Delineating the role of vacancy defects in increasing photocatalytic hydrogen production in an amorphous metal organic framework coordinated graphitic carbon nitride

Aswathy Rajan\textsuperscript{a}, S. Kamalakannan\textsuperscript{a}, M. Prakash\textsuperscript{a}, Satheesh Krishnamurthy\textsuperscript{b} and B. Neppolian\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry, SRM Institute of Science and Technology, Chennai- 603203, Tamil Nadu, India

\textsuperscript{b}School of Engineering and Innovation, The Open University, Milton Keynes, MK7 6AA, UK

Email Id: neppolianb@gmail.com, neppolib@srmist.edu.in

Abstract

The instability in aqueous solutions has impeded the effective employment of metal organic frameworks (MOFs) for various photocatalytic applications. Recent literatures have proved that certain support like graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) can improve the water-stability and meet other functionalities responsible for photocatalytic water splitting. To expound on the mechanistic details central to photoactivity of the g-C\textsubscript{3}N\textsubscript{4}/MOF systems, we relate the activity of an amorphous nickel-imidazole framework (aNi-MOF) with different vacancy (carbon and nitrogen) defects engineered g-C\textsubscript{3}N\textsubscript{4} systems. Vacancy defects significantly alter the electronic structure and characteristics of photoexcited charge carriers and thus, the photocatalytic activity of semiconductor photocatalysts. In this framework, by elucidating both the experimental and theoretical studies, carbon defective g-C\textsubscript{3}N\textsubscript{4} with aNi-MOF (C\textsubscript{v}CN/aNi) proves to be a potential candidate to speed up the photocatalytic hydrogen evolution reaction. The results also potentially accord to the reactive interaction between g-C\textsubscript{3}N\textsubscript{4} and aNi-MOF that a Ni-N bond is vital in photoactivity with the carbon defective C\textsubscript{v}CN/aNi photocatalyst producing 3922.01\(\mu\)mol g\textsuperscript{-1} for 3 hours which is \textasciitilde 3900 and 1700 times better than the pristine aNi-MOF and g-C\textsubscript{3}N\textsubscript{4}, respectively. Our report provides an insight into correlating the reactive mechanism in a g-C\textsubscript{3}N\textsubscript{4}/MOF system and the role of defects in photocatalytic hydrogen evolution reactions.

Keywords: Amorphous Metal-Organic Framework, Nickel-Imidazole framework, graphitic carbon nitride, Vacancy defects, Photocatalytic Hydrogen Production
Introduction

Regarded as a “Holy Grail” in chemistry, photocatalytic hydrogen (H\textsubscript{2}) production from water has been extensively studied as a replacement for existing fossil fuels. Different heterogenous photocatalysts including metal oxides, oxynitrides and oxysulphides, carbon based materials, etc., have been utilized for photocatalytic water splitting. However, these catalysts lack structural controllability and needs to improve the efficiency and stability for practical applications.\textsuperscript{1-3} Therefore, metal organic frameworks (MOFs) with high architectural tunability and intrinsic photoactivity have been considered as potential candidates for photocatalytic H\textsubscript{2} production.\textsuperscript{4}

In recent years, MOFs have kindled the interest of researchers as prospective energy harvesting materials due to their synthetic tunability, high surface area, tuneable pore size and structural regularity.\textsuperscript{5} Crystalline metal-organic frameworks (cMOFs) are made up of an infinite array of inorganic nodes connected to organic linkers and retain long-range order. The chemically versatile nature of cMOFs have been of interest for gas storage, selective separation of gases, water harvesting, heterogenous catalysis and drug delivery.\textsuperscript{6,7} In the quest for MOFs with more functionalities and applications, emerged alongside the cMOFs are a class of amorphous metal-organic frameworks (aMOFs) that maintain the fundamental secondary building blocks but lack long-range crystallinity. Most of the research focussed on aMOFs centres around adsorption or separation, electrocatalysis, drug delivery and their synthesis routes are majorly by high-temperature heating, ball milling and pressurizing.\textsuperscript{8,9} With the increasing diverse applications that have been reported for aMOFs, the introduction of defects to structures and understanding the role of defects have been riveting.

These disordered structures or defects are important for heterogenous reactions. Disorders along with electrical structure, charge transport, and surface characteristics are crucial variables controlling the photoactivity of a semiconductor.\textsuperscript{10,11} Semiconductors with lattice disorders may develop mid-gap states, often known as band tail states that extend to and overlap with the conduction band or valence band.\textsuperscript{12,13} As a result of this, the mid-gap states might develop into the active sites for electron-hole excitation and boost semiconductors' optical responsiveness. In addition to providing photoinduced carriers with trapping sites and preventing the recombination of electrons and holes, these controlled disordered defects also increase overall quantum efficiency.\textsuperscript{14} In our previous work, the integration of an amorphous nickel- imidazole framework (aNi-MOF) with graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) demonstrated
that the disordered architecture had effective active sites and improved charge separation to attribute to the enhanced photocatalytic hydrogen evolution from a mixture of water/triethanolamine (TEOA).15

Generally, graphitic carbon nitride (g-C_3N_4) is an organic and non-metal polymeric material and has gained significant attention for photocatalytic water-splitting, due to its advantageous conduction band (CB) edge and visible light active band gap (2.7eV). Nevertheless, the water-splitting ability of pure g-C_3N_4 is constrained by its low specific surface area and relatively higher rate of photoinduced charge carrier recombination.16,17 Numerous studies have been carried out to improve the photocatalytic activity of g-C_3N_4, including developing heterojunctions by coupling with transition metal oxides, dye sensitization, doping with non-metal [e.g. B, S, O] and metal [e.g. Fe, Co, Cu].18-20 Both g-C_3N_4 and MOFs are visible light-active photocatalysts, however when used separately, they have low quantum efficiencies and high recombination rates. Composite photocatalysts of the individual material can surpass the quantum efficiency limit. For example, Wang et. al. coupled UiO-66 with g-C_3N_4 to prepare a quasi-polymeric hybrid photocatalyst efficient in photocatalytic water splitting under visible light irradiation. The effective interfacial charge transfer from photoexcited g-C_3N_4 to UiO-66 was crucial for the increased in H_2 generation.21 Other MOFs like ZIF-67, NH_2-MIL-125 (Ti), etc. have also been integrated to g-C_3N_4 for photocatalytic hydrogen evolution.22-24 Several more cocatalysts, including Pt, complex, and hydrogenase, been introduced into MOFs employing the functional groups to achieve improved H_2 production.25,26 Despite all these studies, the reactive mechanisms involved in a MOF and g-C_3N_4 systems for photocatalytic hydrogen production has not been explored till date. The effect of defects and their role in improving the photocatalytic activity in such systems have also not been studied extensively.

