

Metal-Free Photoredox Upcycling of Chemically Diverse Plastics and Mixed Plastics into High-Value Chemicals under Visible Light

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Abstract: The growing accumulation of plastic waste poses a major global environmental challenge, yet existing chemical recycling technologies remain constrained by high energy demand, narrow substrate scope, intolerance to poly(vinyl chloride) (PVC) and mixed plastic waste, and heavy reliance on precious, toxic, or base-metal catalysts. Here, we report a metal-free, defect-engineered polymeric carbon nitride photocatalyst containing tri-coordinated nitrogen vacancies and oxygen-linked heptazine units (O-V_N-CN) that confronts this challenge under visible light and ambient conditions. Our developed O-V_N-CN catalyst converts chemically distinct commodity plastics, including aliphatic polypropylene (PP), aromatic polystyrene (PS), and halogenated PVC, both individually and as a ternary mixture, into value-added chemicals under a unified set of reaction conditions without substrate-specific modification. Notably, the co-upcycling of ternary PP/PS/PVC mixture represents, to the best of our knowledge, the first demonstration of photocatalytic upcycling of mixed plastics using a recyclable, metal-free heterogeneous photocatalyst under ambient conditions. Mechanistic and computational investigations reveal that the co-existence of tri-coordinated nitrogen vacancies and oxygen-linked heptazine units creates shallow electron-trapping states that enhance visible light absorption, promote charge separation and interfacial transfer, and facilitate the activation of O₂ to •O₂⁻ that actively participates in the C–C bond cleavage and breaks down the polymer chains into value-added small molecules. Synthesized from cheap, abundant urea and ammonium acetate by simple calcination, the catalyst offers a potentially scalable, green and economically compelling route to closing the plastics carbon loop.

Keywords: plastic upcycling; C-C bond cleavage; defect-engineered catalyst; mixed plastics; photocatalysis

1. Introduction

Plastics have become indispensable to modern society. The annual production of plastics has grown exponentially, surging from less than 2 million tonnes in the 1950s to 368 million

tonnes in 2019,^{1,2} and global output is projected to double within the next two decades.³ Despite this enormous production, only 9% of global plastic waste was recycled in 2019; 19% was incinerated, while the remaining 72% accumulated in the environment.⁴ Strategically valorizing plastic waste as

a feedstock for chemicals and energy could simultaneously (i) reduce environmental pollution, (ii) conserve finite fossil resources, (iii) mitigate climate change by offsetting carbon emissions, and (iv) accelerate the transition to a circular economy. Through the transformation of plastic waste into fuels, chemicals, and monomers, we can minimize environmental waste, recover material value, and reduce reliance on virgin resources, supporting sustainable development by closing the loop on plastic usage. Typically, recycling one tonne of plastic conserves roughly 130 million kJ, equivalent to the energy produced by burning 22 barrels of oil. Scaled globally, an efficient plastic recycling technology could save around 3.5 billion barrels of oil, leading to an annual financial saving of about US\$176 billion.⁵

Plastic recycling involves four key approaches: primary (closed-loop), secondary (mechanical), tertiary (chemical), and energy recovery (incineration).⁶ Conventional plastic recycling relies predominantly on mechanical recycling, which generally requires well-sorted and sufficiently clean plastic.⁷ Besides, recycled plastics often possess lower quality than virgin materials, with decreased molecular weights and inferior thermal and mechanical properties. Chemical recycling and upcycling offer an alternative by transforming polymers into monomers, platform chemicals, or other value-added products.⁸ However, these transformations remain fundamentally challenging because many commodity plastics contain chemically stable and kinetically inert C–C backbones.⁹ Conventional thermochemical processes typically require high temperatures and pressures to activate these bonds, leading to substantial energy consumption and limited product selectivity.¹⁰

This challenge becomes considerably more complex for compositionally mixed plastic waste. Most catalytic processes are optimized for a single polymer because different plastics possess distinct backbone structures, substituents, bond dissociation energies, and degradation pathways.¹⁰ Consequently, a reaction environment that effectively activates one polymer may be ineffective or even incompatible with another.¹¹ This chemical disparity is exemplified by polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS), three widely used addition polymers with markedly different structural characteristics. PP contains a saturated, methyl-substituted hydrocarbon backbone dominated by inert C–C and C–H bonds, whereas PS contains pendant aromatic groups that alter radical stability and oxidative cleavage pathways.¹² PVC presents an additional challenge because cleavage of its C–Cl bonds and dehydrochlorination can generate chloride-containing species that corrode equipment, poison catalysts, or interfere with the conversion of coexisting polymers.¹³ Within a mixed-plastic feedstock, these chemically distinct polymers may compete for catalytic active sites and reactive oxygen species, undergo oxidation at substantially different rates, and generate mutually interfering intermediates.¹⁴ Their simultaneous conversion

therefore requires a sufficiently versatile catalytic system to activate chemically distinct polymer backbones, tolerate chlorine-containing species, and direct divergent reaction pathways toward value-added products under a common set of reaction conditions.

Photocatalysis offers a promising approach to plastic upcycling by using light-generated charge carriers and reactive radical species to activate strong chemical bonds under comparatively mild conditions.^{15,16} Modern semiconductor photocatalysis traces back to the seminal 1972 report by Fujishima and Honda on photoelectrochemical water splitting using an illuminated TiO₂ electrode,¹⁷ which established that band-gap excitation can drive thermodynamically uphill chemistry under ambient conditions. Just nine years later, Kawai and Sakata reported the first photocatalytic decomposition of plastics, converting poly(vinyl chloride) and other solid wastes into H₂ over a Pt/TiO₂ photocatalyst,¹⁸ representing the foundational milestone of all subsequent photocatalytic plastic conversion work. The introduction of metal-free graphitic carbon nitride (g-C₃N₄) photocatalyst by Domen and co-workers in 2009¹⁹ marked a major advance in the development of inexpensive, polymer-based semiconductors, while the contemporaneous emergence of visible-light organophotoredox catalysis from the groups of MacMillan,²⁰ Yoon,²¹ and Stephenson²² reshaped how single-electron-transfer manifolds are accessed under mild conditions.

Complete photocatalytic mineralization of plastics typically yields CO₂ and H₂O. Since CO₂ is a greenhouse gas, upcycling plastics into valuable products represents a more sustainable goal. The following representative works define the present frontier. To escape the energy penalty of pyrolysis, Scott and co-workers achieved a landmark by using Pt/ γ -Al₂O₃, a noble-metal-based catalyst, to convert polyethylene into liquid alkylaromatics at 280 °C.²³ Subsequently, the Chen group introduced solar-thermal catalysis, lowering the depolymerization temperature of polyesters to 150 °C.²⁴ In a pioneering ambient-temperature work, Reisner and co-workers employed Cd-based CdS/CdO_x quantum dots to upcycle polyurethane, polylactic acid and PET,²⁵ however requiring 10 M NaOH pretreatment to partially hydrolyze the plastics into monomers before photocatalytic reactions. Remarkably, Soo and co-workers demonstrated upcycling of plastics with resin codes 2–7 without pre-treatment using commercially sourced vanadium(III) acetylacetonate but with a long reaction duration of 4 to 7 days.²⁶ Moving to metal-free systems, McInnes and co-workers upcycled PS to benzoic acid, formic acid and acetophenone using p-toluenesulfonic acid in carcinogenic benzene solvent.²⁷ Ma and co-workers used graphitic carbon nitride for PS upcycling,²⁸ however requiring an impractical 2.5:1 catalyst-to-plastic ratio at 150 °C. Critically, all of these works process a single plastic per reaction. Li and co-workers reported a breakthrough mixed-plastics-to-methane conversion but required a costly single-

atom Ru catalyst with high-temperature H_2 pre-treatment,²⁹ and Ma and co-workers processed PVC/PET simultaneously using metal-based $ZnCl_2$ and a toxic chlorine-containing ionic liquid.³⁰ Therefore, a recyclable, inexpensive, metal-free photocatalytic system capable of upcycling chemically distinct PP, PVC, and PS individually and as mixed plastic feedstocks under the same reaction conditions has yet to be established.

