Radiation | Temperature (°C) | Conversion (%) | Selectivity (%) | Azoxy- | Azo- | Aniline |
|-----|----------------|-------------|-----------|----------------|---------------|-------|------|--------|
| 1   | SiO₂/CdS/Rh⁵   | 7.7         | 436 nm, 25 h | RT              | 80            | 68             |
| 2   | Au/TiO₂⁶        | 14.4        | >430 nm, 12 h | 98             | 0             | 99             |
| 3   | Cu/Graphene⁷    | 92.2        | >400 nm, 5 h | 90              | 98            | N/A            |
| 4   | TiO₂/N₂/Pt⁷     | 57.1        | 530 nm, 24 h | RT             | >99           | 0              |
| 5   | Au/TiO₂-Ag⁸     | 7.6         | >450 nm, 10 h | RT             | 100           | 0              |
| 6   | N₂O/P/CdS⁹      | 6.2         | >420 nm, 24 h | RT             | 99            | 0              |
| 7   | g-C₃N₄⁵         | 0.1         | 450 nm, 12 h | 97              | 95            | 5              |
| 8   | g-C₃N₄⁵         | 0.1         | 410 nm, 5 h  | 95              | 96            | 94             |
| 9   | A-g-C₃N₄⁸      | 0.1         | 450 nm, 12 h | 95              | 99            | 0              |
surface area (112 m² g⁻¹) compared to that of g-C₃N₄ (49 m² g⁻¹) shows a negligible performance in photocatalytic nitrobenzene reduction under similar reaction conditions (Table 1, entry 9).

Under 410 nm irradiation, azobenzene is gradually formed in a two-step reduction reaction; firstly, nitrobenzene is converted to azoxybenzene, which is then subsequently reduced to azobenzene (Fig. 1a). In contrast, azoxybenzene has been found to be the main product throughout the 450 nm irradiation course (Fig. 1b). Under both irradiation conditions, the nitrobenzene reduction can reach high conversion (>95%) with high selectivity (>94%) without the formation of aniline. We estimate that the quantum efficiencies (QE) are 1.4 and 0.4% for the synthesis of azoxybenzene and azobenzene under 410 and 450 nm irradiation, respectively (Supplementary Equations 1 and 2). It should be noted that such QEs are relatively high considering that the reactions involve 6e⁻ and 8e⁻ charge transfer processes, respectively, to achieve azoxy- and azobenzene. We also observed that the selectivity to aniline remains very low (<5%) even under UV irradiation until most nitrobenzene molecules (>82%) had been converted (Supplementary Table 1).

**Up-scaling**. The photoconversion of nitrobenzene into the value-added azoxybenzene by using the g-C₃N₄ photocatalyst shows a huge potential for scaling-up to industrial level, both in terms of the nitrobenzene starting concentration and the reaction volume. As shown in Fig. 1c, the high selectivity and conversion observed at low nitrobenzene concentration (8 mM) are maintained at higher nitrobenzene concentrations (24 and 40 mM) under identical reaction conditions. We observed that prolonged irradiation times are required to reach full conversion (12, 60, and 168 h, for 8, 24, and 40 mM of nitrobenzene, respectively), which may be caused by the reduction of light transmission to the photocatalyst due to the increased light absorption of azoxybenzene.