Inspired by these findings, in extension to our earlier studies on aNi-MOF/ g-C_3N_4 system,15 we used a temperature controlled synthetic route to introduce carbon and nitrogen vacancies into the polymeric framework of g-C_3N_4 and a solvothermal pathway for its coordinative integration into aNi-MOF. It is expected that introducing vacancy defects (carbon and nitrogen) in the g-C_3N_4 may be an effective approach to scrutinise the reactive mechanism between aMOFs and g-C_3N_4 systems and also, an effort was made to investigate the effect of vacancies on photocatalytic activity. On correlating the photoactivity and the defects, it is observed that an active bonding with the Ni^{2+} ion from the extended framework of aNi-MOF with the N containing species in the g-C_3N_4 was critical. Thus, the C-defective aNi-MOF/ g-C_3N_4 system (C,CN/aNi) proved to be a potential candidate for photocatalytic water splitting with
3922.01 µmol g⁻¹ hydrogen production in comparison to 2750.93 µmol g⁻¹ and 776.112 µmol g⁻¹ produced by the non-defective (CN/aNi) and N-defective (N,CN/aNi) aNi-MOF/ g-C₃N₄ systems respectively. This work in support with the theoretical data integrates the concepts of defect chemistry with photoelectrochemistry, to analyse the changing electronic structure, associated charge transfer, and correlated reactive mechanisms involved in the photoreactivity of g-C₃N₄ coordinated MOF systems for the first time.

**Experimental Section**

*Reagents and Characterisation Studies*

2-methyl imidazole (2MI), Nickel nitrate hexahydrate (Ni(NO₃)₂, 6H₂O), Melamine, and other organic solvents used for the experimental studies were purchased and used without further purification.

The synthesised photocatalyst's crystal phases were studied with a Cu Kα radiation (λ=1.5406 Å) X-ray diffractometer (PANaltical Xpert powder diffractometer). Fourier-transform infrared (FT-IR) spectra were measured on a Shimadzu, IRTracer-100 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on PHI VersaProbe III Scanning XPS Microprobe. The morphology of synthesised samples was characterised by a high-resolution scanning electron microscopy (HRSEM) from Thermo Fisher Scientific, Apreo S and high-resolution transmission electron microscopic (HRTEM; JEOL Japan, JEM-2100 Plus microscope). The UV–vis diffuse reflectance (UV-DRS) spectra were obtained by a Shimadzu, UV-3600i Plus UV–vis spectrophotometer. A fluorescence spectrophotometer from Agilent was used for collecting photoluminescence (PL) spectra.

*Synthesis of amorphous nickel- imidazole MOF (aNi-MOF)*

Ni(NO₃)₂. 6H₂O, the metal precursor, and 2MI, the linker was dissolved separately in a 1:2 ratio in 15 mL of DMF solvent and ultra-sonicated for 20 min. The separate solutions were mixed together and treated solvothermally at 150 °C for 12 h. The powder sample was collected, subjected to multiple washes with DMF and methanol, and then vacuum dried at 80 °C.
Synthesis of g-C$_3$N$_4$ (CN)

A certain amount of melamine was calcined at a temperature of 530 °C for 4 h, and the resultant product was collected and milled to a fine powder. Finally, it was then marked as CN and placed in an airtight container for future use.

Synthesis of C vacant g-C$_3$N$_4$ (C$_v$CN)

Two step thermal oxidation treatments have been reported for the synthesis of ultrathin carbon defective g-C$_3$N$_4$ systems.$^{27}$ Thus, 500 mg of as prepared g-C$_3$N$_4$ was placed in a covered ceramic ark and reheated for 4 h at 530 °C. It was then stored in an air-tight container and named as C$_v$CN.

Synthesis of N vacant g-C$_3$N$_4$ (N$_v$CN)

In reference to previous studies,$^{28}$ in a boat shaped ceramic plate, 500 g as-prepared g-C$_3$N$_4$ was placed, then it was heat-treated for 4 h in an atmosphere of nitrogen at 600 °C. Finally, it was stored in an air-tight container for further use and labelled as N$_v$CN.

Synthesis of g-C$_3$N$_4$/aNi-MOF composites

A solvothermal method similar to that used for aNi-MOF synthesis was followed for the preparation of g-C$_3$N$_4$/MOF nanocomposites except that 150 mg of the various g-C$_3$N$_4$ (CN, C$_v$CN and N$_v$CN) was first sonicated in a 30 mL DMF solvent for 20 min after which the metal precursor and linker were added. The samples were labelled as CN/aNi, C$_v$CN/aNi and N$_v$CN/aNi when the starting precursor for g-C$_3$N$_4$ synthesis were bare (CN), carbon defective g-C$_3$N$_4$ (C$_v$CN) and nitrogen defective g-C$_3$N$_4$ (N$_v$CN), respectively.

Synthesis of Cobalt- imidazole MOF (ZIF-67)

Co(NO$_3$)$_2$. 6H$_2$O and 2MI, the linker was dissolved separately in a 1:2 ratios in 15 mL of DMF solvent and ultra-sonicated for 20 min. The separate solutions were mixed together and treated solvothermally at 150 °C for 12 h. The powder sample was collected, subjected to multiple washes with DMF and methanol, and then vacuum dried at 80 °C.

