C₃N₅: A Low Bandgap Semiconductor Containing an Azo-Linked Carbon Nitride Framework for Photocatalytic, Photovoltaic and Adsorbent Applications

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Supporting Information

ABSTRACT: Modification of carbon nitride based polymeric 2D materials for tailoring their optical, electronic and chemical properties for various applications has gained significant interest. The present report demonstrates the synthesis of a novel modified carbon nitride framework with a remarkable 3:5 C:N stoichiometry (C₃N₅) and an electronic bandgap of 1.76 eV, by thermal deamination of melamine. Characterization revealed that in C₃N₅ polymer, two ₁-s-heptazine units are bridged together with azo linkage, which constitutes an entirely new and different bonding fashion from g-C₃N₄ where three heptazine units are linked together with tertiary nitrogen. Extended conjugation due to overlap of azo nitrogens and increased electron density on heptazine nucleus due to the aromatic π network of heptazine units lead to an upward shift of the valence band maximum resulting in bandgap reduction down to 1.76 eV. XRD, He-ion imaging, HR-TEM, EELS, PL, fluorescence lifetime imaging, Raman, FTIR, TGA, KPFM etc. clearly show that the properties of C₃N₅ are distinct from pristine carbon nitride (g-C₃N₄). When used as an electron transport layer (ETL) in MAPbBr₃ based halide perovskite solar cells, C₃N₅ outperformed g-C₃N₄ in particular generating an open circuit photovoltage as high as 1.3 V, while C₃N₅ blended with MA₃FA₃⁺Pb(1-x)BrₓI₃ perovskite active layer achieved a photoconversion efficiency (PCE) up to 16.7%. C₃N₅ was also shown to be an effective visible light sensitizer for TiO₂ photoanodes in photoelectrochemical water splitting. Because of its electron-rich character, the C₃N₅ material displayed instantaneous adsorption of methylene blue from aqueous solution reaching complete equilibrium within 10 min, which is significantly faster than pristine g-C₃N₄ and other carbon based materials. C₃N₅ coupled with plasmonic silver nanocubes promotes plasmon-exciton coinduced surface catalytic reactions reaching completion at much low laser intensity (1.0 mW) than g-C₃N₄ which showed sluggish performance even at high laser power (10.0 mW). The relatively narrow bandgap and 2D structure of C₃N₅ make it an interesting air-stable and temperature-resistant semiconductor for optoelectronic applications while its electron-rich character and intrasheet cavity make it an attractive supramolecular adsorbent for environmental applications.

INTRODUCTION

The last few decades have witnessed the rise of semiconducting, all-organic polymers as excellent metal-free and visible light-active materials for various optoelectronic and energy harvesting applications.1 Although impressive improvements in performance have been achieved, particularly for plastic solar cells, the synthesis procedures for semiconducting polymers are cumbersome and difficult to scale up,2 and the organic semiconductors themselves are unstable under the action of heat, light and/or ambient air.3 Consequently, there are scalability concerns related to semiconducting polymers,4 and requirement of heavy encapsulation to achieve even modest durability in the photovoltaic application. The same concerns, related to oxidative stability and durability, have also ruled out the use of semiconducting polymers in photocatalytic applications.

A very different approach toward forming and exploiting all-organic, polymeric semiconductors in optoelectronic and energy harvesting applications consists of using doped and...
Among graphenic semiconductors, graphitic carbon nitride (g-C3N4), composed of tris-s-triazine (s-heptazine, C6N7) units bridged together with nitrogen atoms to give a 2D graphic structure has gained significant interest due to its astonishing electronic, optical and physicochemical properties. The major advantages of graphenic semiconductors are their chemical robustness and the simplicity of synthesis. Several graphenic semiconductors are synthesizable using solvothermal synthesis and/or solid-state reactions, and graphenic semiconductors are perfectly stable in ambient conditions up to temperatures of several hundred degrees Celsius. As a result of this exceptional stability, almost no structural or chemical degradation of photocalytic action is observed even after several reuse cycles.

The somewhat wide bandgap of g-C3N4 means that it can absorb only the ultraviolet and blue fraction of solar spectrum (\(\lambda < 450\) nm), which limits its performance in photocatalytic and photovoltaic applications. Doping with various heteroatoms such as P, F, B and S has been utilized to improve the visible light absorption profile and efficiency. Like all semiconductors, g-C3N4 suffers the innate drawback of carrier recombination detrimental to catalytic and photocatalytic processes. Many surface modification approaches such as increasing the surface area via soft and hard templating, using two or more precursors, transformation of bulk material into sheets, doping with metals (Ag, Cu, Rh, Pt, Na, etc.) and metal oxides (CoOx) for electron and hole capture, coupling with other semiconductors/metal complexes to form heterojunctions, and blending with graphene have been employed to improve the photocatalytic and catalytic performance of g-C3N4. However, less attention has been paid to chemical structure modification, which can lead to the generation of a more robust, band edge tuned g-C3N4 framework with entirely new physicochemical properties for efficient catalytic/photocatalytic applications. It has been found that addition of extra nitrogen-rich moieties in the g-C3N4 scaffold to increase the N:C ratio from 4:3 ratio in CN can reduce the bandgap significantly, due to a more extended conjugated network and the participation of the lone pair on the N atom with the \(\pi\) conjugated system of heptazine motif. Vinu et al. demonstrated the synthesis of N-rich carbon nitride (MCN-8) using 3-amino-1,2,4-triazole to afford \(\text{C}_6\text{N}_7\), stoichiometry resulting in a significant decrease in bandgap (2.2 eV) due to extended conjugation. However, this increase in N:C ratio to 5:3 (from the 4:3 ratio in g-C3N4) was due to the presence of the N-rich 1,2,4-triazine moiety linked to the heptazine motif and not because of the direct incorporation of the extra N atom in the heptazine nucleus. The same group has also reported the synthesis of mono- and diamino-s-triazine based carbon nitride materials (i.e., MCN-ATN, MCN-4 and MCN-9) with \(\text{C}_6\text{N}_7\) to \(\text{N}_2\text{C}_6\text{N}_8\) stoichiometry using 3-amino-1,2,4-triazine/ammonoguanidine hydrochloride precursor and SBA-15/KIT-6 templating material. The N-rich 1,2,4-triazine or 1,2,4,5-tetrazine moieties were bridged together with tertiary nitrogen in a similar fashion to triazine based carbon nitride and a significant decrease in band gap was observed due to the addition of extra nitrogens. In a recent report, mesoporous triazole and triazine framework modified carbon nitride materials with \(\text{C}_6\text{N}_8\) empirical formula was synthesized by using 5-amino-1H-tetrazole (5-ATTZ) precursor and their hybrid with graphene displayed excellent performance in the oxygen reduction reaction. Fang et al. reported the synthesis of nitrogen self-doped graphitic carbon nitride (C3N_x) by heating hydrazine treated melamine in a sealed ampule. In \(\text{C}_6\text{N}_{4+x}\), the excess N atoms replace terminal C atoms in the heptazine nucleus and the excess charge on the N atom gets redistributed leading to electron-rich heptazine motifs due to which \(\text{C}_6\text{N}_{4+x}\) possessed a narrower bandgap (2.65 eV) with concomitant shifts in the conduction and valence band edge positions (\(E_{\text{CB}} = -0.98\) eV and \(E_{\text{VB}} = +1.67\) eV). In these N-rich carbon nitrides, the N-rich triazine or heptazine based unit remains linked together with tertiary nitrogen, \(\text{N}(\text{C}_3)\), and increased stochiometric N:C ratio was due to the replacement of C via N in triazine or heptazine ring system. Similarly, carbon-rich \(\text{C}_3\text{N}_4\) network also facilitates bandgap narrowing and efficient charge separation due to the extended conjugated network. Zhang et al. reported the hydrothermal synthesis of low bandgap, C-rich \(\text{C}_3\text{N}_4\) materials with extended conjugated networks using melamine (as heptazine ring source) and glucose (as carbon source) precursors. However, the use of melamine and other C and N sources can afford only \(\text{C}_3\text{N}_4\) structures possessing randomly distributed domains within the \(\text{C}_3\text{N}_4\) framework due to the uncontrolled reaction and these regions work as trap centers. Melem (2,5,8-triamino-s-heptazine) considered the smallest monomeric unit of \(\text{C}_3\text{N}_4\) framework, provides the opportunity to manipulate chemical structure by incorporating other units in the \(\text{C}_3\text{N}_4\) framework in a more controlled fashion. Shiraiishi et al. reported the synthesis of modified CN-polydimide framework (g-C3N4/PDI) by solid-state reaction between melem and electron deficient pyromellitic dianhydride (PMDA) and demonstrated that the band edge positions of g-C3N4/PDI could be tuned by limiting the number of PDI units in the framework. Heterostructured \(\text{C}_4\text{N}_4\)-emembods of conductive, in-plane, \(\pi\) conjugated carbon rings incorporated in the \(\text{C}_3\text{N}_4\) matrix were prepared by thermal dehydrogenation reaction between glucose and melem, and the obtained \(\text{C}_4\text{N}_4\) heterostructure achieved fast spatial charge transfer from g-C3N4 to C4N4 motif facilitating efficient water splitting. The replacement of amino functionalities on melem/melamine by nitrogen-rich functionalities, i.e. azide (\(-\text{N}_3\)), expedted the synthesis of low-N rich carbon nitride, i.e. 2,5,8-triazido-s-heptazine, \((\text{C}_6\text{N}_7)(\text{N}_3)\_3\) which after thermal heating afforded N-rich carbon nitride. Likewise, triazine containing N-rich CN was also synthesized by thermal annealing of 2,4,6-triazido-1,3,5-triazine [cyanuric triazine, \((\text{C}_3\text{N}_3)(\text{N}_3)\_3\)] and polyvinyl alcohol. However, the synthesis procedure involved sodium azide and concomitant shock sensitive explosion hazards; furthermore, azide intermediates are highly undesirable.