Figure 1d and e depict the reactions scaled-up in volume (to 0.8 and 80 L corresponding to an 80 and 8000-fold volume increase compared to the lab-scale reactions) performed under solar irradiation (i.e., without the use of artificial light sources). The yellow catalyst suspension gradually turned orange, indicating the formation of azo- and azoxybenzene. The colour change of the liquid caused by the formation of azo- and azoxybenzene was even more obvious after centrifugation. Gas chromatography (GC) analysis reveals that the high selectivity (~90%) towards azoxybenzene was achieved for both up-scaled tests (Fig. 1f and g). The solar irradiation favours the formation of the same compound as that formed under blue light irradiation (450 nm, azoxybenzene), which suggests that the reduction of nitrobenzene to azoxybenzene is more favourable than that of the conversion of azoxybenzene to azobenzene. The formation of azobenzene will only take place when nitrobenzene has been fully converted to azoxybenzene. We estimate the QE of the 8000-fold
azoxybenzene can be synthesised with excellent conversion and selectivity from the \( p,\text{-}p \)-chloro-, \( p,\text{-}bromo-\), and \( p,\text{-}i\)odo nitrobenzene, respectively (Table 2, entries 1–6). Likewise, the \( o,\text{-}o \) ′-dichloro- and \( m,\text{-}m \)′-dichloro- substituted azo- and azoxybenzene can also be selectively synthesised from the corresponding \( o\),chloro nitrobenzene and \( m\)-chloro nitrobenzene (Table 2, entries 7–10). Furthermore, the photoconversion of \( p\)-nitrotoluene, \( p\)-nitroanisole and \( p\)-nitrobenzotrifluoride into their corresponding azo- and azoxybenzene can also be achieved with very high conversion and selectivity in a controlled manner (Table 2, entries 11–16). We have also examined the photoconversion of four di-substituted nitrobenzene precursors (\( p\)-Cl, \( m\)-F; \( p\)-Cl, \( m\)-CF\(_3\); \( p\)-CH\(_3\), \( m\)-CH\(_3\); and \( p\)-CF\(_3\), \( m\)-CF\(_3\)) (Table 2, entry 17–24). All of these di-substituted nitroaromatic compounds can be converted into their corresponding azo- and azoxy-aromatic products with high selectivity, indicating that more complicated azoxy- and azo-aromatic compounds can be synthesised via this approach. In addition, the photosynthesis of asymmetric azobenzenes can also be realised with a reasonable selectivity (Supplementary Table 6).

**Reaction mechanism.** We propose that the excellent performance of the \( g\text{-}C_3N_4 \) photocatalyst for nitrobenzene photo reductions can be associated with the efficient utilisation of photogenerated

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### Table 2 Photocatalytic reduction of various nitroaromatic compounds to azoxy- (I) and azo- (II) aromatic compounds using the \( g\text{-}C_3N_4 \) photocatalyst

| Entry | \( R \) | Light (nm) | Time (h) | Conversion (%) | Selectivity (%) | Ratio |
|-------|--------|------------|----------|----------------|-----------------|-------|
|       |        |            |          |                | I + II | Amine I | I + II | Amine II |
| 1     | \( p\)-Cl | 410        | 8        | 100            | 100 | 0     | 2     | 98      |
| 2     | \( p\)-Br | 410        | 12       | 100            | 100 | 0     | 92 | 8       |
| 3     | \( p\)-I  | 410        | 20       | 95             | 90 | 10    | 99 | 1       |
| 4     | \( o\)-Cl | 410        | 14       | 92             | 100 | 0     | 5 | 95      |
| 5     | \( m\)-Cl | 410        | 38       | 98             | 96 | 4     | 94 | 6       |
| 6     | \( p\)-CH\(_3\) | 410 | 60       | 100            | 100 | 0     | 4 | 96      |
| 7     | \( p\)-CF\(_3\) | 410 | 36       | 95             | 100 | 0     | 82 | 8       |
| 8     | \( m\)-CH\(_3\) | 410 | 12       | 100            | 100 | 0     | 82 | 92      |
| 9     | \( m\)-OCH\(_3\) | 410 | 20       | 96             | 91 | 9     | 72 | 93      |
| 10    | \( p\)-CF\(_3\) | 410 | 20       | 100            | 100 | 0     | 0 | 100     |
| 11    | \( p\)-CH\(_3\) | 410 | 40       | 90             | 100 | 0     | 93 | 7       |
| 12    | \( p\)-CF\(_3\) | 410 | 20       | 90             | 100 | 0     | 95 | 5       |
| 13    | \( p\)-Cl, \( m\)-F | 410 | 12       | 90             | 100 | 0     | 95 | 5       |
| 14    | \( p\)-Cl, \( m\)-CF\(_3\) | 410 | 30       | 90             | 100 | 0     | 95 | 5       |
| 15    | \( p\)-CH\(_3\), \( m\)-CH\(_3\) | 410 | 60       | 100            | 100 | 0     | 95 | 5       |
| 16    | \( p\)-CF\(_3\), \( m\)-CF\(_3\) | 410 | 22       | 90             | 100 | 0     | 95 | 5       |