Synthesis of g-C$_3$N$_4$/ ZIF-67 composites
The synthesis of g-C$_3$N$_4$/ZIF-67 composites were similar to the solvothermal synthesis of g-C$_3$N$_4$/aNi-MOF composites except that instead of Ni (NO$_3$)$_2$, the metal precursor used is Co(NO$_3$)$_2$. The samples were labelled as CN/ZIF-67, C$_v$CN/ ZIF-67 and N$_v$CN/ZIF-67 when the starting precursor for g-C$_3$N$_4$ synthesis were bare (CN), carbon defective g-C$_3$N$_4$ (C$_v$CN) and nitrogen defective g-C$_3$N$_4$ (N$_v$CN), respectively.

**Photocatalytic measurements**

The photocatalytic hydrogen production reaction was studied both under a 300W Xenon Lamp and simulated solar light (1.5 AM$_0$) of 1 sun intensity and. In a 100 mL Pyrex reactor, 5 mg of the photocatalyst sample was dispersed in an aqueous TEOA solution (10 vol%, 50 mL). To eliminate any dissolved oxygen present in the reactor, the system was then purged with nitrogen gas for 20 min before the light irradiation. A gas chromatograph with molecular 5 °A column and thermal conductivity detector (TCD) was employed to measure the amount of evolved gas (Shimadzu GC-2014). All the samples were irradiated for a period of 3 hours.

**Photoelectrochemical Analysis**

The photoelectrochemical characteristics of the synthesised photocatalysts were investigated using an Ag/AgCl reference electrode, a Pt counter electrode, and glassy carbon coated with the suitable photocatalyst as a working electrode. In the study, a 1:1 mixture of water and ethanol was ultrasonically dissolved with 2.5 mg of catalyst using 0.005 mL of Nafion. An Biologic SP150 electrochemical workstation was used to evaluate the electrochemical analysis after the slurry was drop casted onto a glassy carbon (GC) electrode. 0.1 M Na$_2$SO$_4$ solution was the electrolyte that was employed. The illumination source was 300 W SSEM, Photo Emission Tech, USA made 1.5 AM solar simulator .

**Computational Details**

To analyse the photocatalytic hydrogen evolution reaction (HER) at the CN/ aNi material, periodic boundary calculations were performed. The interactions between the aNi-MOF and CN were accurately described using the dispersion term (DFT+D3). The
CP2K/Quickstep package was used to perform these periodic calculations. The CN/ aNi system electron densities were expressed using the Gaussian plane wave (GPW) basis. This mixed GPW enables the expression of the valance electron densities and pseudopotentials. Here, MOLOPT-TZVP basis sets were used to represent the C, N, and H atoms, while the Ni atom was represented by the DZVP-MOLOPT-SR-GTH basis set (SR stands for short-range). An orbital transformation (OT) and plane-wave cutoff (400 Ry) were incorporated. All atoms in the complex systems were freely optimized throughout the simulation. The binding energies of CN/ aNi at were calculated by below equation,

\[ E_{\text{ads}}(\text{CN/ aNi}) = E_{\text{CN/ aNi}} - (E_{\text{aNi-MOF}} + E_{\text{CN}}) \]  

where \( E_{\text{ads}}(\text{CN/ aNi}) \) is the total energy of the CN/ aNi and \( E_{\text{aNi-MOF}}, E_{\text{CN}} \) are the energies of aNi-MOF and CN, respectively. Then, we generated the electron density profile from the computed complex systems at the PBE+D3/TZVP level to interpret the accumulation and depletion of electrons between the aNi-MOF and CN systems and their charge transfer phenomena thereof. The interfacial charge transfer was calculated by restrained electrostatic potential (RESP) charge analysis. The electron density plot is expressed using the following equation

\[ \Delta \rho = \rho((\text{CN/aNi})) - \rho((\text{CN})) - \rho(\text{aNi-MOF}) \]  

where \( \rho((\text{CN/aNi})) \) is the charge density of the aNi-MOF at CN and \( \rho(\text{aNi-MOF}) \) is the charge density of aNi-MOF. The structural minimization was done until the forces of all-atoms below 0.0001 eV/Å. Furthermore, we used optimized geometries for finding the projected density of states (PDOS) of each elements. We removed one carbon atom and one nitrogen atom to model a C\text{v}CN and N\text{v}CN, respectively.

**Results and Discussions**

The highly crystalline g-C\text{3}N\text{4} (CN) is mainly assembled by C and N atoms. Thus, the key approach to understand the reactive mechanism between the aNi-MOF and g-C\text{3}N\text{4} system would involve introducing carbon and nitrogen vacancies in g-C\text{3}N\text{4} systems. The introduction of vacancies into the polymeric framework of g-C\text{3}N\text{4} modifies the atomic arrangement and chemical groups. Varying characterization techniques are employed to identify the introduced vacancies and their interaction with the aNi-MOF.
Figure 1. (a) XRD patterns and (b) FTIR spectra of g-C₃N₄ (CN), vacancy defective g-C₃N₄ (carbon vacancy- CᵥCN and nitrogen vacancy- NᵥCN), aNi-MOF and g-C₃N₄/MOF (CN/aNi, CᵥCN/aNi and NᵥCN/aNi) composites, (c) XPS Survey spectra and (d) C 1s spectra of CN, CᵥCN and NᵥCN, (e) C/N ratios of CN, CᵥCN and NᵥCN as obtained by XPS and HRSEM elemental analysis.