Building on the recent advances from the Loh group on metal-free, recyclable visible light photoredox catalysis,³¹ herein, we report a metal-free heterogeneous organophotoredox system for the upcycling of chemically distinct PP, PS, PVC and their ternary mixture into value-added chemicals under visible light irradiation at ambient conditions. This was realized through our rationally designed surface-defect-engineered polymeric carbon nitride bearing tri-coordinated nitrogen vacancies and oxygen-linked heptazine units (O- V_N -CN). Comprehensive structural, electronic, and photophysical analyses reveal that the concurrent regulation of vacancy defects and interunit oxygen linkages generates defect-associated electronic states, promotes visible light harvesting, and facilitates photogenerated charge carrier separation and oxygen activation. In contrast, pristine carbon nitride without structural modification shows minimal activity under identical reaction conditions. To the best of our knowledge, this is the first demonstration of photocatalytic upcycling of mixed plastics using a recyclable, metal-free heterogeneous photocatalyst under ambient conditions.

2. Experimental procedures

2.1. Chemical reagents

For the synthesis of photocatalysts, analytical grade urea ($\geq 99.0\%$) and ammonium acetate ($\geq 97.0\%$) were purchased from Sigma-Aldrich. Polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), and 1,2-dichloroethane (DCE) were also purchased from Sigma Aldrich and used as received without any purification. Oxygen (99.8% purity) was supplied by Leeden National Oxygen Ltd. Deionized water ($>18\text{ M}\Omega\cdot\text{cm}$ resistivity) was used in the experiments wherever mentioned.

2.2. Synthesis of O- V_N -CN, V_N -CN and CN photocatalysts

The surface-engineered carbon nitride with tri-coordinated nitrogen vacancies and O-linked heptazine units (denoted as O- V_N -CN) was facilely prepared as follows: In a typical synthesis, 40 g of urea was mixed with 2 g of ammonium acetate by grinding until the solid mixture was homogeneous. The resulting solid was placed into porcelain crucibles, covered, and transferred to a muffle furnace before being subjected to calcination at 550°C for 4 h in air with a ramping rate of $5^\circ\text{C}/\text{min}$. After the furnace cooled down naturally to room temperature, the solids were ground and underwent a second-step heat

treatment in air at the same ramping rate and temperature for 2 h. Finally, the sample was collected and ground. For comparison, the control sample with nitrogen vacancies but without O-doping (denoted as V_N -CN) was synthesized using the same procedures, except it was only subjected to one-step calcination. Another control sample, pristine carbon nitride without surface modifications (denoted as CN) was synthesized following the same procedures as V_N -CN, except that ammonium acetate was not added.

2.3. Materials characterization

The surface morphology and elemental composition of our developed samples were revealed through transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) mapping using a FEI Tecnai G2 20 S-Twin operating at an accelerating voltage of 200 kV. For the preparation of TEM specimens, the solid samples were dispersed in ethanol, and a drop of the sample suspension was placed onto the copper grid. The powder X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (Bruker D8 Discover) with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The chemical environment of the samples was analyzed using X-ray photoelectron spectroscopy (XPS) with a Phoibos 100 spectrometer (SPECS, Germany) with a monochromatic Al- $\text{K}\alpha$ X-ray source. Prior to deconvolution, the binding energies were calibrated by setting the C 1s signal from adventitious carbon to 284.6 eV. To determine the specific surface area of the samples, a multipoint Brunauer-Emmett-Teller (BET) N_2 adsorption-desorption isotherm was performed at 77 K using a Micromeritics ASAP 2020. Prior to the analysis, the samples were degassed at 150°C for 8 h to remove adsorbed species. The elemental compositions of the samples were determined using an elemental analyzer (Elementar UNICUBE). Steady-state photoluminescence (PL) spectra of the samples were recorded with a fluorescent spectrometer (Perkin Elmer LS55). Electron paramagnetic resonance (EPR) spectra were recorded with a continuous-wave X-band Bruker ELEXSYS E500 EPR spectrometer at a center field of 3,521 G, sweep width of 250 G, and microwave frequency of 9.87 GHz. The optical properties of the photocatalysts were elucidated from an Agilent Cary 100 Ultraviolet-Visible (UV-vis) spectrophotometer equipped with an integrating sphere, with a scanning range of 200–800 nm.

2.4. Photoelectrochemical analysis

The photoelectrochemical properties of the samples were assessed using a Metrohm Autolab electrochemical workstation. The setup involved a standard three-electrode quartz cell, comprising a Pt rod and Ag/AgCl saturated with KCl as counter and reference electrodes, respectively. The working electrode was prepared by coating a fluorine-doped tin oxide (FTO) coated glass slide with the sample suspension in ethanol, covering an electroactive area of $1\text{ cm} \times 1\text{ cm}$. Throughout the

experiments, these three electrodes were immersed in an electrolyte comprised of 0.5 M Na₂SO₄ at pH 7. The visible light source was provided by a 500 W Xenon arc lamp (CHF-XM-500 W) equipped with a UV cut-off filter to eliminate wavelengths below 400 nm.

2.5. Density functional theory (DFT) calculations

Density functional theory (DFT) calculations were carried out using the Vienna *ab initio* Simulation Package (VASP, version 6.1.0).^{32,33} The electron-ion interactions were represented using the projector-augmented wave (PAW) method.³⁴ Electron exchange and correlation were described using the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional (GGA-PBE).³⁵ A $3 \times 3 \times 1$ Monkhorst–Pack mesh was used to sample the Brillouin zone, and the kinetic-energy cutoff for the plane-wave basis set was fixed at 400 eV. The electronic energy convergence criterion was set to 10^{-5} eV. All structures were fully relaxed until the residual force on each atom was less than $0.03 \text{ eV } \text{\AA}^{-1}$. The optimized structural models are presented in figures in Section 3.4 and Figure S7 and S8.

The Gibbs free-energy change for each elementary reaction step was determined using:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE represents the electronic-energy difference between the reactants and products of each elementary reaction step, while ΔZPE and ΔS represent the corresponding changes in zero-point energy and entropy, respectively. The zero-point energies of the adsorbed intermediates were derived from vibrational-frequency calculations.

2.6. Photocatalytic upcycling of plastics

In a typical experiment, 300 μmol of the single repeat unit of plastic resin was added to a 15 mL Schlenk tube containing 5 mL of DCE solvent and 5 mg of our developed photocatalyst. The Schlenk tube was then connected to a balloon filled with O₂, and the reaction mixture was subjected to blue LED irradiation (two units, 50 W, $\lambda_{\text{max}} = 448 \text{ nm}$) with continuous stirring at room temperature. The product yields were quantified after 24 h of reaction. A series of plastic resins, including PVC, PS, and PP were evaluated under identical experimental conditions. The applicability of the photocatalytic system to mixed plastic feedstocks was further evaluated using a ternary mixture of PS, PP, and PVC. For mixed plastics upcycling, PS, PP, and PVC (0.3 mmol each) were transferred to the same Schlenk tube containing 5 mL of DCE and 5 mg of photocatalyst. While more plastics were loaded into the Schlenk tube, the catalyst loading and the volume of solvent remained unchanged. Similarly, photoreactions were performed under identical conditions, and the product yields were quantified after 24 h of photoreaction using NMR spectroscopy with pivalic acid serving as the internal standard. All plastic conversion

experiments were conducted in an air-conditioned laboratory. The LEDs were equipped with heat sinks and external cooling fans were positioned to face the reaction mixtures to dissipate the heat generated during irradiation and maintain the reaction temperatures within the range of 25–30 °C.

3. Results and discussion

To determine whether concurrent control over the defect chemistry and interunit bonding configuration of polymeric carbon nitride could overcome the limited activity of the pristine material toward plastic C–C bond cleavage, we developed three metal-free photocatalysts, which are pristine graphitic carbon nitride (CN), carbon nitride with artificially induced tri-coordinated nitrogen vacancies (V_N-CN), and carbon nitride with the co-existence of tri-coordinated nitrogen vacancies and oxygen-linked heptazine units (O-V_N-CN). With the presence of ammonium acetate during the thermal polymerization of urea and additional thermal treatment in air, the effects associated with nitrogen deficiency and subsequent oxygen incorporation on the photocatalytic plastic upcycling performance will be evaluated progressively. Figure 1 summarizes the overall scope of the study.