Herein, we demonstrated the synthesis of novel modified carbon nitride framework with a \(\text{C}_3\text{N}_3\) stoichiometry by thermal deammoniation of 2,5,8-tri hydrazino-s-heptazine, also known as melem hydrazine (MH), as a safe and environmentally benign precursor (Figure 1). The obtained carbon...
nitride modified framework was denoted as C$_3$N$_5$ due to its 3:5 C:N stoichiometric ratio. Characterization studies revealed that the C$_3$N$_5$ framework contains heptazine moieties bridged together by azo linkage (−N=N−). The presence of azo linkage extends the $\pi$ conjugated network due to overlap between the $p$ orbitals on N atoms constituting the azo bond and $\pi$ system of heptazine motif, which resulted in the reduction of the electronic bandgap to 1.76 eV. C$_3$N$_5$ displayed improved photosensitization properties at longer wavelengths for solar water splitting. Further, because of the increased electron charge density on the ring nitrogen, C$_3$N$_5$ exhibited instantaneous adsorption of methylene blue from aqueous solution. Solar cell devices fabricated using low bandgap C$_3$N$_5$, as an electron transporting layer (ETL) in MAPbBr$_3$ based perovskite solar cells demonstrated improved power conversion efficiency (PCE), open circuit voltage ($V_{oc}$) etc. compared to solar cells made from g-C$_3$N$_4$ based ETL due to tuned band alignment. Blending a small amount of C$_3$N$_5$ (4.0 wt %) with MA$_x$FA$_{1-x}$Pb(I$_{0.85}$Br$_{0.15}$)$_3$ perovskite active layer led to an increase in PCE up to 16.68% with $V_{oc}$ of 1.065 V and $J_{sc}$ of 22.87 mA/cm$^2$ higher than conventional and g-C$_3$N$_4$ blended solar cell architectures. Compared to g-C$_3$N$_4$, C$_3$N$_5$ exhibited a remarkably enhanced performance in the plasmon-exciton codriven photoreduction of 4-nitrobenzenethiol to 4,4′-dimercaptoazobenzene.

### RESULTS AND DISCUSSION

Melem (2,5,8-triamino-s-heptazine) served as the precursor monomeric unit for the synthesis of C$_3$N$_5$ polymer. Melem was synthesized by heating melamine at 425 °C overnight followed by purification in boiling water. The obtained melem was treated with hydrazine hydrate (NH$_2$NH$_2$·H$_2$O, 55% in water) in an autoclave at 140 °C for 24 h. The treatment of melem with hydrazine transformed amino (−NH$_2$) functionalities into hydrazino (−NH−NH$_2$) functionalities, which afforded melem hydrazine, MH (2,5,8-trihydrazino-s-heptazine). The obtained white melem hydrazine was subjected to programmed heating at 450 °C for 2 h to obtain orange colored C$_3$N$_5$ polymer (Figure 2) (see Supporting Information for experimental details). Melem hydrazine has a highly...
hydrogen bonded structure which facilitates the formation of an azo-bridged heptazine framework by thermal condensation. Previously, Gillan also reported the formation of similar azo-bridged functionalities by heating nitrogen-rich 2,4,6-cyanuric triazine or triazido-1,3,5-triazine (C3N3(N3)3) to form differential composition triazine based carbon nitride.25,26 In the same report, Gillan suggested that transformation of cyanuric triazine into azo-bridged triazine carbon nitride framework proceeded through the nitrene intermediate (C3(N3)2N:') and that the formation of C3N5 from melem hydrazine might proceed via a similar intermediate due to the thermolabile nature of hydrazine functionalities. The structures of melem, melem hydrazine and hydrogen bonded melem hydrazine are given in Supporting Information (Figure S1).

The surface morphology of the C3N5 polymer was investigated using a He-ion microscope equipped with an electron flood gun to facilitate positive charge neutralization accumulated from the He-ion beam (Figure 3a). The He-ion images of MHP show a rough, crumpled graphenic scaffold with some erupted morphologies, which indicate that the high polymerization into an irregular sheet-like structure. The temperature treatment of MH monomeric unit facilitated with some erupted morphologies, which indicate that the high

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319 orbitals overlap between bridging azo functionalities and 320 heptazine motifs. The formation of extended $\pi$ conjugated 321 network in C$_3$N$_5$ was also supported by increased UV-vis 322 absorption profile and shorter TRPL lifetime decay (Figures 7 323 and 8). The N K-edges energy loss peaks for g-C$_3$N$_4$ and C$_3$N$_5$ 324 located at 399.8 and 408.5 eV, assigned to 1s-$\pi^*$ and 1s-$\sigma^*$ 325 electronic transition of sp$_2$ hybridized nitrogens in heptazine 326 ring and bridging N, further verify sp$_2$ hybridized nitrogen-rich 327 carbon nitride framework (Figure 4d). Absence of any new 328 peak in N K-edge loss of C$_3$N$_5$ demonstrate bridging nitrogens 329 in C$_3$N$_5$ have almost identical electronic environment like 330 N(C)$_3$ in g-C$_3$N$_4$ via azo nitrogens, C$-N=N-C$, 331 renders a lone pair on azo nitrogens, which contributes to $\sigma^*$ 332 signal and relative intensity of $\pi^*$ signal suppressed. However, 333 the total peak area of the N K-edge peak for C$_3$N$_5$ was 334 increased, which demonstrated addition of extra nitrogens in 335 the carbon nitride framework. The N:C atomic ratio of C$_3$N$_5$ 336 was calculated to be 1.62, which was in close agreement with 337 the theoretical value (1.66) and C:N value obtained from 338 CHNS analysis (1.65). Slightly lower N content might be due 339 to cleavage of azo bond resulting in loss of some nitrogens 340 under high energy electron beam.

Table 1. (a) Elemental Analysis of C$_3$N$_5$ Showing C, H and N wt % and Empirical Formula and (b) XPS Elemental Analysis of C$_3$N$_5$ Showing at. % and Empirical Formula and Their Comparison with Theoretical C$_3$N$_5$ Composition

(a) elemental analysis

<table>
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<th>serial no.</th>
<th>method</th>
<th>N (wt %)</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>empirical formula</th>
<th>N$<em>{emp}$:N$</em>{isol}$ (at. % ratio)</th>
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<td>1</td>
<td>CHN analysis</td>
<td>61.27</td>
<td>31.81</td>
<td>2.68</td>
<td>C$<em>3$N$</em>{4.95}$H$_{1.01}$</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>theoretical wt %</td>
<td>66.02</td>
<td>33.98</td>
<td>—</td>
<td>C$_3$N$_5$</td>
<td>3:2 (60:40)</td>
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(b) XPS elemental analysis

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<th>N (at. %)</th>
<th>C (at. %)</th>
<th>H (at. %)</th>
<th>empirical formula</th>
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<tr>
<td>3</td>
<td>XPS analysis</td>
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<td>36.76</td>
<td>—</td>
<td>C$<em>3$N$</em>{3.16}$</td>
<td>$\sim$3:2 (60.47:39.53)</td>
</tr>
<tr>
<td>4</td>
<td>theoretical at. % value</td>
<td>62.50</td>
<td>37.50</td>
<td>—</td>
<td>C$_3$N$_5$</td>
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353 hydrazino group (−NH−NH2) at elevated temperature and
354 loss of some azo nitrogens.9b,10b As expected, sulfur was not
355 present at measurable levels. Notably, the observed hydrogen
356 might arise from −NH2 and −OH groups present at the edge
357 of the polymeric framework.

To elucidate the chemical structure of MH and C3N5
358 materials, solid-state nuclear magnetic resonance (NMR)
359 spectroscopy using the cross-polarization magic-angle spinning
360 (CPMAS) technique was performed (Figure 5). CPMAS
361 NMR enables the structural investigation of local- and
362 medium-range structure in micro- and nanocrystalline
363 compounds. The 13C CPMAS NMR spectra of melem
364 hydrazine (MH) display three NMR signals at 164, 160 and
365 154 ppm (Figure 5a). The 13C NMR signals at 164 and 160
366 ppm originated from N2C−NHNH2 carbons while the
367 resonance at 154 ppm was observed from CN3 carbons of
368 the heptazine nucleus. The observed signals were in good
369 agreement with the reported NMR spectra for MH and melem
370 based structures.18a,24,30 The CPMAS NMR spectrum of C3N4
371 exhibits two 13C NMR signals of approximately equal intensity
372 at 164 and 166 ppm for N2C−N=N=N− and CN3 carbons
373 (Figure 5b).24,30,31 The N2C−NHNH2 carbon signal of MH
374 located at 160 ppm arising due to C−H functionalities
375 disappeared in the 13C NMR of C3N5, which confirms removal
376 of −NHNH2 protons and formation of an azide linkage during
377 polymerization step agreeing with 15N CPMAS NMR,
378 vide infra. Furthermore, the appearance of equally intense (Cc:Ce/
379 1:1.07) 13C peaks in the 13C NMR spectrum of C3N5 suggests
380 that heptazine units are in the presence of a symmetric azo
381 bridging motif (where Cc corresponds to central carbons in
382 ring and Ce to external carbons bonded to azo N). A slight
383 shift to higher frequency in CN3 carbon peaks from 154 ppm
384 in MH to 156 ppm in C3N5 suggests shielding of carbons due
385 to N 2p overlap of azo and aromatic π system, which extends
386 the π conjugated network.32
The $^{15}$N CPMAS NMR spectrum of MH exhibits four signals, $-207, -252, -273$ and $-317$ ppm (Figure 5c).\(^{23}\) The $^{15}$N NMR signal at $-207$ ppm and another weak signal at $-273$ ppm were assigned to (NC$_3$) and (NC$_3$)$_2$ nitrogens of the heptazine motif,\(^{36,39,40,41}\) while the peaks at $-252$ and $-317$ ppm assigned to NH$_2$ and NH terminal nitrogens of hydrazino moiety.\(^{35,36}\) The transformation of MH to C$_3$N$_5$ proceeds with removal of NH$_3$ and formation of azo linkage which was evident from the disappearance of NH$_2$ and NH peaks at $-252$ and $-317$ ppm in the $^{15}$N NMR spectrum of C$_3$N$_5$ (Figure 5d). The two NMR peaks in the $^{13}$N NMR spectra of C$_3$N$_5$ at $-197$ and $-248$ (weak) ppm were attributed to NC$_2$ and NC$_3$ nitrogens of heptazine skeleton while another peak at $-271$ ppm arose from $-N=N-$ (and residual NHs) type nitrogens. As the N atoms are in similar chemical environments, a semiquantitative CPMAS NMR analysis of the $^{15}$N peak areas achieved by peak integration of NC$_2$ and NC$_3$ and $-N=N-$ resonances was found give a ratio of 1.00:0.18:0.54, which was in good agreement with the theoretical value (1.00:0.17:0.5) calculated for C$_3$N$_5$ polymeric structure containing heptazine units interconnected with azo linkage (Figure S1). Furthermore, $^1$H NMR of MH gave an intense peak at 5.11 ppm due to NH and NH$_2$ hydrogens (Figure S4). This intense peak disappeared in the $^1$H NMR spectra of C$_3$N$_5$ further confirming the removal of NH hydrogens and a very broad peak centered at 9.18 ppm appeared due to intercalated hydrogen, and residual carboxy and aldehyde hydrogens (essential for the CPMAS approach to function whereby $^1$H magnetization is transferred to $^{13}$C and $^{15}$N). All these NMR results validate the successful synthesis of a modified carbon nitride framework.