Figure 1a shows XRD patterns of g-C₃N₄ (CN), vacancy defective g-C₃N₄ (carbon vacancy- CᵥCN and nitrogen vacancy- NᵥCN), aNi-MOF and g-C₃N₄/MOF (CN/aNi, CᵥCN/aNi and NᵥCN/aNi) composites. All CN based samples represent a typical g-C₃N₄ composition without any impurity. Specifically, g-C₃N₄ has a stacked structure, and as explained by Lotsch et al. the in-plane structure in the g-C₃N₄ planes is made of regularly cohered strands of hydrogen.
bonded polymeric melon units with NH$_2$/NH groups resulting in two basic XRD peaks around 27.5° and 12.9°.\textsuperscript{35} The weak intensity at 12.9° corresponds to the in-plane structural packing motif and the one at 27.5° attributes to the (002) plane arising from long-range interplanar stacking of aromatic systems or the interlayer reflection of graphitic structure.\textsuperscript{20} When vacancies are present in the CN framework, two significant properties connected with these two peaks are seen. First is the shift in the peak at 27.5° to slightly higher 2θ values, which is indicative of a reduction in the interplanar stacking distance. This shift in peak can be explained as an enhanced interlayer stacking order accounted by the greater 600 °C condensation temperature and double calcination of CN, in case of N$_v$CN and C$_v$CN respectively. By isothermally tempering the synthesised g-C$_3$N$_4$ in a closed quartz vessel at 600 °C for 10 h, Thomas et al. stated a shortest interlayer distance of 0.319 nm in coherently-ordered carbon nitride. The other characteristic is the significantly reduced long-range order of the in-plane structural packing in the CN nanosheets, which is indicated by the considerably weakened and expanded peak at 13.1°.\textsuperscript{36} In this context, the direct polycondensation at 600 °C of the CN in presence of N$_2$ for synthesising N$_v$CN and double calcination of CN for C$_v$CN, in an open ampule will undoubtedly effect in the marked loss of lattice carbon or nitrogen atoms so that the spaces between strands will have a broader distribution range. As evident from the structural nature of g-C$_3$N$_4$, C and N are in the ratio 3:4, this necessarily lowers the long-range order of the strands, causing a reduced intensity in case of N$_v$CN in comparison to the C$_v$CN samples. Additionally, in order to compare the structure of the attained aNi-MOF with the ordered crystalline structures of nickel-imidazole framework, in reference to our previous study, a crystalline Ni-MOF was synthesised and the amorphous counterpart was compared (Figure S1).\textsuperscript{15} A wide peak around 14° was seen in the XRD pattern of aNi-MOF, demonstrating the amorphous nature of the Ni-MOF. The successful integration of CN and defective CN systems to the aNi-MOF was confirmed by the broad peak around 14°.\textsuperscript{37}

FT-IR spectroscopy was used to understand the interactions among CN, defective CN and aNi-MOF systems. The structure of defective CN systems (N$_v$CN and C$_v$CN) is basically the same as that of CN, though vacancy defects have been introduced in the graphitic carbon nitride framework. The spectra of CN, N$_v$CN and C$_v$CN show typical IR patterns of graphitic carbon nitride and are displayed in Figure 1b. The presence of secondary and primary amines that are only partially condensed is indicated by the broad peaks at about 3000–3500 cm$^{-1}$ (and their intermolecular hydrogen bonding).\textsuperscript{35} The peaks ranging from 1200 to 1800 cm$^{-1}$ are arising from the bridging C-NH-C units or the trigonal C−N(−C)−C (full condensation). The
fundamental melon units with NH/NH₂ groups are identified by the absorption band at about 810 cm⁻¹, which results from the breathing modes of triazine rings. After the introduction of vacancies to CN, some peaks shifted to lower frequencies in case of N_vCN and C_vCN. Nevertheless, the intensity of the peak at 3200 cm⁻¹ (corresponding to amino groups) increases in the C_vCN sample compared to N_vCN due to the removal of tertiary carbon and the concomitant formation of more amino groups. However, the characteristic peaks attributed to the C-N and N-H bonds from 1200-1800 cm⁻¹ and 3000 cm⁻¹ to 3500 cm⁻¹, respectively are observed with decreased intensity in the g-C₃N₄/MOF composites (N_vCN/aNi, C_vCN/aNi and CN/aNi) representing the effective coordination of Ni²⁺ to the –NH₂ groups of g-C₃N₄. In the FTIR spectra of aNi-MOF, the characteristic absorption bands in the range of 670 cm⁻¹- 1400 cm⁻¹ attributes to the stretching to bending modes of the methyl imidazole(MI) ring and the bands around 1200 cm⁻¹ related to the C=N (stretch mode) in 2-MI. The sharp band at 476 cm⁻¹ originating from Ni-N stretch in all the nanocomposites explained that a coordination polymer similar to aNi-MOF was formed. The Ni-N bond intensity in the composites was in the order of C_vCN/aNi > CN/aNi > N_vCN/aNi implying a better integration of C_vCN in comparison to the N_vCN and CN to the aNi-MOF.

To further understand the electronic properties of the systems in particular to core levels changes with respect to functionalisation, X-ray photoelectron spectroscopy (XPS) were performed. Typical XPS survey spectra of CN contain 3 sharp peaks at 287, 398 and 531 eV corresponding to C 1s, N 1s and O 1s respectively (Figure 1c). The slight O 1s signal arises from the absorbed H₂O and CO₂ on the catalyst surface. The quantitative analysis from XPS spectra reveals that the C/N ratio of the C_vCN is < and N_vCN. As seen from Figure 1d, the pristine CN C 1s spectra is fitted by peaks at binding energies at 284.8, 286.3 and 288.10 eV stemming from the adventitious carbon (C-C/C=C), cyano groups or C-NH₂ groups on the edges of heptazine units and the sole three- coordinated carbon (C₃c), respectively. The N 1s peak can be resolved into a major peak centred at 398.5 eV and a minor shoulder peak at 399.68 eV, which, respectively, arise from two-coordinated N atoms (N₂c) and three-coordinated (N₃c) nitrogen atoms in the framework of the heptazine unit (Figure S2). The peak at 401.16 eV originates from NH₂ groups in the heptazine units. The amino group is formed due to the breakage of C-N bond during thermal condensation of CN. As a result of the introduction of vacancies, apparent changes occur in both N 1s and C 1s XPS spectra of CvCN and N_vCN when compared to CN. In case of C_vCN, the C 1s-to-N 1s peak ratio reduces, while that of amino groups to graphitic N increases. The redistribution of excess electrons left by the missed
carbon atoms causes a slight positive shift in the binding energy of C in the C=N-C configuration. The peak area ratio of N-C=N to C=C/ C-C increases in order of C,CN < N,CN < CN. The lower graphitic carbon functionalities suppress the photocarrier charge recombination and carbon vacancies improve the electrical conductivity and mobility of photogenerated charge carriers.