3.1. Photocatalytic upcycling of chemically distinct and mixed plastics

We first established the photocatalytic reaction conditions using PS as a representative substrate. PS provides a structurally well-defined aromatic polymer platform from which both aromatic and C1 oxidation products can be readily tracked, enabling the catalytic performance and product evolution to be systematically evaluated. Initial screening experiments (Table S1) established that O₂-rich conditions, blue-light irradiation ($\lambda_{\text{max}} = 448 \text{ nm}$), and a catalyst loading of 5 mg were the standard conditions for subsequent evaluation. Under the optimized conditions at room temperature, PS was converted into formic acid, benzoic acid, and acetophenone within 24 h (Figure 2a), demonstrating that cleavage of the polymer backbone can proceed under mild conditions with visible light as the only energy input to drive the reaction. The reaction exhibited a pronounced dependence on the solvent environment (Figure 2b). Among the solvents examined, appreciable product formation was observed predominantly in the chlorinated solvents DCE and DCM, with DCE affording the highest photocatalytic activity, whereas EA, THF, EtOH, MeCN, DMSO, and acetone resulted in negligible PS conversion. Since the inactive solvents span a broad range of polarities, this suggests the pronounced solvent dependence is unlikely to be governed by solvent polarity. Instead, it may arise from the favorable polymer-solvent interactions that promote PS chain accessibility, thereby facilitating interfacial contact with the heterogeneous photocatalyst and molecular oxygen. Nevertheless, DCE is a chlorinated solvent with recognized environmental concerns, which must be handled with care during experiments.

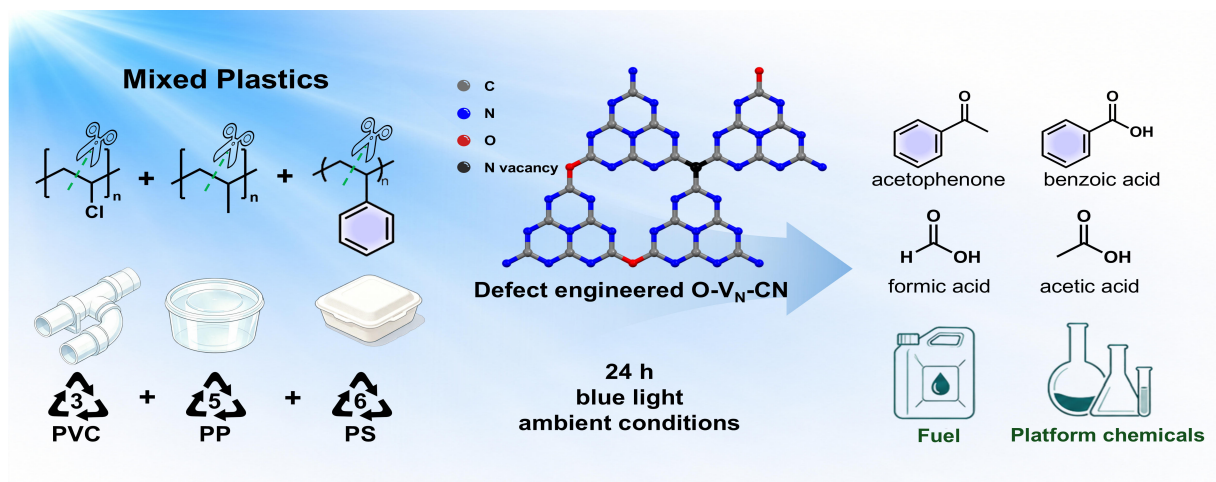


Figure 1. Schematic overview of the metal-free photocatalytic upcycling of mixed plastics into value-added chemicals over O-V_N-CN catalyst under visible light irradiation at ambient conditions.

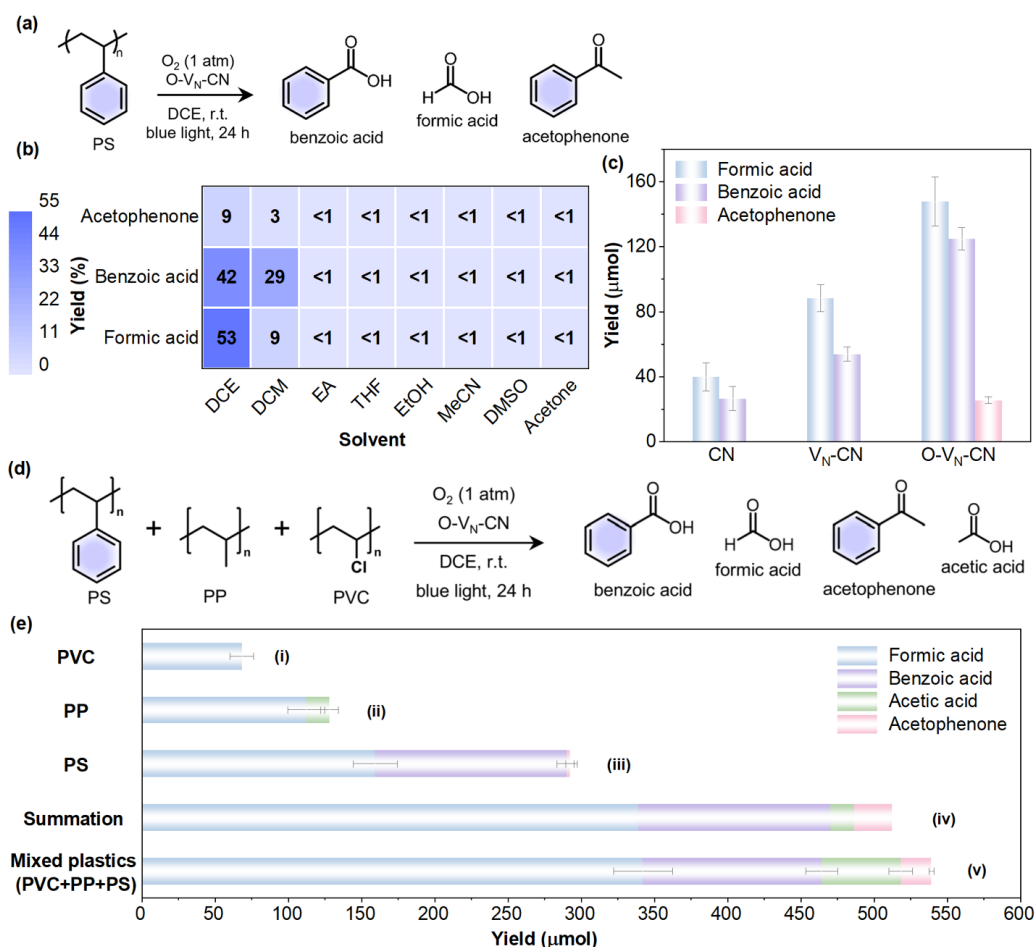


Figure 2. (a) Photocatalytic upcycling of PS into benzoic acid, formic acid, and acetophenone. (b) Effect of solvent on the product yields from PS conversion. (c) Comparison of the photocatalytic activities of CN, V_N-CN, and O-V_N-CN toward PS conversion. (d) Photocatalytic co-upcycling of a ternary mixture of PS, PP, and PVC. (e) Product distributions obtained from the individual conversion of (i) PVC, (ii) PP, and (iii) PS, (iv) theoretical summation of the products from the three individual-polymer reactions, and (v) experimental conversion of the ternary PS/PP/PVC mixture containing 0.3 mmol of each polymer. Experimental data are presented as the mean of three independent runs, with error bars representing the standard deviation.

With the reaction conditions established, we next investigated how structural modification of the photocatalyst influences PS upcycling (Figure 2c). Pristine CN exhibited only modest activity, whereas introducing tri-coordinated nitrogen vacancies in V_N -CN substantially improved product formation. Further structural modification to generate O- V_N -CN with oxygen-linked heptazine frameworks resulted in the highest photocatalytic activity, affording 148 μmol (49.3%) of formic acid, 125 μmol (41.6%) of benzoic acid, and 25.6 μmol (8.5%) of acetophenone after 24 h of visible light illumination (Figures 2c and S1). In particular, O- V_N -CN afforded approximately 2.3- and 4.7-fold higher benzoic acid yields than V_N -CN and pristine CN, respectively. The formation of acetophenone was detected only in the reaction using the O- V_N -CN photocatalyst, showing that co-engineering the catalyst changes not only the extent of conversion, but also the accessible product distribution. To confirm the products were generated from the photocatalytic reactions, a series of control experiments were carried out under three different conditions: (i) without light irradiation, (ii) without oxygen, and (iii) without photocatalyst. In all cases, a negligible amount of products was formed (Figure S2), attesting that the photocatalyst, oxygen, and light are prerequisites for the formation of formic acid, benzoic acid, and acetophenone.

Notably, the high photocatalytic activity exhibited by O- V_N -CN in chlorinated DCE prompted us to examine PVC, which remains particularly challenging for catalytic valorization because chloride species and HCl released during conversion can corrode reaction systems and poison metal-based catalysts.³⁶ Remarkably, O- V_N -CN converted PS, PP, and PVC (Table S2) under the same ambient photocatalytic conditions despite the distinct chemical structures of the polymers (Figure 2e). The product distributions reflected the structures of the parent polymers: styrenic PS afforded formic acid, benzoic acid, and acetophenone; PP yielded predominantly formic and acetic acids; and PVC produced formic acid as the major quantified product. These substrate-dependent product distributions demonstrate selective depolymerization and oxidation pathways governed by the molecular structures of the parent polymers, rather than complete mineralization into CO_2 and H_2O .