General reaction conditions: 8 mM substrates, 30 mW cm\(^{-2}\) light intensity, 10 mM KOH, and 50 mg catalyst in 10 mL isopropanol under deaerated condition

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**Photoconversion of other nitroaromatic compounds.** By tuning the irradiation wavelength of the light sources, we have further demonstrated the versatility of the \( g\text{-}C_3N_4 \) catalyst for controlled photoconversion of various nitroaromatic compounds into their corresponding azoxy- or azo-compounds (Table 2). The compounds \( p\),\text{-}p′-dichloro-, \( p\),\text{-}p′-dibromo-, and \( p\),\text{-}p′-iodoazo- and azoxybenzene can be synthesised with excellent conversion and selectivity from the \( p\)-chloro-, \( p\)-bromo-, and \( p\)-iodo nitrobenzene, respectively (Table 2, entries 1–6). Likewise, the \( o\),\text{-}o′-dichloro- and \( m\),\text{-}m′-dichloro- substituted azo- and azoxybenzene can also be selectively synthesised from the corresponding \( o\)-chloro nitrobenzene and \( m\)-chloro nitrobenzene (Table 2, entries 7–10). Furthermore, the photoconversion of \( p\)-nitrotoluene, \( p\)-nitroanisole and \( p\)-nitrobenzotrifluoride into their corresponding azo- and azoxybenzene can also be achieved with very high conversion and selectivity in a controlled manner (Table 2, entries 11–16). We have also examined the photoconversion of four di-substituted nitrobenzene precursors (\( p\)-Cl, \( m\)-F; \( p\)-Cl, \( m\)-CF\(_3\); \( p\)-CH\(_3\), \( m\)-CH\(_3\); and \( p\)-CF\(_3\), \( m\)-CF\(_3\)) (Table 2, entry 17–24). All of these di-substituted nitroaromatic compounds can be converted into their corresponding azo- and azoxy-aromatic products with high selectivity, indicating that more complicated azoxy- and azo-aromatic compounds can be synthesised via this approach. In addition, the photosynthesis of asymmetric azobenzenes can also be realised with a reasonable selectivity (Supplementary Table 6).
when using the g-C₃N₄ photocatalyst, whereas the A-g-C₃N₄ sample and pristine TiO₂ (Degussa Aerosil® P25) showed much slower rates in O₂ depletion. We have further rationalised that such efficient reduction can be linked to the adsorption energy of the surface adsorbed hydrogen atoms (H_ads) that was generated by isopropanol oxidation during irradiation, as probed by post-mortem temperature programmed desorption (TPD, Fig. 2b and Supplementary Fig. 12). The pre-irradiated (3 h under reaction-like conditions without nitrobenzene) and subsequently vacuum dried g-C₃N₄ sample showed no H₂ desorption peak. This indicates that H_ads is only adsorbed weakly on the catalyst surface, enabling it to react rapidly with the surface adsorbed nitrobenzene to form azo- or azoxy-benzene (Fig. 2c). In contrast, the A-g-C₃N₄ sample prepared identically showed two H₂ desorption peaks, suggesting a relatively strong adsorption of the photogenerated H_ads on A-g-C₃N₄, which prevents the use of the H_ads for efficient reduction reactions. The in-situ X-ray photoelectron spectroscopy analysis (XPS, Supplementary Fig. 13) also confirms that the H_ads binds strongly on the A-g-C₃N₄ surface, resulting in a significant shift of the N1s peak. In contrast, the N1s peak of g-C₃N₄ remains unchanged upon irradiation, indicating that the H_ads only loosely binds to the g-C₃N₄ surface, thus, making the catalyst ideal for the nitrobenzene reduction (Supplementary Fig. 13). In addition, the N1s peak intensity also remains unchanged, indicating that nitrogen does not leach out from the g-C₃N₄ catalyst. Furthermore, the g-C₃N₄ shows a significantly higher photocurrent compared to that of A-g-C₃N₄, indicating that the charge separation is also promoted by the ordered structure of g-C₃N₄ (Supplementary Fig. 14).