The depth distribution of C and N vacancy defects in C,CN and N,CN compared to CN can be examined by XPS and XRD due to their varying depths of detection. Conferring from XPS, the surface atomic ratio of carbon to nitrogen increases from 0.69 in the CN to 0.72 in the nitrogen-deficient N,CN and decreases to 0.66 in case of carbon defective C,CN. The significantly diminished peak at 13.1° and 27.5° in the XRD pattern strongly shows that vacancies exist both in the bulk and on the surface. This can be explained by the loss of nitrogen and carbon atoms that took place during the condensation process of the CN precursor. As seen from Figure 1e, the element analysis also demonstrates that the C,CN has a smaller C/N ratio (0.63) than that of CN (0.68) and N,CN (0.74). Moreover, the introduced vacancy defects do not noticeably modify the morphology of C,CN, N,CN and CN and is evident from the morphological studies by SEM and HRTEM [Figure S3]. The thermal polycondensation reaction of CN undergoes an intermediary melem formation with the release of NH₃, H₂O, and CO₂ gases to form dense layers of nanosheet like structure. The structure for N,CN and C,CN are also similar. However, the aNi-MOF had an interwoven nanowire like structure [Figure S3].
Figure 2. XPS Spectra for N1s spectra of as-prepared nanocomposites (a) CN/aNi, (b) C\textsubscript{v}CN/aNi and (c) N\textsubscript{v}CN/aNi patterns (d ) UV–Vis DRS spectra of all prepared catalysts, and (e) Mott Schottky plots for C\textsubscript{v}CN/aNi, CN/aNi and N\textsubscript{v}CN/aNi.

Having confirmed the C and N vacancy defects in C\textsubscript{v}CN and N\textsubscript{v}CN, respectively, the successful integration and bonding of aNi-MOF to the graphitic carbon nitride systems were further studied with their XPS. The integration of aNi-MOF to CN and defective CN samples (N\textsubscript{v}CN and C\textsubscript{v}CN) were validated by the presence of Ni in the C\textsubscript{v}CN/aNi, CN/aNi and N\textsubscript{v}CN/aNi survey spectra (Figure S4). The C1s spectra of C\textsubscript{v}CN/aNi, CN/aNi and N\textsubscript{v}CN/aNi contain three major peaks at 288.10 eV, 286.33 eV and 284.8 eV ascribed to N–C=N, -NH\textsubscript{2}/C=N and C–C groups, respectively (Figure S5).\textsuperscript{15} The C\textsubscript{v}CN/aNi has higher number of -NH\textsubscript{2} groups induced by the carbon defective C\textsubscript{v}CN polymeric structure than CN and N\textsubscript{v}CN. These C-NH\textsubscript{2} groups were beneficial to coordinate aNi-MOF with Ni\textsuperscript{2+} ion during the integration of CN. After effective integration of CN and aNi-MOF, -NH\textsubscript{2}/C=N bonds were increased in C\textsubscript{v}CN/aNi > CN/aNi > N\textsubscript{v}CN/aNi and N-C=N bonds were decreased in N\textsubscript{v}CN/aNi < CN/aNi < C\textsubscript{v}CN/aNi.
Moreover, slight moves in N-C=N and -NH₂/C=N bonds of g-C₃N₄/aNi-MOF defective systems were detected in contrast to g-C₃N₄ (CᵥCN, NᵥCN/aNi and CN) after incorporation with aNi-MOF.

The N ls spectra of CᵥCN/aNi, CN/aNi and NᵥCN/aNi as represented in Figure 2 (a,b, and c) were deconvoluted into three peaks 398.5 eV, 399.68 eV and 401.16 eV resulting from the pyridinic, pyrrolic and graphitic nitrogen functional groups of g-C₃N₄, respectively. In particular, pyridinic N groups are more prevalent than pyrrolic and graphitic N groups in case of defect-free g-C₃N₄. According to the vacancy defect created, different degrees of dangling -NH₂ groups at CN are created. Thus, CᵥCN and CN displayed fewer pyridinic groups than NᵥCN which can be ascribed to the greater number of dangling -NH₂ groups. Also, the percentage of various C and N bonding in the CᵥCN/aNi, CN/aNi, and NᵥCN/aNi were significantly altered in comparison to the pure CN. These changes of bonding percentages in CᵥCN/aNi, CN/aNi and NᵥCN/aNi were directly linked to the coordinative bonding of Ni²⁺ ions to aNi-MOF. The more the C vacancy in CN, the more the percentage of N available for coordinate bonding of aNi-MOF to CN. Thus, the percentage rate of coordination in CᵥCN/aNi, CN/aNi and NᵥCN/aNi increases in NᵥCN/aNi > CN/aNi > CᵥCN/aNi. Therefore, CᵥCN/aNi has more pyrrolic N accounting from the higher dangling bonds of -NH₂ in CᵥCN which can be coordinated to the uncoordinated centres of aNi-MOF. Equally, CN/aNi also exhibited a greater intensity of pyrrolic-N bond than NᵥCN/aNi, depending on its differing dangling -NH₂ groups. Further, there was a slight shift in graphitic-N bonding of CᵥCN/aNi, CN/aNi and NᵥCN/aNi compared to CᵥCN, CN and NᵥCN, respectively, which approves of the effective incorporation of g-C₃N₄ with aNi-MOF. This description provides an idea about the bonding involved in the aNi-MOF and g-C₃N₄ system.