Fourier transform infrared (FTIR) spectroscopy was employed to determine the change in functional moiety in the material (Figure 6a–d). The FTIR spectrum of melem shows characteristic broad peaks at 3109 cm$^{-1}$ due to the combined symmetric and antisymmetric stretch vibrations of $-NH_2$ and $-OH$ ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$) groups. The IR bands at 1595, 1411, 1230 and 1078 cm$^{-1}$ are ascribed to the C–N stretch ($\nu_{\text{C-N}}$) of heptazine (C$_3$N$_5$) aromatic nucleus (Figure 6a).\(^{18a,31b,34a,35}\) The N–H stretch band ranging from 3153 to 2895 cm$^{-1}$ for MH was found to become broader due to combinatorial symmetric and asymmetric N–H stretches of $-NH_2$–$NH_2$ group in MH, which confirms the successful transformation of $-NH_2$ moiety in melem to $-NH_2$–$NH_2$ in melem hydrazine (Figure 6b). The broadening of the NH peak was attributed to strong intermolecular hydrogen bonding in MH molecules.\(^{35,36}\) However, all stretching and bending peaks due to heptazine aromatic ring skeleton remain preserved, which indicates that the heptazine motif remains unchanged during the hydrazine treatment. Additionally, some new peaks emerged at 1095 and 965 cm$^{-1}$ implicating the N–N stretch and $-NH_2$ rocking vibration, respectively.\(^{18a,36,37}\) Graphitic carbon nitride shows characteristic peaks at 3145 cm$^{-1}$ due to residual $-NH_2$ and $-OH$ stretch and 1639–1145 cm$^{-1}$ due to triazine ring stretch and 798 cm$^{-1}$ for triazine ring bending vibration was in good agreement with the reported literature (Figure 6c).\(^{37,38}\) After conversion of MH to C$_3$N$_5$ by thermal annealing, the intensity of $-NH_2$–$NH_2$ peak of MH was diminished which implicated the transformation of $-NH_2$–$NH_2$ group into azo ($-N=N-$) linkage through the removal of NH$_3$ (Figure 6d). It is important to note that vibration of symmetrical $-N=N-$ azo linkage is forbidden due to which no new sharp peak due to azo functionalities was observed.

The possibility of $\text{–NH–NH–}$ bond can be neglected due to the absence of any strong N–H band; however, very weak broad peaks arise due to some residual $\text{–NH}_2$ present at the edge of the polymeric framework. This fact was well supported by CHNS analysis, which showed the presence of only one H for each stoichiometric C$_3$N$_5$ unit (Table 1). Further, other peaks of MH at 1095 and 965 cm$^{-1}$ due to N–N stretch and $-NH_2$ rocking vibration disappear in C$_3$N$_5$, which confirmed the transformation of hydrazine group into azo moiety. Peaks corresponding to the C$_3$N$_5$ framework at 1542, 1315 and 887 cm$^{-1}$ were absent in C$_3$N$_5$, which suggests an entirely different network of C$_3$N$_5$ in comparison to g-C$_3$N$_4$.

The changes in phase structure and crystalline nature of melem, MH, g-C$_3$N$_4$ and C$_3$N$_5$ were investigated through the measurement of X-ray diffraction (XRD) (Figure 6). The XRD pattern of melem demonstrated a series of peaks located at 12.5°, 13.6°, 16.7°, 18.4°, 19.7°, 22.0°, 25.2°, 27.2° and 30.4°\(^{46}\) in close agreement with previous reports (Figure 6e).\(^{38,39}\) The XRD results indicate the absence of any melamine impurity in the melem sample.\(^{40,41}\) Because of the transformation of melem into melem hydrazine, the XRD pattern of MH changed, with new peaks being observed at $2\theta$ values of 7.3°, 7.9°, 8.4°, 12.9°, 13.7°, 14.8°, 25.1° and 28.0° (Figure 6f). Bulk g-C$_3$N$_4$ shows two distinct XRD peaks at $2\theta$ values of 27.1° and 13.0° indexed to the 002 and 100 planes of carbon nitride materials (Figure 6g). The 002 peak with a 0.32 nm interplanar spacing was correlated to interplanar stacking of sheets while 100 peaks with a 0.68 nm spacing was specific to in-plane structural packing of heptazine units (Figure 6g).\(^{18b,39b,40b,41}\) The XRD pattern of C$_3$N$_5$ exhibits one broad 002 peak at 27.6°\(^{40}\) corresponding to 0.33 nm interplanar sheet distance. The slight increase in $2\theta$ value and $d$ spacing can be explained due to repulsion between electron-rich $\pi$ conjugated C$_3$N$_5$ sheets as in graphite (0.34 nm) (Figure 6h). Further, the absence of 100 peak, a specific feature of in-plane packing, suggests distortion in the carbon nitride framework and broadening of the nanochannel distance between heptazine units due to azo ($-N=N-$) bridging linkage, further consistent with $^{13}$C and $^{15}$N NMR resonance broadening above, suggesting local medium-range disorder. Also, bridging of two heptazine units with two nitrogens through in-plane lattice packing is less efficient in C$_3$N$_5$, which was responsible for the absence of any expected peak at lower $2\theta$ values. These XRD results clearly support the distinct structure of C$_3$N$_5$, possessing azo linkage.

Raman spectra of melem acquired using 632 nm laser excitation show characteristic fingerprint peaks of melem at 435, 469 and 697 cm$^{-1}$ due to heptazine ring (C$_3$N$_5$) breathing modes and a broad hump at 1452 cm$^{-1}$ due to $-NH_2$ bending mode (Figure 5a).\(^{18a,40a}\) Raman spectra of MH demonstrate many signature peaks correlated to the core at 472, 744 and 1529 cm$^{-1}$, which were shifted in comparison to melem due to functionalization while other peaks due to various vibrations of the heptazine nucleous and hydrazine group were observed at 127, 342, 537, 985, 1159, 1314 and 3071 cm$^{-1}$, in good agreement with the reported literature (Figure 5b).\(^{18a,23a,45b,41}\) The Raman spectra of g-C$_3$N$_4$ display many prominent peaks due to the heptazine framework at 471, 697 and 706 cm$^{-1}$ (heptazine ring breathing modes) and two additional peaks at 1542 and 1639 cm$^{-1}$ corresponding to $-NH_2$ bending mode and graphitic G band (Figure 5c).\(^{23,24,25}\) Further, the presence of a broad hump extended from 1100 to 1600 cm$^{-1}$ suggests multilayer stacking of g-C$_3$N$_4$ sheets.\(^{1,12}\) In the Raman spectra of C$_3$N$_5$, only trace peaks of melem
514 hydrazine motif are observed which indicates the complete transformation of MH to C$_3$N$_5$. Two small peaks were observed at 1085 and 1161 cm$^{-1}$ due to the mixed vibration of heptazine motif and azo stretch (Figure S5d). A sharp peak at 1609 cm$^{-1}$ originated due to the C=N stretching mode.

Figure 7a displays the diffuse reflectance UV–vis (DR-UV–vis) spectra of g-C$_3$N$_4$ and C$_3$N$_5$. The DR-UV–vis spectra of g-C$_3$N$_4$ shows a characteristic absorption peak around 200 and 400 nm with a band tail extended up to 450 nm due to charge transfer from the populated valence band of the nitrogen atom (2p orbitals) to the conduction band of the carbon atom (2p orbitals) of carbon nitride. The less intense absorption band at 330 nm is due to $\pi\rightarrow\pi^*$ transition in the conjugated network while another intense peak at ca. 387 nm appeared due to n→$\pi^*$ transition from nitrogen nonbonding orbital to the aromatic nonbonding orbital.

The DR-UV–vis spectrum of C$_3$N$_5$ demonstrates a drastic change in the UV–vis absorption profile in comparison to g-C$_3$N$_4$ due to a more extended $\pi$ conjugated network (Figure 7a). A broad absorption peak around 393 nm in UV–vis spectrum of C$_3$N$_5$ was attributed to n→$\pi^*$ transition from nitrogen nonbonding orbital to the $\pi$ conjugated nonbonding orbital. The absorption spectrum of C$_3$N$_5$ was red-shifted showing band tailing up to 670 nm, due to an extended $\pi$ conjugated network arising from the overlap.
between N 2p orbitals of bridging azo moieties and N 2p in heptazine $\pi$ conjugated system. Further residual –NH$_2$ also contributes to the delocalized aromatic $\pi$ conjugated system. Because of this, the position of the valence band gets upshifted and $\pi \rightarrow \pi^*$ transition occurs at relatively low energy which facilitates the absorption of a large fraction of the visible spectrum and results in the sample displaying an orange color. Further, the optical bandgaps of g-C$_3$N$_4$ and C$_3$N$_5$ were determined using a Tauc plot by plotting a graph between ($\alpha h\nu$)$^{1/2}$ vs $h\nu$ and extrapolation of the linear tangent to abscissa; where $\alpha$ is absorption coefficient, $h$ is plank constant and $\nu$ is light frequency (Figure S6a). From the Tauc plot, the value of bandgap for g-C$_3$N$_4$ was estimated to be 2.65 eV corresponding to a band-edge at a wavelength of 467 nm, in good agreement with the bandgap values reported in the literature. The bandgap value of C$_3$N$_5$ was calculated to be 1.76 eV corresponding to a band-edge at a wavelength of 707 nm.