As is widely accepted, co-upcycling of mixed plastics is a significant challenge, with most existing studies confined to single-component feeds. PVC-containing feeds are particularly problematic; hence extensive separation and sorting are typically required to avoid catalyst deactivation. Encouraged by the tolerance of O- V_N -CN for PVC conversion, we further challenged O- V_N -CN with a ternary mixture of PS + PP + PVC (Figure 2d). Each polymer was introduced at the same loading (0.3 mmol each) as in its individual reaction, while the photocatalyst loading and solvent volume remained unchanged, resulting in a threefold increase in total plastic loading. Remarkably, the mixed feedstock was simultaneously converted into

formic acid, benzoic acid, acetic acid, and acetophenone, with product amounts comparable to the theoretical summation of the corresponding individual-plastic reactions (Figure 2e). This indicates that combining the three plastics did not substantially suppress the formation of the quantified products under the tested conditions. It also demonstrates the tolerance of our photocatalytic system to PVC and mixed plastic streams, suggesting its potential to reduce the need for extensive upstream sorting. As far as we know, this work represents the first demonstration of the photocatalytic co-upcycling of mixed plastics using a heterogeneous, metal-free, and recoverable photocatalyst. This was achieved through a facilely synthesized, scalable, and inexpensive O- V_N -CN catalyst, highlighting its potential as a green and sustainable catalyst for plastic waste valorization.

3.2. Morphology and structural characterization

To elucidate the superior performance of the O- V_N -CN catalyst, we systematically conducted a series of materials characterizations to reveal the chemical, physical, structural, electronic, and optical properties of our developed catalysts, aiming to uncover the reasons behind the photocatalytic enhancement. As disclosed by TEM images (Figures 3a and S3a), pristine CN formed by direct calcination of urea exhibited the characteristic stacked layered structure of graphitic carbon nitride. Upon the introduction of ammonium acetate during thermal polymerization, V_N -CN retained the overall layered morphology but displayed a more loosely stacked and porous structure (Figure S3b), suggesting that gas evolution during thermal treatment disrupted the compact stacking of the carbon nitride layers. Following the second-step thermal treatment in air, O- V_N -CN underwent more pronounced morphological reconstruction and appeared as highly exfoliated nanosheets with rough and curled edges (Figure 3b,c). In addition, the nearly transparent appearance of O- V_N -CN suggests its ultrathin thickness, which shortens photogenerated charge carrier diffusion paths to facilitate the transportation of charge carriers from the interior to the surface for redox reactions to take place. Meanwhile, the rough and curved edges, formed as a result of minimizing surface energy and van der Waals forces to maintain structural stability, are beneficial for photoreactions, as these rough edges can serve as surface active sites. Furthermore, numerous pores were observed on the exfoliated nanosheets (Figure 3d), indicating the pivotal role of ammonium acetate as a gas bubble template, in which the pores were generated by the gases released during the acylation reaction between urea and ammonium acetate, along with the delamination of stacked sheets to enlarge the surface exposure for photoreactions. The EDX mapping of O- V_N -CN reveals the co-existence of C, N, and O elements, which are distributed homogeneously throughout the sample (Figure 3e-h). Since graphitic carbon nitride should contain only C and N elements,

the presence of additional O elements suggests that the introduction of ammonium acetate in the thermal polymerization

process of urea leads to the introduction of foreign oxygen atoms into the structure.

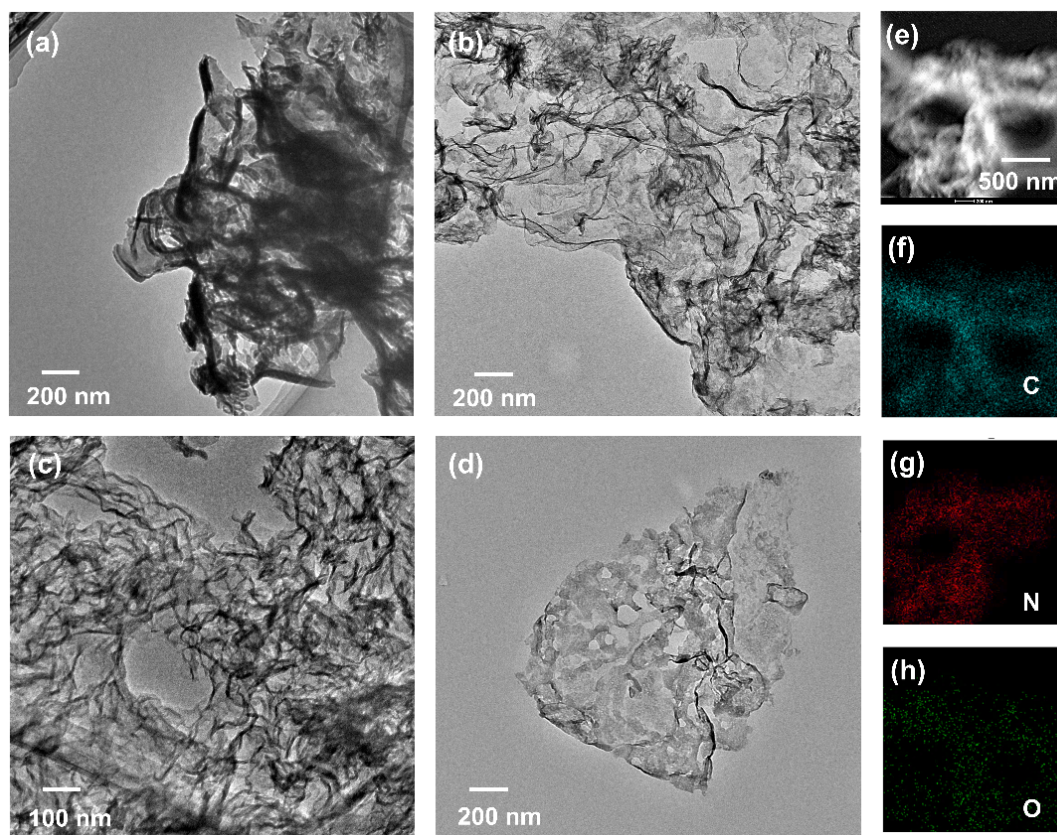


Figure 3. TEM images of (a) CN and (b–d) O-V_N-CN. (e) STEM image of O-V_N-CN and the corresponding EDX mapping showing (f) C, (g) N, and (h) O elements.

The porous, ultrathin structure of O-V_N-CN endows it with good textural properties, as evidenced by the BET analysis. The BET specific surface areas and pore size distributions of our developed photocatalysts were determined by the nitrogen adsorption-desorption isotherms. Based on Figure 4a, all the samples exhibited a Type III isotherm with an H3 hysteresis loop, demonstrating the mesoporous characteristics of our samples. The specific surface areas of CN, V_N-CN, and O-V_N-CN were estimated as 33.35, 70.12, and 120.35 m²/g, respectively. This indicates the specific surface area of engineered O-V_N-CN is 3.6-fold larger than that of pristine CN, thereby offering more active sites for surface reactions to take place. As shown in the Barrett-Joyner-Halenda (BJH) pore size distribution in Figure 4a inset, there is a greater abundance of small pores present in the O-V_N-CN compared to CN and V_N-CN, which are beneficial for the photocatalytic reactions.