It is expected that these g-C₃N₄/aNi-MOF systems containing vacancy defects would have a large effect on the optical properties of g-C₃N₄ and aNi-MOF. Thus, their optical properties were studied by UV–vis absorption spectroscopy. As seen from Figure 2d, an additional absorption band known as the Urbach tail ranging from 450 to 600 nm is formed in the nitrogen-deficient NᵥCN and the absorption edge at around 470 nm blue shifted to 450 nm in case of CᵥCN compared to CN. With longer wavelength, a red- shift in the Urbach tail edge is observed with increasing nitrogen vacancies and for carbon vacancies, a blue shift in light absorption edge is usually reported. For aNi-MOF, an intense absorption band centered at 455 nm was observed due to the $^3T_1(F) \rightarrow ^3A_2(P)$, d-d transition. Furthermore, a
broader and stronger absorption tail, starting at ≈550 nm and extending to the NIR region (800–1400 nm), is also clearly observed for the g-C₃N₄/aNi-MOF composites (CvCN/aNi, CN/aNi and NvCN/aNi). The repeated reflections of incident light in the nanowire-like structure may be the reason for the increased light absorption of g-C₃N₄/aNi-MOF systems in the visible range (550–800 nm), while the presence of nitrogen and carbon vacancies may be the cause of the greater NIR absorption. Additionally, analysis of the transformed Kubelka–Munk function versus the energy of the light absorbed reveals that the intrinsic bandgap decreases from 2.68 to 2.3 eV as a result of nitrogen vacancies in case of NvCN and the bandgap increases to 2.72 eV in case of carbon defective CvCN due to quantum confinement effect. Similar optical absorption changes were also reported by Niu et.al. for nitrogen defective g-C₃N₄ and for holey g-C₃N₄ carbon vacancy defects by Liang et. al.²⁸,⁴² In case of the g-C₃N₄/aNi-MOF composites (CvCN/aNi, CN/aNi and NvCN/aNi), the tail absorption usually arising from the the intrinsic defects (ID) such as C and N deficiencies which produce mid-gap states overlapping with the conduction band (CB) becomes prominent. These mid-gap states, also referred to as CB tail states, originate from the hybridisation of C and N 2p orbitals of g-C₃N₄.

According to the UV-DRS measurement of the nanocomposites, the bandgaps are 2.67 eV, 2.73 eV and 3.2 eV for CvCN/aNi, CN/aNi and NvCN/aNi, respectively.

To ensure that the as-synthesised CN, aNi-MOF and their nanocomposites are suitable for photocatalytic hydrogen production under visible light irradiation, we investigated their electronic band structure by analysing the Mott–Schottky plots which represent the apparent capacitance as a function in varying frequency ranges. All the photocatalysts, as depicted in Figure 2e, have positive slopes in their Mott-Schottky plots, which is a clear indication of the n-type nature of semiconductors.⁴³ CvCN/aNi has a lower slope on the Mott-Schottky plot than NvCN/aNi and CN/aNi, indicating a higher electron donor density. Presumably brought on by carbon vacancies, a high donor density is particularly beneficial for enhancing photocatalytic activity due to the improved mobility of charge carriers and electrical conductivity. With reference to the saturated calomel electrode (SCE), the flat band potentials for all of the as-prepared samples were determined to be -1.79, -1.89 and -1.92 on the x-intercept in the Mott-Schottky plot respectively, for CvCN/aNi, CN/aNi and NvCN/aNi. The 0.10 V conduction band downshift may be a result of carbon vacancies in CvCN and the nanosheet structure of CN. Besides this, the lower flat band potential suggests that CvCN/aNi has a better electrical conductivity than CN/aNi. The valance band potentials of CvCN/aNi, NvCN/aNi and CN/aNi are respectively calculated to be 1.49, 1.35 and 1.79eV by consolidating with the bandgaps
obtained from the UV-DRS spectra (Figure S6). On comparing with the potential of H₂/H⁺ and O₂/H₂O, it is observed that all the photocatalysts fulfil the thermodynamical condition for the photocatalytic water splitting for hydrogen production.

Figure 3: Photocatalytic Hydrogen evolution activity for the prepared photocatalysts (a) Under Xenon Lamp, (b) Stability studies for the g-C₃N₄/aNi-MOFs under Xenon Lamp (3 h cycle, 5 mg photocatalyst, 10 vol% aqueous TEOA); (c) Electrochemical Impedance Spectra (EIS) of prepared catalysts and (d) Photocurrent for CᵥCN/aNi, NᵥCN/aNi and CN/aNi.

The photocatalytic hydrogen production rate of the prepared catalysts and their stability was studied under a 300W Xenon Lamp and solar simulator (1.5AM₀ with 100 mW/cm²) in the presence of aqueous solution of 10 vol % triethanolamine (TEOA) as the hole scavenger (Figure 3a and Figure S7). As matched to the pristine (CᵥCN, NᵥCN, CN and aNi-MOF), g-C₃N₄/aNi-MOFs (CᵥCN/aNi, NᵥCN/aNi and CN/aNi) showed a boosted photocatalytic hydrogen production rate. The hydrogen evolution as a function of reaction time (3 hours) is depicted in Figure 3a and is in the relative order of CᵥCN/aNi (3922.01 μmol g⁻¹) > CN/aNi (2750.93 μmol g⁻¹) > NᵥCN/aNi (776.112 μmol g⁻¹) >
$N_vCN$ (8.3 $\mu$mol g$^{-1}$) $>$ $C_vCN$ (7.3 $\mu$mol g$^{-1}$) $>$ CN (2.4 $\mu$mol g$^{-1}$) $>$ aNi-MOF. Thus, it is very evident that the introduction of vacancies greatly affects the hydrogen evolution. The $C_vCN/aNi$ showed a marked improvement in the hydrogen evolution compared to CN while the $N_vCN/aNi$ photoactivity decreased. Hence proving that a strong Ni$^{2+}$-N bond is critical in reactive mechanism between CN and aNi-MOF. In case of $C_vCN/aNi$ with C vacancy, the percentage chances for Ni$^{2+}$-N formation is higher compared to CN/aNi and the $N_vCN/aNi$. Though both the introduced vacancies are highly beneficial in improving the visible light harvesting and charge separation efficiency of CN, the catalytic performance is greatly facilitated by Ni$^{2+}$-N and substantiating why $C_vCN/aNi$ is a better catalyst.