Photoluminescence (PL) spectra were collected by exciting samples using 360 nm photons to probe radiative recombin- 
tion (Figure 7b). The PL spectrum of melem consists of an intense emission peak centered at 441 nm, which is indicative of efficient charge separation between the bulk and the surface. Such charge transfer excitonic states involving the bulk and the surface have also been observed in other conjugated organic semiconductors that possess an extended $\pi$-conjugated network that prevents radiative recombination by delocalizing the Frenkel exciton. However, because of the conductive conjugated surface, nonradiative charge recom- bination can take place over new localized states in the sheets scaffold.

In order to investigate the lifetime of excited charged species, and charge separation processes, we collected time- 
resolved photoluminescence (TRPL) spectra of g-C$_3$N$_4$ and C$_3$N$_5$ using a single photon picosecond pulsed laser at a 
wavelength of 405 nm. Figure 8 displays the PL lifetime decay curves of g-C$_3$N$_4$ and C$_3$N$_5$. The PL decay curve was fitted 
trirexponentially using the following equation:

$$I(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3}$$

where, $A_1$, $A_2$ and $A_3$ represent the normalized amplitudes of each decay component and $\tau_1$, $\tau_2$ and $\tau_3$ are values of the lifetime components, respectively. The existence of three radiative lifetimes in the fitted PL lifetime spectra of g-C$_3$N$_4$ and C$_3$N$_5$ was in good agreement with previously reported carbon nitride based materials. The obtained values of lifetimes and their fractional components are given in Table 2.

The three components in the PL lifetime decay curve of g-C$_3$N$_4$ can be assigned to various energy states in g-C$_3$N$_4$ formed by the overlap of C and N sp$^2$ and sp$^3$ hybridized orbitals and the presence of lone pairs of electrons, which allow for various radiative transitions. g-C$_3$N$_4$ is composed of tri-$s$- 
triazine (C$_3$N$_6$) units interconnected with tertiary nitrogen atoms where C–N sp$^2$ hybridized state constitute high energy $\sigma$ and $\sigma^*$ molecular orbitals while C–N sp$^3$ hybridization gives rise to a conjugated network resulting in low energy $\pi$ bonding and $\pi^*$ antibonding orbital, which constitutes the valence and conduction bands, respectively. The presence of unbonded lone pairs of electrons on pyridinic N atoms creates energy levels just below the $\pi$ bonding orbital and their overlap with the $\pi$ conjugated system can further decrease the energy of the $\pi$ molecular orbital resulting in the reduction of the bandgap.

The first two shorter lifetime components of 3.31 and 0.75 ns with 34% and 63% contribution in g-C$_3$N$_4$ correspond to charge carrier recombination from $\sigma^*$ and $\pi^*$ antibonding to $\pi$ MO. The third longer lifetime component of 25.02 ns with 610 relative low contribution originated due to intersystem crossing (ISC) of electron from $\sigma^*$ and $\pi^*$ orbital followed by radiative relaxation to conjugated $\pi$ orbital and trap-assisted radiative recombination. The two lifetimes of C$_3$N$_5$ at 8.10 and 2.11 ns with 72% and 26% contributions in the PL decay curve were significantly longer lived in comparison to g-C$_3$N$_4$, strongly suggesting that the introduction of azo moiety extends $\pi$ conjugated network which facilitates better charge carrier mobility on C$_3$N$_5$ sheets (delocalized the exciton, as mentioned previously) and prevents faster charge carrier recombination. Further, because of extended conjugation, the difference between $\sigma^*$ and $\pi^*$ bands gets decreased, which is also evident in Mott–Schottky measurement (Figure S6b). The low energy difference between $\sigma^*$ and $\pi^*$ accelerates the transfer of electrons from $\sigma^*$ and $\pi^*$ orbital via intersystem crossing followed by radiative relaxation, which was evident from higher percentage contribution of the third lifetime component (73%).

The average lifetime ($\tau_{avg}$), which is regarded as coherent measure to evaluate the rate of spontaneous emission, was calculated from the three lifetime components using the following expression:

$$\tau_{avg} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

From eq 2, the average lifetimes of g-C$_3$N$_4$ and C$_3$N$_5$ were calculated to be 12.43 and 4.40 ns, respectively. The decreased lifetime of the C$_3$N$_5$ in comparison to g-C$_3$N$_4$ coupled with the very weak photoluminescence of C$_3$N$_5$ (as shown in Figure 7b) is indicative of fast quenching of the C$_3$N$_5$ luminescence. The fast quenching might originate from improved charge separation in C$_3$N$_5$ due to a larger conjugated $\pi$ network but might also be due to stronger nonradiative transitions. Fast exciton dissociation with concomitant high carrier mobility can result in photogenerated electrons finding trap sites (and moving to them) and recombining by nonradiative processes. The aforementioned processes are highly likely in C$_3$N$_5$ since the presence of azo bonds extends the $\pi$ network because of overlap of N 2p orbital on azo nitrogens with the $\pi$ network of heptazine motif due to which electrons can move within C$_3$N$_5$ scaffold freely. The lower PL lifetime of C$_3$N$_5$ in comparison to g-C$_3$N$_4$ was consistent with steady-state PL where C$_3$N$_5$ shows prodigious quenching in its PL spectrum.

### Table 2. PL Lifetime of Phogenerated Charge Carrier and Their Relative Contribution in g-C$_3$N$_4$ and C$_3$N$_5$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>Average Lifetime ($\tau_{avg}$) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$</td>
<td>3.31 [0.34]</td>
<td>0.75 [0.63]</td>
<td>25.02 [0.05]</td>
<td>12.43</td>
</tr>
<tr>
<td>C$_3$N$_5$</td>
<td>8.10 [0.07]</td>
<td>2.11 [0.26]</td>
<td>0.28 [0.73]</td>
<td>4.40</td>
</tr>
</tbody>
</table>
Electron paramagnetic resonance (EPR) spectra of g-C3N4 and C3N5 to elucidate electronic nature and band excited paramagnetic species were collected under dark and UV irradiation at room temperature (Figure 8b). The EPR spectra of g-C3N4 under dark conditions exhibits an intense Lorentzian EPR resonance signal located at a g-factor of 2.003. The observed EPR signal originated due to the presence of unpaired electrons in the sp_2 hybridized aromatic π-system which was in good agreement with previous reports. The EPR signal intensity of g-C3N4 increased after UV irradiation, attributed to populated unpaired electrons in the conduction band due to π−π* and N nonbonding to π* (n−π*) transition followed by slow relaxation via ISC. The observed EPR signal of C3N5 was also observed at 2.003 g-value, which implies basic graphitic heptazine skeleton remains intact in C3N5 framework. Further, after irradiation with UV light, the EPR signal intensity of C3N5 was also enhanced due to increased numbers of unpaired electrons in the conduction band. However, the overall EPR signal intensity of C3N5 in both the dark and under UV illumination was significantly weaker in comparison to g-C3N4, which was attributed to a lesser number of unpaired electrons in C3N5, which in turn can be taken as evidence of the presence of extra N atoms outside the heptazine nucleus in comparison to conventional N-rich carbon nitride materials where N atoms substitute C atoms in the heptazine motif. It is well documented in the literature that substitution of sp^3 hybridized +4 state C atom in heptazine motif with sp^2 hybridized +3 state N atom will liberate extra electrons in the aromatic system, which will distort electronic symmetry and also increase EPR signal intensity. However, in the case of C3N5, the additional N atom makes an azo bond with an N atom outside the ring via π overlap and the extra electrons remain in the form of lone pairs (Figure 8d).

Fluorescence lifetime imaging microscopy (FLIM) of samples at different spots was used to probe the homogeneity of samples and to determine the nature of the fluorescence (Figure S7). The PL spectra of g-C3N4 samples obtained from different spots exhibited identical emission profiles with a sharp intense peak at 480 nm, which was in good agreement with the steady-state PL spectrum (Figure 7b). The slight red shift in the emission peak (Figure S7a) is attributed to the difference in the mechanism of excitation (750 nm two-photon excitation source for FLIM, 360 nm single photon excitation in Figure 7b). Furthermore, the emission spectrum of C3N5 displays two relatively weak peaks centered around 410 and 490 nm which likely originated from some relatively smaller C3N5 polymeric fragments and heptazine networks (Figure S7c). The smaller fragments are consistent with a lesser number of MH units and therefore exhibit PL properties closer to that of C3N4. FLIM images of g-C3N4 were brighter than C3N5, which further supports our inference that the charge separation process was dominant in C3N5 samples (Figure S7b,d). The C3N5/MB samples obtained after methylene blue dye adsorption displayed relatively strong PL and brighter FLIM images due to the presence of MB in the composite (Figure S7c,f). The absence of PL quenching in the C3N5/MB composite further suggests the absence of photoinduced charge transfer between the methylene blue and C3N5.