The crystallographic structures of our developed samples were disclosed by X-ray diffraction (XRD). As shown in Figure 4b,c, two distinct XRD peaks at 12.9° and 27.3° were observed, corresponding to the in-plane structure of repeated heptazine units (100) and the interlayer arrangement of π -conjugated C–N heterocycles (002) in g-C₃N₄, respectively.³⁷

Compared to bulk CN, both V_N-CN and O-V_N-CN exhibited weaker XRD peaks, indicating decreased structural ordering associated with the formation of more exfoliated nanosheet structures during ammonium acetate-assisted thermal polymerization. It is worth noting that O-V_N-CN exhibited the lowest peak intensity among the samples, along with a slight shift of the peak at 27.3° towards the lower 2 θ angle region. This suggests the disruption of the in-plane structure due to the insertion of foreign oxygen atoms into O-V_N-CN, and the replacement of nitrogen atoms with larger-sized oxygen atoms leads to an increased interlayer distance.³⁸

To elucidate the atomic chemical environment of the photocatalysts, XPS analysis was performed. The XPS survey spectrum (Figure 4d) reveals the co-existence of C, N, and O elements in the O-V_N-CN sample, well agreeing with the chemical composition of the sample obtained from EDX mapping. Bulk CHNS/O elemental analysis further reveals that O-V_N-CN exhibits a lower nitrogen content and a higher oxygen content than in CN and V_N-CN, suggesting the substitutional doping during the second thermal treatment (Table S3). Figure 4e shows the high-resolution N 1s spectra of the samples. Three characteristic peaks centered at 401.3, 400.1, and 398.7

eV can be assigned to amino functional groups (C-NH_x, $x = 1, 2$), tertiary N (N-C₃, N3_c), and sp² hybridized N bonded to C (C=N-C, N2_c), respectively. It is worth noting that the normalized area of the N-C₃ peak reduced from 0.32 for the pristine CN to 0.26 and 0.23 for V_N-CN and O-V_N-CN, respectively. This suggests N3_c is the most probable nitrogen-deficient site (Figure 4g), allowing O atoms to be doped into the lattice by substituting the N atoms. Since a tri-coordinated N site was replaced with a foreign O atom, the O atom serves as a bridge to connect the heptazine units. Figure 4h presents a proposed representative model in which oxygen bridges adjacent heptazine units. Room-temperature EPR spectra in Figure 4f revealed the presence of a signal at $g \approx 2.003$, which is characteristic of unpaired electrons localized with the π -

conjugated carbon nitride framework.^{39–41} The signal intensity increased from CN to V_N-CN, consistent with the formation of nitrogen-vacancy-associated paramagnetic centers. O-V_N-CN exhibited the strongest EPR signal, suggesting that the concurrent introduction of nitrogen vacancies and oxygen-linked heptazine units further modifies and stabilizes the vacancy-associated unpaired electrons, in which the defect-associated electrons may serve as electron-rich sites for the adsorption and activation of molecular O₂. Together with the XPS results, these findings further support the proposed coexistence and electronic interaction of nitrogen vacancies and oxygen-linked heptazine units in O-V_N-CN, providing prerequisites for investigating their roles in the photocatalytic upcycling of plastics.

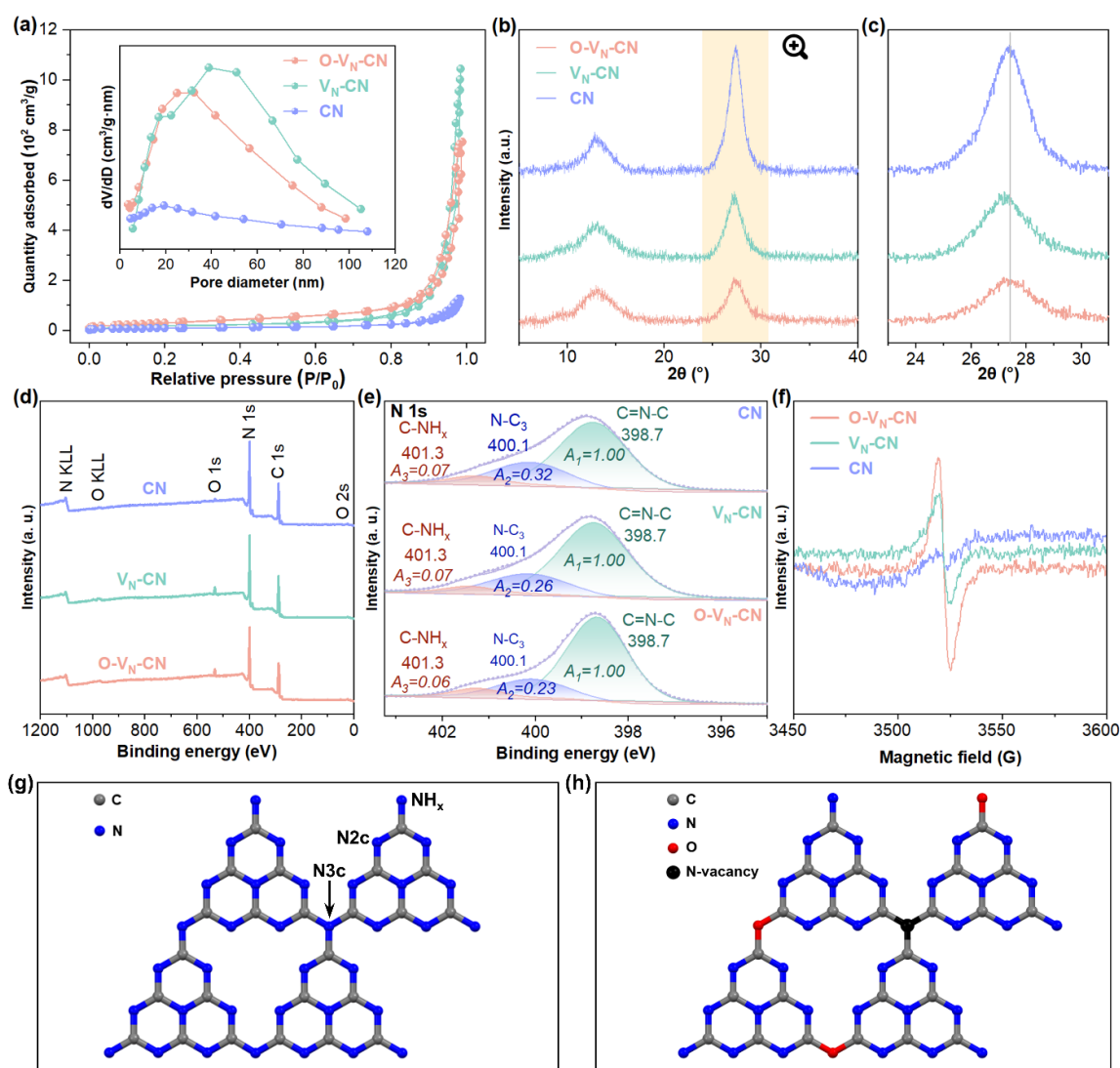


Figure 4. (a) N₂ adsorption-desorption isotherms of CN, V_N-CN, and O-V_N-CN (inset shows the respective pore size distribution). (b) XRD patterns; (c) enlarged XRD patterns in the 2θ range of 23–31°. (d) XPS survey spectra, (e) high-resolution N 1s XPS spectra, and (f) EPR spectra of CN, V_N-CN, and O-V_N-CN. Proposed structural models of (g) CN and (h) O-V_N-CN containing tri-coordinated nitrogen vacancies and oxygen-linked heptazine units, as inferred from the characterization results.

3.3. Defect-mediated optoelectronic properties and charge carrier dynamics

Having established evidence supporting the co-existence of nitrogen vacancies and oxygen-linked heptazine units in O-V_N-CN, the effects of these artificially induced defects on the optical properties of the photocatalysts were firstly investigated. Based on the UV-Vis absorption spectra in Figure 5a, the optimal O-V_N-CN photocatalyst displays not only the inherent optical absorption between 200 and 450 nm that arises from the characteristic π - π^* electron transitions in the heterocyclic aromatics, but also displays a slight uplift of the absorption tail between 450 and 600 nm that is ascribable to the n - π^* electron transitions triggered by the lone pairs of electrons within the graphitic carbon nitride framework.³⁷ In comparison to pristine CN, both V_N-CN and O-V_N-CN displayed significant red-shifting of the absorption edge, where

the absorption edge extended from 451 nm for CN to 510 and 538 nm for V_N-CN and O-V_N-CN, respectively. The enhanced photoabsorption, along with the stark alteration of sample color from cream to dark yellow is a classical phenomenon attributed to the sub-band excitation of electrons from the midgap states to the conduction band (CB), which manifests the alteration of electronic band structures in V_N-CN and O-V_N-CN.⁴² From the Tauc plots in Figure 5b, the bandgaps of CN, V_N-CN, and O-V_N-CN were estimated as 2.80, 2.66, and 2.40 eV, respectively. This suggests that the presence of nitrogen vacancies led to bandgap narrowing in V_N-CN, and the doping of O atoms to bridge the heptazine frameworks further reduced the bandgap of O-V_N-CN, allowing a broader range of the solar spectrum to be harnessed for the generation of more electron-hole pairs to participate in photocatalytic applications.