Further, the photocatalytic hydrogen evolution reactions were conducted in the presence of various hole scavengers (TEOA, lactic acid, glycerol, and methanol) (Figure S8). The hydrogen evolution recorded for $C_vCN/aNi$ was in the order of TEOA (3922.01 $\mu$mol g$^{-1}$) $>$ glycerol (491.8 $\mu$mol g$^{-1}$) $>$ methanol (421.2 $\mu$mol g$^{-1}$) $>$ lactic acid (20.8 $\mu$mol g$^{-1}$). In addition, the initial pH of the reaction media greatly affects the photocatalytic hydrogen generation. A maximum amount of 3922.01 $\mu$mol g$^{-1}$ hydrogen was evolved at a pH of 11 while negligible amount of H$_2$ was produced at higher acidic and basic pH values. This may be because of the less adsorption of TEOA to the surface of the photocatalyst and the weakened ability of donating electrons by the electron donor TEOA as it undergoes protonation. In higher alkaline medium, the electrostatic repulsive force in the reaction media does not allow the adsorption of TEOA onto the photocatalyst and thus the reduction in photoactivity at higher pH values. Additionally, Figure 3b shows the stability studies for synthesised photocatalysts achieved under 300 W Xenon lamp source (cycle of 3 hrs each). Remarkably, the hydrogen production rate for the as-synthesised g-C$_3$N$_4$/aNi-MOFs did not effectively diminish even after 5 cycles.

To further gain insights on the possible photocatalytic mechanism, the charge transfer and separation efficiency on the photocatalytic property were studied. An effective strategy to characterise the separation and recombination rates of charge carriers of a photocatalyst is photoluminescence (PL). In addition to the intrinsic band edge emission, defects can also create near-band emission (Figure S9). Interestingly, both the intrinsic emission and the near band emission decrease when the vacancy defect increases. The significant reduction in PL emissions suggests an increase in the separation efficacy of photoexcited charge carriers. Furthermore, the near band emission/ intrinsic emission ratio increases with increasing vacancy density. Figure S4 depicts a broad emission peaks cantered at 430 nm is observed for all the samples. The emission spectra of the samples also show numerous small peaks, which could
indicate the presence of numerous distinct emission centres. The extended lifetime of intrinsic fluorescence may be related to the faster transport rate of photocarriers caused by the quantum confinement effect in the CN nanosheets. Such similar variations in the PL spectra was obtained for other defective samples and composite catalysts as well.

In addition to the effect of introduced vacancies on the light absorption, we also elucidate that the induced vacancies may also potentially improve the separation efficiency of photoexcited charge carriers. The charge transfer resistance was described using EIS Nyquist plots (Figure 3c). The semicircle radius of Nyquist plots for C\textsubscript{v}CN/aNi, N\textsubscript{v}CN/aNi, and CN/aNi samples are smaller than that of C\textsubscript{CN}, N\textsubscript{CN} and CN samples, which directs that the carrier transport efficiencies increase with the increase of vacancy defects. This is in accordance with the photocurrent measurement in Figure 3d, signifying that the introduction of C vacancies in a g-C\textsubscript{3}N\textsubscript{4}/aNi-MOF system is advantageous to better binding of aNi-MOF with the g-C\textsubscript{3}N\textsubscript{4} and thus better transport of carriers occurs leading to the increased PEC performance. This marks the better conductivity of C\textsubscript{v}CN/aNi and is in line with the findings of the Mott–Schottky tests. Therefore, designing suitable vacancy defects can be beneficial to achieve the highest enhancement in photocatalytic hydrogen production performance.

The experimentally observed effects of N and C vacancy in g-C\textsubscript{3}N\textsubscript{4} and its role in effective binding with an amorphous metal organic framework (aNi-MOF) were correlated by the Density functional theory (DFT). Theoretical calculations were done in order to shed more light on the reactive mechanism involved between aNi-MOF and g-C\textsubscript{3}N\textsubscript{4}. C and N vacancies were introduced onto the CN framework to study its effects in photocatalytic hydrogen evolution reaction. The aNi-MOF decorated could increase the HER-active sites in CN, and these electrocatalytic synergistic effects are combined to provide the CN/aNi hybrid catalyst its high HER performance. We constructed a perfect CN/aNi composite model as the interface. Based on this CN/aNi model, a vacancy defect introduced composite model was constructed by removing some of the surface C atoms and N atoms of CN to form C\textsubscript{v}CN and N\textsubscript{v}CN defects (Figure 4a, b and c). As is evident, the creation of C and N defects distorts the nearby atoms. The charge density analyses were used as a starting point for investigating the effect of defect on the electronic structures (Figure 5a, b and c). Obviously, charge transfer occurs at the interface of defective CN/ aNi interface.
Figure 4. Optimized geometries of (a) CN/aNi, (b) C\textsubscript{v}CN/aNi and (c) N\textsubscript{v}CN/aNi complex systems. The lowest interaction distances between aNi-MOF and CN were given in Å.