The synthesized C3N5 material was explored for dye adsorption studies using methylene blue (MB) as a model dye. Methylene blue is a staining dye widely used in the paper, textile and leather industries which also constitutes a good example of a colored water contaminant, which due to its excellent visible light absorption, reduces light penetration in aqueous ambient and adversely affects aquatic flora and fauna. All dye adsorption studies were carried out at room temperature and under dark conditions. UV−vis spectra of MB solutions during dye adsorption experiments (for experimental details, see Supporting Information). MB has a sharp peak at 664 nm due to π−π* transition and a shoulder around 614 nm which represents MB present in dimeric and polymeric π stacked forms in water (Figure 9a). After the addition of C3N5 sample into methylene blue solution, the color of the solution instantaneously turned green. The green solution after centrifugation turned completely colorless, which demonstrated the prompt adsorption of MB dye over the surface of C3N5 and subsequent settling of the MB adsorbed C3N5 during centrifugation. The obtained solid after centrifugation (denoted as C3N5/MB) exhibits a sharp absorption peak intermediate between C3N5 and MB with a broad peak centered at 680 nm. The redshifting in the peak of
734 C\textsubscript{3}N\textsubscript{5} from 664 to 680 nm is attributed to the transformation
735 of MB into monomeric form and some degree of ground state
736 charge transfer from C\textsubscript{3}N\textsubscript{5} to MB during adsorption on the
737 surface of C\textsubscript{3}N\textsubscript{5}. The dye adsorption performance of C\textsubscript{3}N\textsubscript{5} was
738 much higher than g-C\textsubscript{3}N\textsubscript{4}. MB is a well-known cationic dye
739 possessing positive charge centered on the S atom in aqueous
740 solutions.\textsuperscript{58} On the other hand, the surface of C\textsubscript{3}N\textsubscript{5} material
741 has electron-rich character due to the presence of secondary N
742 (NC\textsubscript{2}) in heptazine moieties, terminal \(-\text{NH}_2\) and \(\pi\) extended
743 network. Therefore, electrostatic interactions between the
744 positively charged MB molecule and negatively charged C\textsubscript{3}N\textsubscript{5}
745 are likely responsible for the instantaneous adsorption.\textsuperscript{54,59} To
746 confirm negative charge on the surface of C\textsubscript{3}N\textsubscript{5}, \(\zeta\)-potential
747 measurement was performed which depicts average surface
748 charge of \(-36.2\) mV and proves the electron-rich surface of
749 C\textsubscript{3}N\textsubscript{5} (Figure S8).\textsuperscript{54} Further, MB can also adsorb on the surface
750 of C\textsubscript{3}N\textsubscript{5} via \(\pi\)–\(\pi\) stacking between aromatic conjugated
751 network of MB and \(\pi\) framework of C\textsubscript{3}N\textsubscript{5} (Figure 9b).\textsuperscript{60} To
752 investigate the role of surface specific properties in the
753 enhanced adsorption profile, Brunauer–Emmett–Teller
754 (BET) surface area (\(S\textsubscript{BET}\)), pore volume (\(V_p\)) and pore
755 diameter (\(r_p\)) of g-C\textsubscript{3}N\textsubscript{4} and C\textsubscript{3}N\textsubscript{5} were measured by N\textsubscript{2}
756 adsorption and desorption. The obtained BET surface area,
757 pore volume and pore diameter for g-C\textsubscript{3}N\textsubscript{4} were found to be
758 11.47 m\textsuperscript{2} g\textsuperscript{-1}, 0.095 cm\textsuperscript{3} and 19.13 nm while these values for
759 C\textsubscript{3}N\textsubscript{5} were found to be 1.78 m\textsuperscript{2} g\textsuperscript{-1}, 0.002 cm\textsuperscript{3} g\textsuperscript{-1} and 16.98
760 nm, respectively. The obtained surface values indicate a
761 decrement in the surface area of C\textsubscript{3}N\textsubscript{5} in comparison to g-
762 C\textsubscript{3}N\textsubscript{4}. The relatively low surface area of C\textsubscript{3}N\textsubscript{5} might be due to
763 the less gas evolution (three NH\textsubscript{3} per heptazine unit) from
764 melam hydrazine precursor during thermal annealing step
765 while the formation of g-C\textsubscript{3}N\textsubscript{4} from melamine precursor
766 releases six NH\textsubscript{3} molecule per heptazine unit. Further,\textsuperscript{77} hydrogen bonded melem hydrazine precursor might promote
767 in-plane cross-linking of heptazine units leading to a stacked
768 sheets type structure which reduces the effective accessible
769 surface area. Contrarily, in g-C\textsubscript{3}N\textsubscript{4} ring formation and
770 polymerization step can produce cross-linking between sheets
771 giving a porous structure with high surface area. The obtained
772 results suggest that an electronic interaction between C\textsubscript{3}N\textsubscript{5} and
773 MB is responsible for the superior adsorption performance of
774 C\textsubscript{3}N\textsubscript{5} rather than an increased surface area.

To investigate whether the nature of adsorption was
776 chemisorption or physisorption, and to explore the possibility
777 of any chemical bonding, the C\textsubscript{3}N\textsubscript{5}/MB composite was
778 analyzed using NMR spectroscopy. The \(\text{\textsuperscript{13}C}\) NMR spectrum
779 of C\textsubscript{3}N\textsubscript{5}/MB composite did not show any change in peak
780 position and intensity of C\textsubscript{3}N\textsubscript{5}, which demonstrated the
781 adsorption of MB on C\textsubscript{3}N\textsubscript{5} to be purely physisorptive in nature
782 (Figure S9d). FTIR, Raman and PL spectra of C\textsubscript{3}N\textsubscript{5}/MB
783 composite displayed various cumulative peaks and signals due
784 to the presence of MB in the C\textsubscript{3}N\textsubscript{5}/MB composite. However,
785 no evident signals for any chemical interaction can be
786 identified, which further supports a purely physical interaction
787 (physisorption) between C\textsubscript{3}N\textsubscript{5} and MB (Figure S9a–c).
788
c\textsubscript{3}N\textsubscript{5}/MB composite displayed various cumulative peaks and signals due
789 to the presence of MB in the C\textsubscript{3}N\textsubscript{5}/MB composite. However,
785 no evident signals for any chemical interaction can be
786 identified, which further supports a purely physical interaction
787 (physisorption) between C\textsubscript{3}N\textsubscript{5} and MB (Figure S9a–c).
788 Additionally, XPS spectra of C\textsubscript{3}N\textsubscript{5}/MB composite were
789 identical to pristine C\textsubscript{3}N\textsubscript{5} samples which revealed that C\textsubscript{3}N\textsubscript{5}
790 signals dominated over MB, and no change in BE value was
791 observed which ruled out the possibility of any chemical bond
792 formation between C\textsubscript{3}N\textsubscript{5} and MB (Figure S10).

To quantify the excellent dye adsorption capacity of C\textsubscript{3}N\textsubscript{5},
794 various parameters such as the adsorption capacity, adsorption
795

Figure 10. Kinetics of MB dye adsorption on g-C\textsubscript{3}N\textsubscript{4} and MB displaying (a) pseudo-first-order fitted curve, (b) pseudo-second-order fitted curve and MB adsorption isotherms fitted by Langmuir and Freundlich model of (c) g-C\textsubscript{3}N\textsubscript{4} and (d) C\textsubscript{3}N\textsubscript{5}, respectively. \(q_e\) is the amount of dyes adsorbed at equilibrium while \(C_e\) is the equilibrium concentration of MB.
796 constants, linear regression correlation coefficient, and
797 adsorption isotherm were measured and compared with
798 pristine g-C3N4 (Figure 10 and Table 3). The adsorption
799 capacity (amount of dye adsorbed) of g-C3N4 and MHP
800 materials was calculated using eq 3:
801
802 Where q is the adsorption capacity, V is the volume of MB
803 solution, m is the mass of the added adsorbent, and C and Ce
804 are the initial and equilibrium concentrations of MB,
805 respectively. The kinetics of methylene blue adsorption on
806 the surface of g-C3N4 and C3N5 were investigated using first-
807 and second-order adsorption kinetics using eqs 4 and 5:
808
809 \[ q_t = q_e (1 - e^{-kt}) \] (4)

810 \[ q_t = \frac{kq_e^2t}{1 + kq_e^2t} \] (5)

Where \( q_e \) is adsorbed amount of dye after reaching equilibrium
809 and \( q_t \) is the adsorbed amount at time \( t \), and \( k \) is the pseudo-
811 first-order or pseudo-second-order adsorption rate constant.
812
The results obtained using pseudo-first-order and pseudo-
813 second-order kinetics are displayed in Table 3 and Figure
814 10a,b. The kinetic studies clearly demonstrate that the
815 prepared C3N5 samples can reach approximately 95%
816 adsorption–desorption equilibrium instantaneously (1 min),
817 and complete adsorption–desorption equilibrium within 10
818 min, which is an extraordinary performance compared to
819 previously reported carbon nitride and carbon based materials
820 which usually take 45 min to achieve equilibrium. 61 In
821 addition, the kinetics study indicated that the adsorption of
822 methylene blue on the C3N5 and g-C3N4 materials follows
823 pseudo-second-order adsorption kinetics, which agreed well
824

| Table 3. Pseudo-First- and Second-Order Kinetic Models of MB Adsorption on g-C3N4 and C3N5 and Langmuir and
Freundlich Adsorption Models Showing Isotherm Constants |
<table>
<thead>
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<tbody>
<tr>
<td>serial no.</td>
</tr>
<tr>
<td></td>
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<td>1</td>
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<td>2</td>
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</tbody>
</table>

| serial no. | sample name | Langmuir | Freundlich |
| --- |
| | | \( Q (mg \cdot g^{-1}) \) | \( b (L \cdot mg^{-1}) \) | \( R^2 \) | \( K (mg^{-1} \cdot L \cdot g^{-1}) \) | \( n \) | \( R^2 \) |
| 1 | g-C3N4 | 6.03 | 0.13 | 0.97 | 1.21 | 0.43 | 0.96 |
| 2 | C3N5 | 42.32 | 0.05 | 0.98 | 2.40 | 0.78 | 0.97 |

Figure 11. (a) XPS valence band spectra of C3N5 for determining energy levels. (b) Density of state revealing band structure of g-C3N4 and C3N5. (c) Linear sweep voltammogram showing current–potential characteristics of g-C3N4 (blue) and C3N5 (red) measured in 0.1 M Na2SO4 solution AM1.5G light irradiation (100 mW cm^{-2}) and under dark conditions. (d) Light on–off showing photocurrent response vs applied voltage by using 450 nm wavelength light (54.15 mW cm^{-2}) for g-C3N4 (blue) and C3N5 (red).
with previous reports. For isotherm studies, standard solutions of 5, 10, 15, 20, 25 and 30 ppm MB in water were prepared; 50 mL of these standard solutions was placed in a beaker and 50 mg of the adsorbents was added to them. The solutions were kept under strong stirring for 30 min under dark conditions to reach equilibrium, and then the concentration of methylene blue was calculated using UV−vis spectroscopy (see Supporting Information for details). The adsorption isotherms of methylene blue were investigated in terms of the Langmuir61a,62 and Freundlich models (eqs 6 and 7, respectively), and the results for g-C3N4 and C3N5 are displayed in Figure 10c,d, respectively; the relevant constants are reported in Table 3. It can be seen from Figure 10 and Table 3 that the value of R2 extracted by employing the Langmuir isotherm model was higher than the R2 value obtained from the Freundlich isotherm model, indicating that the Langmuir model representing complete monolayer coverage on homogeneous sites was successful in predicting the adsorption of methylene blue on both g-C3N4 and C3N5.64

\[ q_e = \frac{QbC_e}{(1 + bC_e)} \]  

(6)

\[ q_e = KC_e^n \]  

(7)

Where \( q_e \) is adsorbed amount of dye after reaching equilibrium (mg g\(^{-1}\)), \( R \) is correlation coefficient, \( Q \) is the monolayer adsorption capacity (mg g\(^{-1}\)), \( b \) is the adsorption coefficient (L mg\(^{-1}\)), \( C_e \) is the equilibrium concentration and \( K \) is the Freundlich constant.