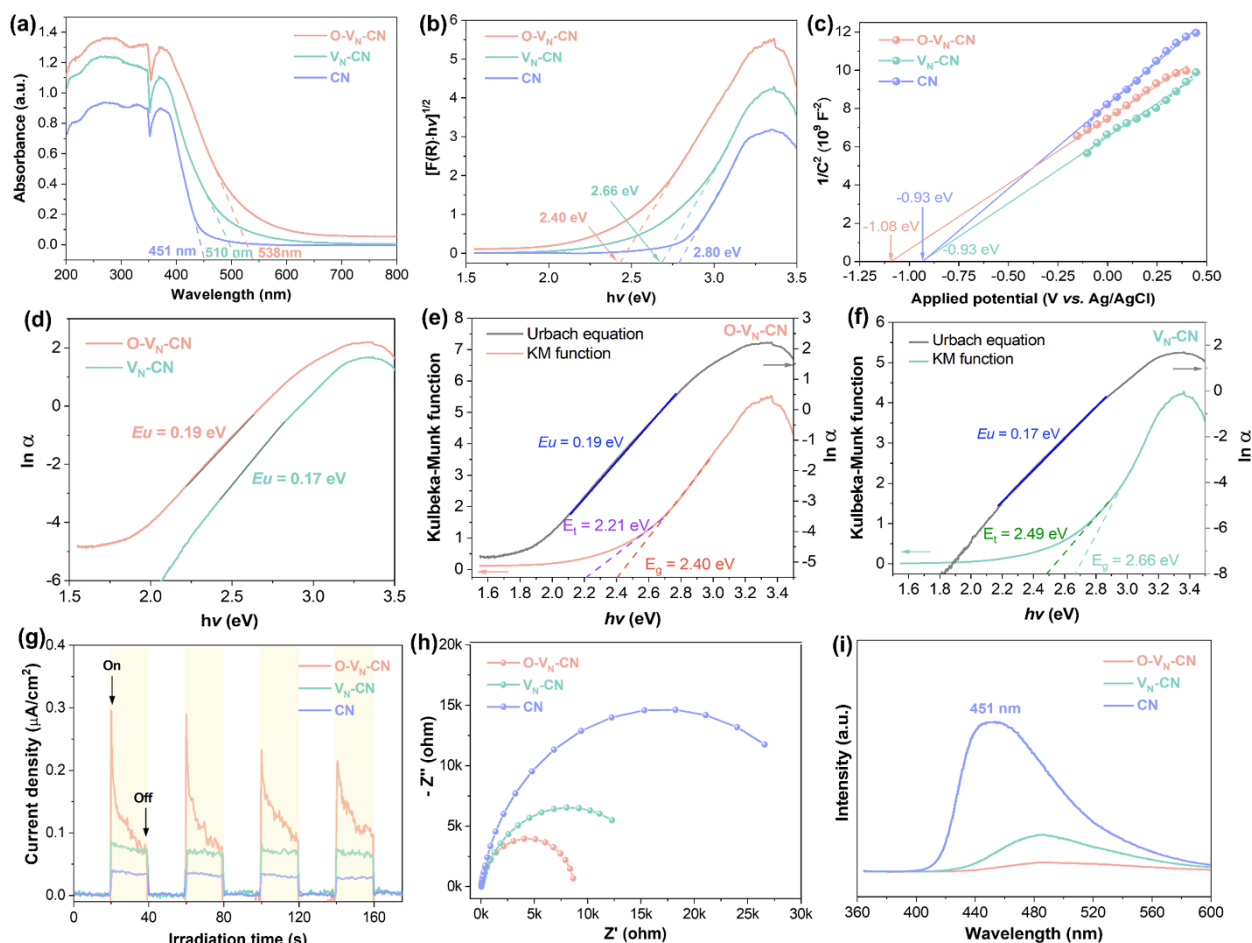


Figure 5. (a) UV-vis absorption spectra, (b) Tauc plots, and (c) Mott-Schottky plots of CN, V_N-CN, and O-V_N-CN. (d) Urbach plot of V_N-CN and O-V_N-CN. Combination of Urbach and Tauc plots for (e) O-V_N-CN and (f) V_N-CN. (g) Transient photocurrent responses, (h) Nyquist plots, and (i) room-temperature steady-state PL spectra of CN, V_N-CN, and O-V_N-CN.

Since the band edge positions greatly affect the separation and transport of photogenerated electron-hole pairs, the electronic band structures of our developed photocatalysts were systematically investigated to elucidate the flowchart of charge

carriers. Based on the Mott-Schottky analysis in Figure 5c, positive slopes were observed for all samples, indicating that the intrinsic *n*-type semiconductor characteristic of graphitic carbon nitride remained unchanged after the introduction of nitrogen

defects and oxygen doping. For *n*-type semiconductors, the Mott-Schottky equation is given by:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0 N_D} (E - E_{fb} - \frac{k_B T}{e}) \quad (1)$$

where *C* is the capacitance of the space charge region, *e* is the electron charge, ϵ is the dielectric constant of the photocatalyst, ϵ_0 is the vacuum permittivity, N_D is the number of donors, *E* is the applied voltage, E_{fb} is the flat band potential, k_B is Boltzmann's constant, and *T* is the absolute temperature. From Equation (1), plotting $1/C^2$ versus *E* should yield a straight line, from which the E_{fb} of the photocatalyst can be determined by the intercept of the extrapolated straight line with the *x*-axis. From Figure 5c, the E_{fb} of CN, V_N -CN, and O- V_N -CN were estimated as −0.93, −0.93, and −1.08 V vs. Ag/AgCl, respectively, corresponding to −0.73, −0.73, and −0.88 V vs. NHE, using the conversion formula ($E_{NHE} = E_{Ag/AgCl} + 0.197$ V). According to the rule of thumb, the CB minimum (CBM) of an *n*-type semiconductor is typically −0.3 V from E_{fb} . Thus, the CBM for CN, V_N -CN, and O- V_N -CN were inferred to be −1.03, −1.03, and −1.18 V vs. NHE, respectively. Combining the bandgap energies determined from Tauc plots, the valence band maximum (VBM) was *ca.* 1.77, 1.63, and 1.22 V vs. NHE for CN, V_N -CN, and O- V_N -CN, respectively. Based on the UV-Vis absorption spectra in Figure 5a, both V_N -CN and O- V_N -CN exhibited absorption tails, indicating the presence of vacancy-induced midgap states that position judiciously below the CB of the photocatalysts. The energy levels of the band tails, often referred to as Urbach tails, can be ascertained using the Urbach plot, described by the following expressions:

$$\alpha = \alpha_o \exp\left(\frac{h\nu}{Eu}\right) \quad (2)$$

$$\ln \alpha = \left(\frac{1}{Eu}\right)h\nu + \ln \alpha_o \quad (3)$$

where α is an absorption coefficient, α_o is a constant, $h\nu$ is the incident photon energy, and *Eu* denotes the Urbach energy, which can be approximated from the inverse of slope for the $\ln \alpha$ vs. $h\nu$. From the Urbach plots in Figure 5d, the *Eu* values were estimated as 0.17 and 0.19 eV for V_N -CN and O- V_N -CN, respectively, suggesting the gap from the CBM to the midgap states. The relatively small *Eu* values indicate the close distance of the midgap states to the CBM, signifying that the midgap states serve as shallow trap states which not only facilitate the separation of photogenerated charge carriers, but also allow a lower-energy excitation pathway for secondary electron excitation by harnessing the long-wavelength photons.⁴³ The presence of shallow trap states in V_N -CN and O- V_N -CN was further confirmed by accessing the transition energy (E_t) by extrapolating the Tauc plot to the *x*-axis (Figure 5e,f). In good agreement with the *Eu* evaluation, the exact levels for the defect states were obtained from E_t analysis, further affirming

the extrinsic sub-bands induced by tri-coordinated $N3_C$ defects located well below the CB of V_N -CN and O- V_N -CN. Since the vacancies-induced defect states are located not far below the CB, this suggests that these shallow trap states can serve as excellent sites for trapping the photogenerated electrons, allowing the O_2 molecules to be spontaneously activated to superoxide radicals ($\bullet O_2^-$) via one-electron oxygen reduction. In addition, the upshifting of the CB level of V_N -CN and O- V_N -CN is highly desirable, rendering stronger reduction power for $\bullet O_2^-$ formation ($E_{O_2/\bullet O_2^-} = -0.33$ vs. NHE), where these $\bullet O_2^-$ radicals play pivotal roles in cleaving the bonds in plastics. The estimated electronic band structures of CN, V_N -CN, and O- V_N -CN are illustrated in Figure 6d.