We have further explored the origin behind the high selectivity of the nitroaromatic photoversion into azoxy- or aza-aromatics by probing the photo reaction of the intermediates (Fig. 2d and Supplementary Table 4). Since all reactions were performed under deaerated conditions, we have ruled out the pathway involving initial reduction to aniline followed by partial oxidation to azo-/azoxy benzene. This has been also confirmed experimentally by a control reaction starting with aniline, where no N-N coupling products were formed under irradiation. According to previous mechanistic studies, nitrobenzene undergoes a gradual photocorrection process during which nitrosobenzene (NBS) and N-phenylhydroxylamine (NPH) are initially formed27,28. The NBS and NPH will then be further reduced to azo- and aza-aromatics via path (I) or to amines via path (II). The as-formed azo-aromatics may also get photoreduced into amines via path (III). We have observed that the photoreduction of NBS or of an NBS/NPH mixture (1:1 in molar ratio) results exclusively in the formation of azo- and azoxybenzene (conversion >97%) when g-C₃N₄ was used as photocatalyst. In contrast, the photoreduction of NBS exhibits a non-selective
behaviour when TiO₂ was used as photocatalyst ([azobenzene+ azoxybenzene]: amine = 44:56). The presence of NPH in the reaction (NBS: NPH = 1:1) further drives the reaction to favour the formation of the amine ([azobenzene + azoxybenzene]: amine = 18:82). Surprisingly, the photoreduction of azobenzene to amine (path III) has been found to be inactive for both g-C₃N₄ and TiO₂. These control experiments suggest that the g-C₃N₄ photocatalyst facilitates the N–N coupling of NBS and NPH (path I) and inhibits the reduction of NBS and NPH (path II), thus resulting in a high selectively of the nitroaromatic photoconversion into azo- and azoxy-aromatic products. Since the affinity of the aromatic molecules can be enhanced by π-π coupling effect of the tri-s-triazine unit in g-C₃N₄, we consider that the photogenerated NBS and NPH are co-adsorbed on the g-C₃N₄ surface, thus, promoting the N-N coupling for the formation of azo- and azoxy-compounds (path I). In contrast, other photocatalysts (i.e., TiO₂) without such π-π bonding interaction possibly facilitates the reduction via path (II) to form amines.

**Discussion**

The redox potentials of isopropanol/acetone and nitrobenzene/azoxybenzene, respectively, are ~0.1 and ~0.8 V as referenced to the standard hydrogen electrode (SHE)³¹,³². Therefore, the photoexcited e⁻ in the conduction band (CB) of g-C₃N₄ is energetically favourable to initiate the nitrobenzene reduction, as depicted in Fig. 3a. Meanwhile, the isopropanol that serves as the electron donor will be oxidised into acetone, resulting in the formation of two protons and the injection of two electrons into the valence band (VB) to fill the hole (h⁺). Since previous calculations reveal that the highest occupied molecular orbital (HOMO, equivalent to the VB) of the g-C₃N₄ mainly originates from the p-orbital of the two-coordinated N atoms, it is reasonable to speculate that the oxidation of isopropanol takes place on these sites (Fig. 3b)³³. It should also be noted that the negatively charged surface of g-C₃N₄ under basic conditions³⁴ is beneficial for the deprotonation of isopropanol, thus, an improved nitrobenzene conversion is expected due to the enhanced isopropanol oxidation.