To check whether C3N5 material displays any visible light induced dye degradation activity, 50 mL of 50 ppm MB containing solution was charged with 50 mg of C3N5 catalyst and stirred in the dark for 30 min to reach adsorption−desorption equilibrium. Subsequently, the obtained suspension was irradiated under simulated sunlight (AM1.5G, 100 mW cm\(^{-2}\)). After every 10 min, 1 mL of sample was withdrawn and centrifuged to remove solid C3N5 and the supernatant liquid was analyzed with UV−vis spectroscopy. The UV−vis analysis indicated that the concentration of MB solution does not change even after 8 h of irradiation. These results suggest that C3N5 is not active for dye degradation, which might be because of unfavorable band alignment. To understand the band structure of C3N5, Mott−Schottky plots were obtained in 0.5 M Na2SO4 solution (Figure S6b). From the Mott−Schottky plot, the flat band positions of g-C3N4 and C3N5 were found to be −1.05 and −0.91 V vs Ag/AgCl, respectively, which can be considered the conduction band position if the Fermi level lies just below conduction band (strong n-type character). Using the bandgap values obtained from the Tauc plot (2.65 eV for g-C3N4 and 1.76 eV for C3N5), the positions of the valence band edge for g-C3N4 and C3N5 were calculated to be +1.60 and +0.85 V vs Ag/AgCl, respectively. Since the standard band edge positions are usually expressed with reference to NHE, the CB and VB positions of g-C3N4 were calculated to be −0.85 and +1.04 V vs NHE at pH 0, while CB and VB positions of C3N5 were found to be −0.72 and +1.04 V vs NHE at pH 0.

XPS valence band spectra of C3N5 was collected to further information regarding the band structure (Figure 11a). The intersecting point obtained by extrapolation of XPS VB spectra on x and y axes gave the value of valence band maximum (VB\(_{\text{max}}\)). The VB\(_{\text{max}}\) of C3N5 was calculated to be +0.95 eV, which was approximately the same (+1.05 V) obtained from the Mott−Schottky measurements and UV−vis data. Further, by using XPS VB and optical bandgap (1.76 eV) values, the CB\(_{\text{min}}\) and VB\(_{\text{max}}\) of C3N5 were calculated to be −0.79 and +0.97 eV, while for g-C3N4, CB\(_{\text{min}}\) and VB\(_{\text{max}}\) positions were found to be −0.85 and +1.80 eV, respectively.

Figure 11b shows a schematic illustration of the density of states (DOS) distribution in C3N5 and g-C3N4.

The dye degradation process begins with the reaction with OH radical originating from photogenerated holes in the valence band of the semiconductor. The oxidation potential of water to generate OH radical (H2O/O2) is +2.38 V vs NHE at pH 0, which requires highly oxidative holes. Another route for the generation of OH radicals is the reduction of O2 to O•− anion radical (O2/O2•−, −0.33 V vs NHE at pH 0) at the conduction band followed by reaction with protons to afford OH radicals.63,65 However, for this process required protons should be derived from water oxidation (H2O/O2•− +1.23 V vs NHE at pH 0).61c Unfortunately, the valence band position of C3N5 is just +1.04 V vs NHE, which cannot facilitate water oxidation thus explaining the absence of photocatalytic activity for MB degradation. Nyquist plots of g-C3N4 and C3N5 determined with electrochemical impedance spectroscopy (EIS) under dark and AM1.5G irradiation demonstrate that the semicircle for C3N5 was larger than for g-C3N4 which represents a higher charge transfer resistance in C3N5 compared to g-C3N4; a higher charge carrier recombination is indicated in C3N5 (Figure S11).

Because of the unfavorable band edge positions of C3N5 (CB = −0.71 V and VB = +1.04 V vs NHE at pH 0), it is not able to function as a stand-alone catalyst for the photoelectrochemical splitting of water. However, the excellent visible light absorption of C3N5 encouraged us to investigate the photosensitizing effect of C3N5 to increase the photocatalytic performance of TiO2 (a wide bandgap semiconductor).67 The conduction band of C3N5 (−0.72 V vs NHE) was more negative than the conduction band of TiO2 (−0.1 V vs NHE), which favors transfer of photogenerated electrons in the CB of C3N5 to the CB of TiO2.68 To measure photosensitizing performance, C3N5 and g-C3N4 powders were mixed with TiO2 nanoparticles in α-terpineol solution (film-forming agent) followed by drop-casting on FTO/glass substrates coated with a thin (~50 nm) blocking layer of TiO2. A three electrode setup consisting of the samples as the photoanode (working electrode), Pt as cathode (counter electrode) and Ag/AgCl reference electrode was used for photoelectrochemical water splitting experiments in 0.1 M Na2SO4 electrolyte, while a Class A solar simulator was used as the source of AM1.5G simulated sunlight (100 mW cm\(^{-2}\)).

Linear sweep voltammograms of electrodes consisting of C3N5 and pristine g-C3N4 samples mixed with TiO2 NPs are shown in Figure 11a. It can be seen from Figure 11a that the photocurrent density for C3N5 sensitized TiO2 was much higher than g-C3N4 sensitized TiO2. The current density for C3N5 and g-C3N4 sample blended TiO2 sample was found to be 1.52 and 100 μA cm\(^{-2}\) at an applied potential of +0.6 V vs NHE (or 1.23 V vs NHE). To probe the improved photosensitizing performance in the visible region, on−off experiments using a 450 nm LED (54.15 mW cm\(^{-2}\)) were carried out, which clearly show the alternate drop and rise in photocurrents in on−off cycles (Figure 11b). Figure 11b also shows that the magnitude of the photocurrent was higher for the C3N5 sample. A similar pattern in the on−off cycle was observed when samples were irradiated with 505 nm LED.
947 (40.48 mW cm\(^{-2}\)), confirming the improved photosensitizing properties of C\(_3\)N\(_5\) at longer wavelengths (Figure S12). Further, photoelectrochemical water splitting experiment carried out using Na\(_2\)S (2.0 mmol) as hole scavenger showed enhanced photocurrent density, reaching up to 465 \(\mu\)A cm\(^{-2}\) for C\(_3\)N\(_5\) under AM 1.5 G irradiation (>420 nm) (Figure S13). Under identical conditions, the value of photocurrent density for g-C\(_3\)N\(_4\) was found to be 373 \(\mu\)A cm\(^{-2}\) (Figure S13a). A similar pattern was followed at higher wavelengths and calculated current density for C\(_3\)N\(_5\) was found to be 454 and 145 \(\mu\)A cm\(^{-2}\) at 450 and 505 nm, while for g-C\(_3\)N\(_4\) the value of current density was found to be 275 and 80 \(\mu\)A cm\(^{-2}\), respectively (Figure S13b). Photocurrent response of C\(_3\)N\(_5\) as a function of time during light on–off cycle does not change significantly compared to g-C\(_3\)N\(_4\), which demonstrates resiliency of C\(_3\)N\(_5\) under reaction conditions and charge flow (Figure S14). The maximum applied bias photon-to-current efficiency (ABPE) and incident photon-to-current efficiency (IPCE) achieved by C\(_3\)N\(_5\) was 0.059 and 2.33% (at 450 nm), while the value for g-C\(_3\)N\(_4\) was 0.048 and 1.41% (at 450 nm), respectively (Figure S13c,d).

To demonstrate the optoelectronic application of our newly synthesized graphenic semiconductor, we employed C\(_3\)N\(_5\) as the electron transport layer (ETL) in MAPbBr\(_3\) based perovskite solar cells and obtained a good result. Carbon-based materials have frequently been used as hole transport layers (HTLs) or hole collection electrodes in MAPbBr\(_3\) based solar cells, but have almost never been used (effectively) as ETLs to boost the open circuit photovoltage. Using C\(_3\)N\(_5\) as the ETL and with no optimization of any kind, we measured a \(V_{oc}\) of 1.3 V, \(J_{sc}\) of 7.5 mA cm\(^{-2}\) and a FF (fill factor) of 0.4 to obtain a power conversion efficiency (PCE) of 4.2% (Figures S15 and S16 in Supporting Information). Some context is needed to appreciate the significance of the aforementioned result. Methylammonium lead bromide (MAPbBr\(_3\)) is a halide perovskite with an electronic bandgap of 2.23 eV, which has two major advantages for solar cell applications in comparison to the more commonly used methylammonium lead iodide (MAPbI\(_3\)). In theory, it enables the construction of much
higher $V_{oc}$ solar cells that can be used to power electrocatalytic and electrochemical reactions and second, MAPbBr$_3$ is known to have superior ambient stability (less moisture sensitivity) and operational stability (due to the absence of phase transitions and enhanced thermal stability at a high working temperature) compared to MAPbI$_3$. However, until recently, most works in this area failed to achieve the expected high $V_{oc}$ value, and the typical $V_{oc}$ values obtained using were in the range 0.90–1.16 V. The use of carbon based charge transport layers has enabled a dramatic improvement in the performance of MAPbBr$_3$ based photovoltaic devices by generating photovoltages in excess of 1.3 V (as high as 1.6 V) without suffering a corresponding penalty in the short circuit current ($I_{sc}$). The first such report was by Wu et al. wherein indene-C60 bisadduct (ICBA) was used as the acceptor in conjunction with MAPbBr$_3$ to realize a high $V_{oc}$ perovskite solar cell. Shortly thereafter, Li et al. used carbon nanotubes as an efficient hole collector for MAPbBr$_3$ solar cells and achieved a $V_{oc}$ of 1.4 V. MAPbBr$_3$ sandwiched between modified PEDOT:PSS (hole transport layer) and PC$_6$BM (electron transport layer) resulted in a solar cell with a $V_{oc}$ of 1.52 V while a graphitic carbon anode (with no hole transport layer).