To explore how the O-linked heptazine units and tri-coordinated nitrogen vacancies of O- V_N -CN assisted in photocatalytic reactions, photoelectrochemical measurements were performed to elucidate the interfacial transport kinetics of photogenerated electron-hole pairs. Transient photocurrent responses of our developed samples were investigated under periodic visible light exposure with alternating on-off cycles. This method involves measuring the intensity of photocurrent responses arising from the movement of photogenerated electrons towards the back contact, whereas the photogenerated holes transfer to the photocatalyst-electrolyte interface which are then captured by the electrolyte's reduced species.⁴⁴ Given that the electrodes and electrolyte were prepared identically for each measurement, the photocurrent intensity serves as a direct indicator of the charge carrier generation, transportation, and separation efficiency. From Figure 5g, CN demonstrated poor photocurrent responses, suggesting the intrinsic rapid recombination of photogenerated charge carriers in pristine $g-C_3N_4$. With the presence of tri-coordinated nitrogen vacancies that serve as shallow trapping sites, V_N -CN displayed higher photocurrent intensity, while the co-existence of O-linked heptazine units and nitrogen defects boosted the photocurrent responses of O- V_N -CN. Aside from the improved photocurrent responses that suggest more photogenerated charge carriers to take part in the photocatalytic reactions, the synergistic roles of the internal electric field originating from the O-linked heptazine units and nitrogen defects were revealed by the electrical impedance spectroscopy (EIS) Nyquist plots. Based on the EIS Nyquist plots in Figure 5h, a similar trend to the photocurrent responses was observed, in which O- V_N -CN displayed the smallest arc radius, followed by V_N -CN and lastly CN. Since a smaller arc radius of the Nyquist plots indicates a lower resistance for electron transfer and an improved separation of photogenerated electron-hole pairs that facilitates the interfacial charge transfer,^{45–47} the presence of the opportune defects and foreign atoms in O- V_N -CN greatly boosts the migration and separation of charge carriers. The much depressed Nyquist arc radius of O- V_N -CN suggests its superior interfacial charge transfer efficiency.

The separation efficiency of the photogenerated charge carriers was further elucidated by steady-state photoluminescence (PL) spectroscopy. Under an excitation wavelength of 350 nm, CN exhibited a strong emission peak centered at 451 nm, as shown in Figure 5i. This emission wavelength coincides with the absorption edge of CN as determined from the UV-Vis spectra in Figure 5a, demonstrating intrinsic band-to-band recombination of CN. The observed fluorescence emission arises from energy dissipation corresponding to the bandgap between the CB and VB of CN. For V_N -CN, a significant suppression of the emission peak was observed, suggesting the presence of nitrogen vacancies that act as trapping sites for charge carriers. Consequently, the intrinsic radiative recombination of electron-hole pairs was greatly inhibited. Furthermore, with the co-existence of nitrogen vacancies and foreign oxygen atoms doping, strong PL quenching was observed for O- V_N -CN, demonstrating their synergistic role in retarding the recombination of photogenerated charge carriers. In comparison to CN, significant red-shifting of emission peaks was observed for V_N -CN and O- V_N -CN, offering further evidence for the enhanced light harvesting ability of the defect-engineered samples.

3.4. Catalyst recyclability and underlying mechanism for plastic upcycling

The preceding characterization demonstrates that O- V_N -CN with co-existence of tri-coordinated nitrogen vacancies and oxygen-linked heptazine frameworks exhibits defect-associated mid-gap states, enhanced visible light absorption, facilitated charge carrier transport, and improved separation of photogenerated electron-hole pairs. Next, we examined the stability and recyclability of O- V_N -CN over three consecutive PS upcycling cycles under identical reaction conditions. Each cycle was conducted for 24 h using fresh PS and DCE without adding fresh catalyst. After three consecutive cycles of PS upcycling, O- V_N -CN exhibited 143.2, 117.1, and 23.8 μmol of formic acid, benzoic acid, and acetophenone, respectively (Figure 6a), manifesting remarkable activity retention of 93.6%, 91.5%, and 88.1% relative to the first cycle after 72 h of reaction (24 h each run). The long-term activity demonstrates the stability and reusability of O- V_N -CN as a recoverable metal-free heterogeneous photocatalyst. Besides, no significant changes were observed in the chemical properties and bulk elemental composition of O- V_N -CN recovered after the photocatalytic plastic upcycling reaction (Figure S4 and Table S4).

Following that, we sought to understand the defect-mediated charge-carrier behavior of O- V_N -CN for plastic bond cleavage as modulation of the local coordination and electronic environments is known to influence the adsorption and activation of oxidants and the subsequent generation of reactive oxygen species.⁴⁸ PS was selected as the representative mechanistic substrate because its benzylic C-H sites provide a chemically defined point of oxidative activation, while its aro-

matic and aliphatic carbon fragments can be followed through the formation of benzoic acid, acetophenone, and formic acid (Figure 6c). This avoids the overlapping pathways that would arise from studying the ternary mixture. Selective scavenger experiments reveal that the addition of triethanolamine (TEA), which consumes photogenerated holes, strongly suppressed the formation of all three products (Figure 6b), establishing that oxidative equivalents generated in the valence band are indispensable for initiating polymer activation through direct C-H abstraction. Similarly pronounced inhibition was observed upon the addition of *p*-benzoquinone (BQ) or hydroquinone (HQ), both of which act as superoxide radical ($\bullet\text{O}_2^-$) scavengers. The large drops in product yields provide conclusive evidence that $\bullet\text{O}_2^-$ is the dominant reactive oxygen species and support a superoxide-mediated radical oxidation pathway. This was further supported by the EPR spin-trapped measurements with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), in which no discernible DMPO-adduct signal was observed in the dark, whereas a characteristic DMPO- $\bullet\text{O}_2^-$ signal appeared after 5 min of light irradiation (Figure S5). In contrast, tert-butanol (TBA) produced negligible effect on the product yields, indicating that freely diffusing $\bullet\text{OH}$ radicals are not the principal oxidants under the reaction conditions. Furfuryl alcohol (FFA) caused only little inhibition in the product yields, suggesting that singlet oxygen, if involved, likely makes at most a secondary contribution. Taken together, these results support a reaction pathway in which photogenerated holes participate in the initial oxidation of the polymer, while photoexcited electrons reduce O_2 to $\bullet\text{O}_2^-$ at defect states, which subsequently contribute to oxygenation and C-C bond cleavage. To directly examine the cleavage of the PS backbone, gel permeation chromatography (GPC) measurements were performed (Figure S6). The apparent number-average molecular weight (M_n) of PS dissolved in DCE before photocatalytic reaction (0 h) was 36,784 g/mol. After 24 h of reaction, the M_n dropped substantially to below 400 g/mol, providing direct evidence of extensive PS chain shortening during photocatalysis and consistent with oxidative C-C bond cleavage.

Drawing upon the scavenger experiments, catalytic activity tests, control experiments, physicochemical characterization, GPC and EPR analyses, a plausible mechanism for the plastic upcycling is proposed (Figure 6e). Firstly, our developed O- V_N -CN with a carefully engineered electronic band structure (Figure 6d) allows effective absorption of visible light for the formation of photogenerated charge carriers (Equation (4)). Secondly, the simultaneous introduction of nitrogen vacancies and foreign oxygen atoms not only thwarted the direct recombination of photoinduced charge carriers, but also facilitated the adsorption of oxygen molecules on the nitrogen-vacant sites.⁴⁹ In this case, the photogenerated electrons (e^-) are favourably transferred to the defect-induced midgap states (abbreviated as defect states in Figure 6e), allowing the accumulation of

localized electrons. Upon the adsorption of oxygen molecules on the nitrogen vacancies, these oxygen molecules can be easily activated by the localized electrons, leading to the formation of numerous $\bullet\text{O}_2^-$ anion radicals *via* one-electron oxygen reduction (Equation (5)). In comparison with CN and V_N -CN, the electronically modulated O- V_N -CN exhibited much stronger reduction power owing to the upshifting of the conduction band (CB) position. Since the potential of defect states in O- V_N -CN (-0.99 V) is more negative than the redox potential of $\text{O}_2/\bullet\text{O}_2^-$ (-0.33 V vs. *NHE*), the process of $\bullet\text{O}_2^-$ anion radical

generation can proceed energetically. Meanwhile, the photo-generated holes (h^+) attacked the $-\text{C}-\text{H}$ bond in PS, withdrawing an electron from it and resulting in $\text{C}-\text{H}$ bond activation, leading to the formation of carbon-centered PS radicals (Equation (6)).