We have further explored the possible active sites for the nitrobenzene reduction reaction by employing semi-empirical MO PAC2016 calculations, to estimate the relative adsorption energies of H pairs (two H atoms) on a model crystalline g-C₃N₄ structure consisting of two H-bonded strips with 6 melem units (Supplementary Fig. 15). Since the nitrobenzene reduction requires removal of oxygen by two H atoms through the formation of H₂O, we have evaluated the relative stability of adsorbed H pairs to see if they will identify any significant sites for the reduction. In general, the H-atom pairs are found to be less stable on the crystalline g-C₃N₄ surface (ΔG_H > 0) compared to free H₂, which agrees well with our post-mortem TPD results (Supplementary Table 5). The H pairs prefer to be adsorbed close to each other instead of further apart on the same melem unit, and the most stable adsorption sites are found to be the C-N bond adjacent to a bridging N atom (~ 0.5 eV) and the two-coordinated N atoms in the same ring adjacent to the bridging N atoms between melem units (~ 0.9 eV), as indicated in the Fig. 3(c). Therefore, we speculate that these possible hydrogen adsorption sites are the active sites for the nitrobenzene reduction. In addition, we found that the C-N binding configuration upon H adsorption becomes more stable when occurring on the corner melem unit, where it is only 0.1 eV less stable than free H₂. This could point to even more highly labile H₂ adsorption sites at the edges of the melem strips in real g-C₃N₄. A list of selected adsorption energies are provided in Supplementary Table 5.

Herein, we report on a photocatalytic strategy for controllable and efficient synthesis of a series of industrially important azo- and azoxy-aromatic compounds from their corresponding nitroaromatic precursors under visible light irradiation at RT. The g-C₃N₄ photocatalyst facilitates the light driven N-N coupling of the nitroaromatics, and the weakly adsorbed photogenerated H_ads atoms contribute to the excellent catalytic performance in the multi-electron transfer process. We anticipate that the possibility of scaling-up the reaction with respect to both concentration and volume, and the use of the inexpensive g-C₃N₄ photocatalyst makes the reaction attractive for industrial applications.

**Methods**

**Sample preparations.** The g-C₃N₄ photocatalyst was synthesised via conventional pyrolysis of urea at 550 °C, and the A–G–C–N₄ sample was obtained by post heating of the g-C₃N₄ at 630 °C (Supplementary Fig. 1).

**Price estimation of the photocatalysts.** The prices of photocatalysts listed in Table 1 were estimated according to the catalyst compositions presented in the cited studies (Supplementary Table 2).

**Materials characterisations.** Transmission electron microscopy (TEM), N₂ adsorption-desorption isotherm, X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), and diffuse reflectance spectrometry (DRS) were used for material characterisation (Supplementary Figs 8–11 and Supplementary Table 3). In-situ XPS and post-mortem TPD were performed to analyse the oxidation state change of N and the bond strength of the H_ads to the catalyst surface under reaction conditions (Supplementary Figs 12 and 13). MS (Supplementary Figs 4 and 5) and gas chromatography (GC) were used to investigate the reaction mechanism.

**Photocatalytic process analysis.** A home-built vacuum-gas line was used to perform the photocatalytic reactions (Supplementary Figs 2 and 3). GC was used to determine the concentrations of the reactants and the products.

**Calculations.** The semi-empirical molecular orbital geometry optimisations were performed in MOPAC2016, all using the PM7 Hamiltonian (Supplementary Fig. 15 and Supplementary Table 5)³⁶. All details can be found in the Supplementary Methods and Supplementary Discussion.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon request.

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