Table 4. Photovoltaic Performance of HPSCs Made with Bare PbX$_2$, 4 wt % g-C$_3$N$_4$ and C$_3$N$_5$ in PbX$_2$ Solution under AM1.5 G Solar Simulated Light

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$N$_5$</td>
<td>maximum</td>
<td>1.065</td>
<td>22.870</td>
<td>0.685</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>1.026 ± 0.043</td>
<td>22.560± 1.039</td>
<td>0.654 ± 0.044</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td>maximum</td>
<td>1.030</td>
<td>21.573</td>
<td>0.691</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>0.984 ± 0.042</td>
<td>21.204± 0.565</td>
<td>0.670 ± 0.017</td>
</tr>
<tr>
<td>bare</td>
<td>maximum</td>
<td>1.040</td>
<td>20.344</td>
<td>0.660</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>1.041 ± 0.035</td>
<td>20.394± 0.200</td>
<td>0.647 ± 0.020</td>
</tr>
</tbody>
</table>

Figure 13. (a) Raman spectrum of pristine 4NBT (black), DMAB (yellow) and comparison of SERS spectra of plasmon-exciton coinduced surface catalytic reaction of 4NBT to DMAB on AgNC (purple), AgNC/g-C$_3$N$_4$ (blue) and AgNC/C$_3$N$_5$ (red) under 532 nm laser irradiation at 1.0 mW power and 60 s accumulation time and SERS spectra as a function of laser power for plasmon-exciton coinduced surface catalytic transformation of 4NBT to DMAB on (b) AgNC/C$_3$N$_5$, (c) AgNC/g-C$_3$N$_4$ and (d) AgNC. The gradual lightening of color as a function of laser power represents the transformation of 4NBT to DMAB.
and TiO₂, electron transport layer were used by Liang et al. to realize a MAPbBr₃ solar cell with a \( V_{oc} \) as high as 1.57 V.\(^{7,1} \)

The origin of the poor \( V_{oc} \) values was poorly understood for a long time. Even now, there are two distinct explanations: one based on active layer material quality issues and another based on high interfacial recombination. For instance, vapor deposited MAPbBr₃ films were found to generate high \( V_{oc} \) values in comparison with solution-deposited films, which was attributed to the superior morphology and grain size in the vapor deposited films, and supported the explanation based on active material quality.\(^{7,2} \)

The second explanation was supported by the observation of high \( V_{oc} \) values when hole transport layers with deep HOMO levels were used, indicating that the separation of the electron- and hole-quasi-Fermi levels at the charge extraction interfaces was the controlling mechanism determining \( V_{oc} \).\(^{7,3} \) Our examination of MAPbBr₃ solar cells using C₃N₅ as the ETL provides a way to reconcile the above explanations. On the one hand, the high CB position of C₃N₅ is better aligned with the CB of MAPbBr₃, and enables an optimal value for the electron quasi-Fermi level at the perovskite–C₃N₅ interface. On the other hand, the low dark current observed using C₃N₅ ETI in comparison to both TiO₂ and g-C₃N₄ ETIs (Figure S17 in Supporting Information) indicates suppression of trap-mediated hopping through MAPbBr₃ due to the insertion of C₃N₅ as a midgap state-free barrier layer, thus enabling the circumventing of active layer material quality issues. In summary, it is noteworthy that an unoptimized ETI made with a brand new semiconductor (C₃N₅) that was cast into films from a particulate suspension, generated a \( V_{oc} \) value of 1.3 V, higher than that generated by TiO₂ and g-C₃N₄ ETIs.\(^{7,4} \)

The photovoltaic performance of halide perovskite solar cells is highly dependent on grain size and defects free lattice states and presence of small numbers of defects and trap sites have a detrimental effect. The trap assisted recombination can be minimized by passivating perovskite layer with graphenic materials due to their high carrier mobility and surface area, which can efficiently capture charge and improve transportation behavior resulting in better photovoltaic efficiency.\(^{7,5} \) Further, incorporation of graphenic semiconductors with perovskite precursor provide crystallization surface, which helps in increasing of grain size and minimize defects density at grain boundaries. The increased conjugation in C₃N₅ should lead to electron-rich conductive surface with high carrier density and better carrier mobility than g-C₃N₄.\(^{7,6} \)

To verify this assumption, we have blended MAₓFAₓ₋ₓPbBr₂₋ₓIₓ (\( x=0,0.1,0.2 \)) based perovskite with different wt % of C₃N₅ and g-C₃N₅. Under optimized conditions, 4 wt % doping of g-C₃N₅ and C₃N₅ with respect to PbX₂ was found best performing and C₃N₅ outperformed over g-C₃N₅ and bare PbX₂ based solar cell architecture attributed to better charge separation in more conjugated C₃N₅ scaffold and reduced trap sites.\(^{7,7} \)

Figure 12 shows the \( J–V \) curves of the best performing solar cells devices based on undoped and doped perovskite layers while the photovoltaic performance of solar cells is summarized in Table 4. Solar cells made with a compact undoped perovskite solar cell yielded a short circuit current density (\( J_{sc} \)) of about 20.344 mA/cm², an open circuit voltage \( (V_{oc}) \) of 1.04 V and fill factor (FF) of about 66% resulting in the overall power conversion efficiency (PCE) of about 13.959%. While, perovskite solar cell made with g-C₃N₅-doped perovskite layer show a \( J_{sc} \) of 21.573 mA/cm², \( V_{oc} \) of 1.03 V and fill factor of about 69.1% and corresponding PCE of about 15.344%. C₃N₅-doped perovskite solar cells displayed a PCE value of 16.689% resulting from \( V_{oc} \) of 1.065 V, \( J_{sc} \) of 22.87 mA/cm² and FF of 68.5%.\(^{7,8} \)

Capacitance–voltage measurement on fabricated devices with doped/undoped perovskite layer was measured at 10 kHz frequency in dark to determine bulk properties such as doping density (\( N_{D} \)) and energy equilibrium at the contacts, which is related to the flat-band potential (\( V_{fb} \)).\(^{7,9} \)

Mott–Schottky plots for the devices made with doped and undoped perovskite layer are shown in Figure 13.

\[
\frac{1}{C_p^2} = \frac{2}{ee^\epsilon \epsilon_D r} \left( V - V_{FB} - \frac{kT}{e} \right)
\]

\( r \)

\[
N_D = \frac{2}{ee^\epsilon \epsilon_D n}
\]

\( \epsilon_D \)

\( V_{fb} \) and \( N_D \) were calculated by using eq 8 and eq 9 respectively, where \( C_p \) is the space-charge capacitance (i.e., film capacitance) per unit area; \( \epsilon \) is the dielectric constant of the material, \( \epsilon_0 \) is the vacuum permittivity, \( k \) is Boltzmann constant, \( T \) is temperature in Kelvin, \( e \) is the electron charge and \( V \) is the applied potential. The measured \( V_{fb} \) of bare undoped, g-C₃N₅-doped and C₃N₅-doped perovskite solar cell was found to be 1.12, 1.08, and 1.15 V respectively, while carrier concentration of the respective devices was found to be 1.74 × 10¹⁰, 1.96 × 10¹⁰ and 1.36 × 10¹⁰ cm⁻³. This proves that doping perovskite layer with C₃N₅ significantly improves the charge transport in the device compared to the undoped and g-C₃N₅-doped devices.\(^{7,10} \)

To explore the charge transport characteristics, hole only devices with the architecture of FTO/PEDOT:PSS/Perovskite/Spiro-oMeTAD/Au was measured by the space charge limited current (SCLC) model described by the following equation:

\[
J = \frac{9}{8L} \epsilon_0 \epsilon_r \mu V^2
\]

\( \epsilon_0 \) \( \epsilon_r \) \( \mu \) and \( L \) are permittivity of the free space, relative permittivity of the perovskite, carrier mobility in the perovskite layer and thickness of perovskite layer, respectively. The hole mobility in pure perovskite was found to be 2.55 × 10⁻³ cm²/Vs while that of g-C₃N₅ and C₃N₅-doped perovskite was found to be 3.28 × 10⁻³ cm²/(V s) and 4.33 × 10⁻³ cm²/(V s), respectively (Figure S19).\(^{7,11} \)

To get insight into the charge transfer properties of perovskite solar cells based on undoped and doped perovskite layer, solid-state impedance spectroscopy measurements in the frequency range from 0.1 Hz to 1 MHz at different applied bias under dark conditions were performed. The resulting Nyquist plots were fitted with the circuit shown in inset of Figure 12c,\(^{7,12} \) where \( R_s \) is series resistance, \( R_{rec} \) and \( C \) represent the resistance and capacitance at the interface between the active layer and charge transport layer and \( Q \) is a constant phase element (CPE) with coefficient \( N \). The resulting recombination resistance of different solar cells obtained after fitting the Nyquist plot observed from the low-frequency region at different voltages is shown in Figure 12d–i. The C₃N₅-doped device showed a higher value of \( R_{rec} \) compared to the g-C₃N₅-doped and undoped devices. As the electron and hole transporting layers for all kind of devices are same, the difference in \( R_{rec} \) is mostly governed by the change in the interfacial property of perovskite layer induced by doping with C₃N₅.\(^{7,13} \)
Interfacial recombination is inversely proportional to the recombination resistance; therefore, it can be concluded that the interfacial charge recombination in perovskite solar cells significantly gets suppressed by doping with MHP, while it increases by doping with g-C\(_3\)N\(_4\) resulting in an improved \(V_{oc}\) in C\(_3\)N\(_5\) based device followed by the undoped and doped devices.