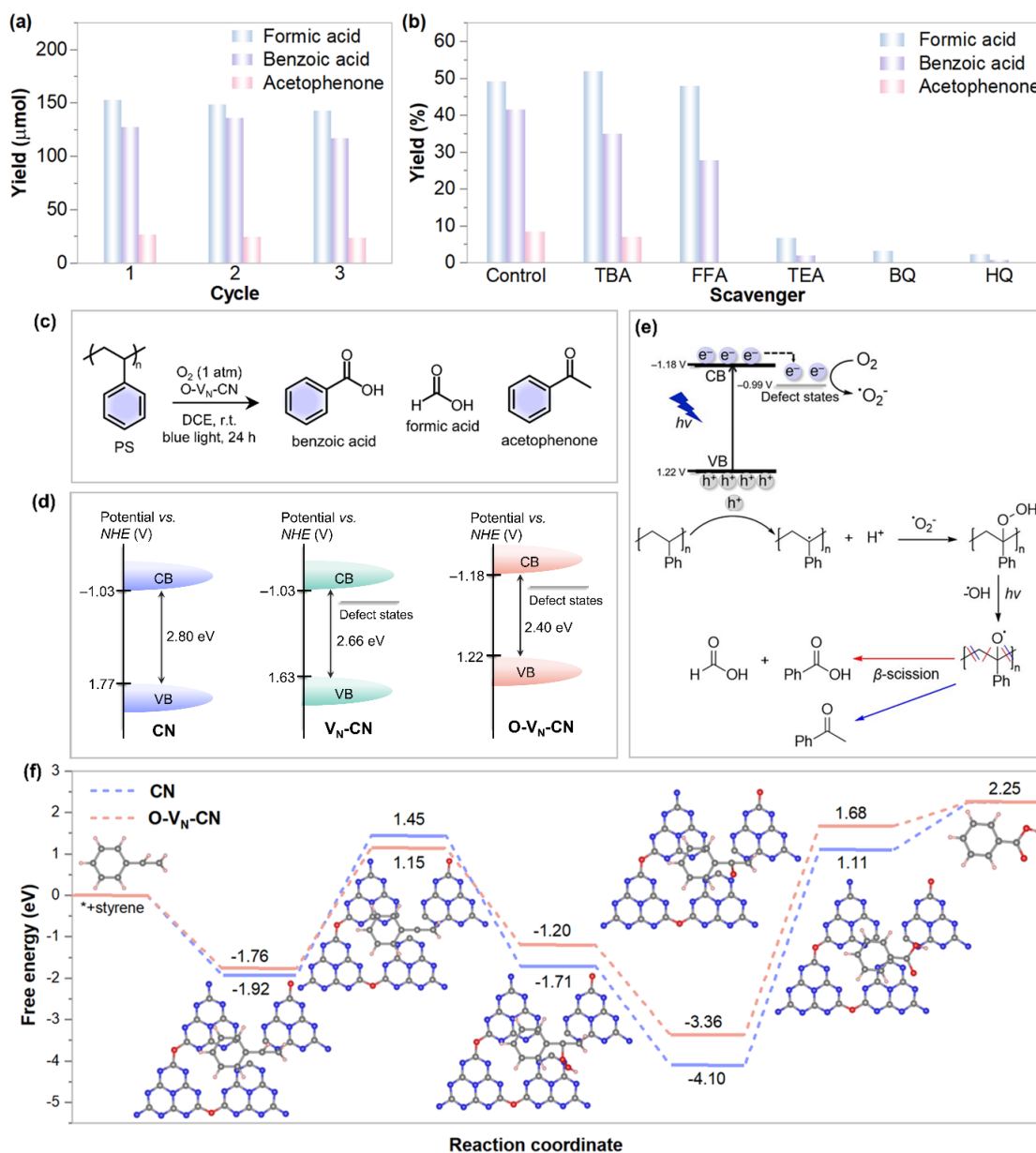
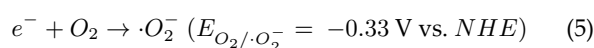
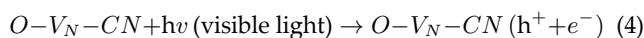


Figure 6. (a) Product yields over three consecutive photocatalytic cycles, with the recovered O- V_N -CN reused with fresh PS and DCE in each cycle. (b) Effects of tert-butanol (TBA), furfuryl alcohol (FFA), triethanolamine (TEA), p-benzoquinone (BQ), and hydroquinone (HQ) on PS conversion. (c) Photocatalytic conversion of PS into benzoic acid, formic acid, and acetophenone. (d) Estimated electronic band structures of CN, V_N -CN, and O- V_N -CN. (e) Proposed reaction pathway involving hole-mediated C-H activation, O_2 reduction to $\bullet\text{O}_2^-$, formation of oxygenated polymer intermediates, and β -scission. (f) DFT-calculated free-energy profiles for styrene conversion over CN and O- V_N -CN.

These PS radicals readily react with $\bullet\text{O}_2^-$ to form intermediates that undergo subsequent oxygenation and β -scission to induce oxidative C–C bond cleavage along the polymer backbone.⁵⁰ Repetition of these oxygenation and β -scission events progressively shortens the polymer chains and generates lower-molecular-weight oxygenated intermediates. Continued oxidation and fragmentation of these intermediates ultimately afford the observed products, including acetophenone, benzoic acid, and formic acid.

Density functional theory calculations further support the role of defect engineering in lowering the energetic demand of the initial polymer activation (Figure 6f). Using styrene as a representative molecular analogue of the PS repeat unit, adsorption and successive oxygenated intermediates were evaluated on CN and O- V_N -CN. The first uphill activation configuration is stabilized on O- V_N -CN relative to CN, decreasing in free energy from 1.45 to 1.15 eV. This reduction is consistent with the ability of the vacancy- and oxygen-modified framework to redistribute interfacial charge and facilitate the formation of an activated polymer-derived species. Subsequent stabilization of oxygenated intermediates provides a pathway toward alkoxy-radical formation and C–C bond scission. Although the calculated profile represents an idealized molecular model rather than the complete heterogeneous polymer interface, this trend agrees with the experimental findings and supports the conclusion that the co-existence of tri-coordinated nitrogen vacancies and oxygen-linked heptazine units modifies both charge utilization and the energetics of substrate activation.

4. Conclusion

We have demonstrated a metal-free, defect-engineered polymeric carbon nitride organophotoredox catalyst, O- V_N -CN, for the upcycling of chemically distinct and mixed plastics under visible light and ambient conditions. O- V_N -CN converts aliphatic PP, aromatic PS, and chlorine-containing PVC into value-added small molecules under a unified set of reaction conditions and, importantly, concurrently upcycles their ternary mixture without substantial loss of activity relative to the combined performance of the individual plastics. Comprehensive structural, optoelectronic, photophysical, mechanistic, and computational investigations reveal that the coexistence of tri-coordinated nitrogen vacancies and oxygen-linked heptazine units creates shallow electron-trapping states, enhances visible-light absorption, promotes charge separation and interfacial transfer, and facilitates the activation of O_2 to $\bullet\text{O}_2^-$, which participate in the selective scission of the kinetically inert C–C backbone for progressive breakdown of polymer chains into value-added small molecules.

Beyond its scientific novelty, the technology is built for impact: the O- V_N -CN catalyst is synthesized by simple calcination from urea and ammonium acetate, which are inexpensive, abundant and globally available. More importantly, its metal-

free nature also avoids the risk of secondary metal pollution, making it a potentially green and sustainable catalyst. By converting an environmental liability into a renewable carbon feedstock for platform chemicals at mild conditions, this work provides a promising foundation for developing economically viable routes towards closing the plastics carbon loop. We anticipate that defect-engineered organophotoredox heterogeneous catalysis will open a broad design space for confronting the global plastic crisis while reclaiming the immense, untapped value locked within plastic waste.

Supplementary Materials

The supporting information can be downloaded at https://ssi.ukscip.com/uploads/7/asset-file/2026/09/asset-file_6fe298c83b0efd058e883adf110dcb2a.pdf.

Author Contributions

X.Y.K. and T.-P.L. conceived the idea, designed the experiments, and acquired funding. X.Y.K., S.R.C., W.-K.C., L.Z., P.T., R.D.W., and S.-P.C. performed the experimental work and analyzed the data. X.Y.K. and T.-P.L. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

The data supporting the findings of this study are available in the article and its [Supplementary Materials](#).

AI Use Statement

The authors declare that no artificial intelligence (AI) tools were used in the preparation of this manuscript.

Conflict of Interest

T.P.L. and X.Y.K. are inventors for a PCT patent application (PCT/SG2025/050271), filed on 22 April 2025 and published as WO 2025/226218 A1 on 30 October 2025. The patent covers the photocatalytic upcycling of a diverse range of plastics and mixed plastics and was filed through NTUitive.

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The authors declare no other competing interests.

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