The low band gap and extended \(\pi\) conjugation of C\(_3\)N\(_5\) makes it an excellent candidate to harvest solar light to drive visible light induced catalytic reaction. Recently, plasmonic materials capable of generating hot electrons, coupled with graphenic materials, have shown wide potential in plasmon-exciton coinduced surface catalytic reactions.\(^7\^9\) The plasmon-exciton coupling for codriven chemical reactions can be measured by surface enhanced Raman spectroscopy (SERS).\(^8\) For plasmonic material. The comparative SERS spectra of NBT adsorbed on bare AgNC, and AgNC decorated on g-C\(_3\)N\(_5\) mW and C\(_3\)N\(_5\) using 532 nm laser and 1 mW laser power are presented in Figure 13a. Normal Raman spectra of the pristine 4NBT powder show three main Raman signals at 1101, 1332 and 1576 cm\(^{-1}\) assigned to S\(\equiv\)C stretch, NO\(_2\) vibration and C\(\equiv\)C stretch, respectively.\(^8\) After irradiating with 532 nm laser with a 1 mW power intensity, the N\(\equiv\)O vibration was decreased and new peaks at 1142 (C\(\equiv\)N stretch), 1389 and 1438 (N\(\equiv\)N stretch) cm\(^{-1}\) assigned to S\(\equiv\)C stretch, NO\(_2\) vibration and C\(\equiv\)C stretch, respectively.\(^8\) For bare AgNC the drop in 4NBT peak was not significant, which showed inefficient surface-plasmon-to-hot-electron conversion to promote plasmon-driven chemical reaction. The AgNC/g-C\(_3\)N\(_5\) showed a slight lowering of 4NBT peak intensity and rise in DMAB peaks; however, the peak was not disappeared suggesting incomplete transformation at lower laser power.
While for Ag/NC/C₃N₅, the N−O vibration peak was completely disappeared at 1.0 mW laser power. Further, we tested laser power dependent SERS spectra on NBT adsorbed samples, which demonstrate complete disappearance of 4NBT peaks for Ag/NC/C₃N₅ even at 0.7 mW, while bare Ag and Ag/NC/30 g-C₃N₅ system could not achieve complete degradation even at 10 mW laser power (Figure S22). Magnified SERS spectra of Ag/NC/C₃N₅ in the 1270–1470 cm⁻¹ region showed a gradual decrease in N−O vibration peak as a function of laser power.

AgNC and completely disappeared at 1.0 mW (Figure S20). A sluggish transformation rate was observed for AgNC/g-C₃N₅ and AgNC as evident from the increase in 4NBT peak at 1332 cm⁻¹ along with DMAB peak at 1389 and 1438 cm⁻¹ as a function of laser intensity. The excellent conversion efficiency of AgNC/g-C₃N₅ assembly was attributed due to better plasmon-to-electron conversion efficiency on conjugated C₃N₅’s surface, which lead to high-density hot electrons to facilitate high catalytic conversion.

We performed thermogravimetric analysis (TGA) analysis of g-C₃N₅ samples to determine the thermal stability of materials (Figure S21). The TGA thermogram of g-C₃N₅ shows two weight loss regimes in the range of 60−150 °C and 500−740 °C (Figure S21a). The first small weight loss (~6%) in the range of 60−150 °C was due to loss of surface adsorbed water molecules. The second major weight loss started from 550 °C, showed slow weight loss (~8%) up to 635 °C due to loss of NH₃ and condensation of heptazine units followed by almost ~70% sharp weight loss in the range of 635−740 °C due to degradation of heptazine moieties.94 Following that, a steady weight loss was observed up to 900 °C due to the removal of residual carbon material. For C₃N₅, an initial small weight loss of 6% in the range of 60−150 °C was attributed due to loss of surface adsorbed and intercalated water (Figure S21b). A second steady weight loss (~34%) observed in the temperature range of 420−630 °C was assigned to loss of bridging azo nitrogens (N=N=N=) and edge decorated NH₂ nitrogens.

The absence of any sharp weight loss for azo nitrogens demonstrates that azo nitrogens were not localized but present in a cross-linked heptazine network. Previous reports on azo-linked polymer also demonstrated excellent thermal stability of such polymers due to the formation of a rigid structure.85 Further, the observed weight loss value was in close agreement with expected weight loss value for azo nitrogen (33.5%) calculated by considering removal of three azo nitrogens (~N=N−N=− shared by two heptazine) from azo-bridged C₃N₁₀ unit, leaving behind C₃N₉-hetzapine unit. These results further validated the presence of azo nitrogens in C₃N₅ polymer. Approximately 38% sharp weight loss in 630−720 °C region was assigned to degradation of heptazine ring system followed by slow weight loss up to 900 °C for residual carbon. Further, to investigate the nature of the product formed at high temperature, we annealed the sample in a closed evacuated quartz tube at 800 °C for 4 h. The orange product turned black and stuck to the wall of the tubes. Raman analysis of the product showed specific D, G band along with the 2D band and demonstrate its transformation into N-doped graphene (Figure S22). Previous reports also demonstrate the transformation of carbon nitride based materials/nitrogenous precursors into N-graphene/N-carbon at higher temperatures.

To understand charge carrier dynamics and recombination mechanisms in C₃N₅, the surface potential changes of the samples under dark and under laser illumination at different wavelengths, were measured using Kelvin Probe Force Microscopy (KPFM) as illustrated in Figure 14. The surface topographical AFM image of g-C₃N₄ and C₃N₅ thin films deposited on bare FTO reveals an average roughness of 20.4 nm and 19 nm, respectively (Figure 14ai,bi). Figure 14aii−v and bi−v displays the surface potential map of g-C₃N₄ and C₃N₅ samples under dark conditions, 635, 520 and 450 nm, respectively. The FTO was grounded and behaves as an electron sink for photogenerated charges, leaving holes behind.

The surface potential map under dark for both g-C₃N₄ and C₃N₅ shows even distribution of charge all over the surface of samples, (Figure 14ai,bi). After illumination with 635 nm laser the contrast of blue spots (positive potential shift) in the surface potential map was increased for both g-C₃N₄ and C₃N₅; however, this change was much intense for C₃N₅. Under 520 nm light, the density of blue spots was slightly higher for g-C₃N₄ than C₃N₅, which drastically increased under 450 nm illumination (Figure 14a (ai,v) and 14b (bi,v)). These observations demonstrate that highest charge generation and accumulation on the surface was at 450 nm for g-C₃N₄ and at 635 nm for C₃N₅ while remaining moderate for both at 520 nm. Further, values of surface potential measured by KPFM under dark condition were found to be +156 and +45 mV for g-C₃N₄ and C₃N₅ respectively, which agreed well with the increased electron density on C₃N₅ than g-C₃N₄ due to contribution of charge from azo motif to heptazine ring system via extended orbital overlap (Figure 14c,d). The high surface negative charge of C₃N₅ was also confirmed by zeta-potential measurements (Figure S8). After illumination with 450 nm light, the surface potential was negatively shifted reaching maximum +40 mV for g-C₃N₄ and +25 mV for C₃N₅. Higher change in contact potential difference (CPD) or SP, i.e. 102 nmV, for g-C₃N₄ was observed due to good absorption at 450 nm for generation of electron−hole pairs and accumulation of negative charge on the sample surface. The broad surface potential peaks and significantly larger CPD shift for g-C₃N₄ were attributed possibly due to the longer lifetime (as confirmed by TRPL, Figure 8a) of g-C₃N₄ charge carriers resulting into delayed recombination of accumulated charge. Under 520 nm illumination, the surface potential values for g-C₃N₄ and C₃N₅ were measured to be 123 and 8 mV, while the change in SP was found to be 33 and 37 mV, respectively. For g-C₃N₄ relatively small CPD shifting at 520 nm can be explained due to its limited absorption at 520 nm wavelength generating fewer numbers of excitons, while in C₃N₅ most of the photogenerated charge get recombined due to faster recombination rate. Interestingly, C₃N₅ showed an unusually high SP shift (77 mV) at 635 nm, while g-C₃N₄ showed an explicitly small CPD shift (30 mV). The exceptional high SP shift at 635 nm demonstrated azo motif plays a certain role in charge carrier generation and stabilization at a longer wavelength. Azo-bridged aromatic compounds are well-known for their visible light absorption due to the presence of azo chromophore (−N=N−) in conjugation with aromatic units. The n−π* transition corresponding to azo nitrogen nonbonding orbital to the π* orbital of conjugated nitrogens in azo moiety occurs at low energy giving visible light absorption.86 In C₃N₅, where electron withdrawing heptazine units (C₆H₅−) were bridged together with azo bonds, these low energy transition can take place at 635 nm resulting into increase CPD shift at 635 nm. The high surface potential of C₃N₅ at 635 nm validates its potential to generate excitons at longer wavelengths.

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We report the synthesis of a modified carbon nitride framework C3N5 polymer containing exceptionally high N:C atomic ratio (5:3) melem hydrazine as the monomeric unit. Extensive characterization of C3N5 with XPS, EELS, NMR spectroscopy and elemental analysis suggested the presence of heptazine moieties bridged by azo nitrogens in the C3N5 framework. Because of the overlap between the π orbitals of C3N5 systems for direct and indirect (equipment use) support. U.K.T. is supported by a graduate student scholarship from Alberta Innovates. Some device fabrication and testing used research infrastructure made possible by a Leaders Opportunity Fund grant to K.S. from the Canada Foundation for Innovation and the Alberta Small Equipment Grants Program. We acknowledge use of the following facilities: the National Research Council - National Institute for Nanotechnology (NRC-NINT) Electron Microscopy Lab, the Cell Imaging Facility, the Analytical Chemistry Laboratory and the University of Alberta Nanofab. Drs. Shihong Xu and Wayne Moffat are kindly acknowledged for assisting in He-ion imaging. CHNS elemental analysis, respectively. We thank Prof. Alkivithes Meldrum for allowing the use of his lab to perform PL lifetime measurements.

## REFERENCES

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