The interfacial defects potentially increase charge density to enhance the adsorption of reactants such as H* and H\textsubscript{2}, as evidenced by the much more significant charge accumulation seen on the defective CN/aNi. The gain/loss of electrons at bare and C and N-defective interface was examined using the Restrained Electrostatic Potential (RESP) charge population analyses. The RESP charges of interfacial atoms in defective CN/aNi have altered more significantly than in the bare CN/ aNi, illustrating the redistribution of electrons (Figure 5). Faster reaction rates and increased catalytic activity are the results of the improved charge transfer effects.\textsuperscript{45}

Figure 4, depicts the optimized geometries of bare, C and N defective CN/ aNi monolayer. The aNi-MOF at CN was stabilized by hydrogen atom of (aNi-MOF) H⋯N (CN) nitrogen atom of aNi-MOF through strong electrostatic interactions. The calculated lowest interaction distance between the bare, C and N defective surfaces are 2.615 Å, 1.764 Å and 2.006 Å, respectively. From these observations, we found that the lowest value observed for C\textsubscript{v}CN/aNi system. This is due to the creation of carbon vacancy results in more nitrogen
percentage and also flipping of imidazolium group of aNi-MOF. These geometrical changes and increment in N-content enhances the electrostatic interaction between the aNi-MOF and heterocyclic group of CN. In order to understand the stability of the complex system, we have simulated the binding energy (BE) analyzes. The calculated BEs of bare, C, and N defective interfacial system is -285.55, -296.85, and -210.96 kcal/mol respectively. This clearly states that the C\textsubscript{v}CN/aNi complex system is more stable than the other two complex systems. This observation is good agreement with experimental and our computed geometries.

We performed a computational analysis on the synthesized CN/aNi catalyst to get in-depth understanding of the adsorption, activation, and reaction processes in order to support the proposed HER mechanism. According to DFT calculations, reactant (R) has two H atoms adsorbed on two different N-sites of bare and C\textsubscript{v}CN and N\textsubscript{v}CN-defective CN/ aNi monolayer with an H-H distance of 1.175 Å and 1.061 Å. At the transition state (TS) the calculated H-H distance is 1.777 Å and 1.243 Å, respectively when complex systems are at close contact (i.e. CN/aNi and C\textsubscript{v}CN/aNi). A poorly adsorbed H\textsubscript{2} molecule (0.789 Å and 0.600 Å) was formed in the product (P) after crossing over the TS. For pure CN/aNi complex system and the system with C defects, the required activation energy barriers are 0.14 eV and 0.08 eV, respectively. This confirms that the C-defective CN/aNi complex system requires less amount of activation energy when compare to bare CN/aNi complex. This approach can significantly boost up the HER reaction when compared to the other complex system. This is also in good correlation with the experimental findings.
Figure 5: Charge density difference plots of (a) CN/aNi, (b) C\textsubscript{v}CN/ aNi and (c) N\textsubscript{v}CN/ aNi complex systems.

The projected density of state analysis can be used to examine the orbital overlap of interacting aNi-MOF with CN monolayer in order to gain more insight on the reactive part.\textsuperscript{46} Figures 6, shows the PDOS plots of bare, C and N defective aNi-MOF decorated CN. It clears that in all our complex systems, N-p orbital presents throughout valance band maximum (VBM) and conduction band minimum (CBM) of energy diagram. This confirms that the strong bonding nature of carbon and nitrogen of CN. Furthermore, the H-s orbital of bare
CN/aNi is weakly hybridized with N-p orbital from 8.1 eV to 9.6 eV of VBM region. This implies the weak electrostatic interaction between them. Also, in case of N-defective complex system the H-s weakly overlaps with the N-p orbital at -7.8 eV to -9.1 eV which specifies the weak binding between the aNi-MOF and CN. However, in C-defective CN/aNi the N-p strongly was hybridized with H-s orbital at -6.4 eV to -7.3 eV. This intermixing of s-p hybridization is due to strong electrostatic interaction between the aNi-MOF and CN surface. It is interesting to note that, in all our complex systems Ni-d orbital persists near Fermi region. Also the most obvious change is that, after the creation of a vacancy, all bands shift towards higher energies, resulting in a partial filling of the VBM. The principal reason of the improvement in HER activity is the sharp increase in the DOS peak value near the Fermi level.\textsuperscript{47} It is observed that broadening and splitting of Ni-d orbital in C-defective system improves the in the catalytic property of the system. Finally, we identified that the CvCN/aNi complex system to be the potential candidate to speed up the HER reaction.

**Figure 6:** The projected density of states a) CN/ aNi b) CvCN/aNi and c) NvCN/aNi

Hence, from the electronic structure calculations and experimental findings, it is confirmed that carbon defective g-C\textsubscript{3}N\textsubscript{4} (C\textsubscript{v}CN) coordinates better with aNi-MOF and helps in speeding up the photocatalytic hydrogen production. Evidently, the interaction via Ni-N bond between the aNi-MOF and g-C\textsubscript{3}N\textsubscript{4} along with other factors are responsible for the improved photocatalytic activity of C\textsubscript{v}CN/aNi. The photocatalytic reaction is thermodynamically supported by C\textsubscript{v}CN/aNi because it can absorb more visible and NIR light, has a lower flat potential, and a higher donor density. Additionally, C\textsubscript{v}CN/aNi has a significantly improved separation efficiency of photogenerated carriers and a considerably higher degree of electron delocalization, as shown by the prolonged lifetime of PL emission. The results also throw light into the reactive mechanism between a g-C\textsubscript{3}N\textsubscript{4} and aNi-MOF.

Based on the critical insights drawn from this work that involve MOF integrated with g-C\textsubscript{3}N\textsubscript{4}, another well-known framework ZIF-67 was integrated with g-C\textsubscript{3}N\textsubscript{4}. The ZIF-67/ g-C\textsubscript{3}N\textsubscript{4}
system followed a similar preparation method as the aNi-MOF/ g-C$_3$N$_4$ and the photocatalytic activity was evaluated. As expected, the photocatalytic hydrogen evolution reaction experiments illustrate that C-defective ZIF-67/ g-C$_3$N$_4$ system (C$_v$CN/ZIF-67) proved to result in better photocatalytic hydrogen evolution with 190.63 µmol g$^{-1}$ compared to non-defective (CN/ZIF-67) and N-defective (N$_v$CN/ZIF-67) ZIF-67/ g-C$_3$N$_4$ systems with 73.54 µmol g$^{-1}$ and 38.76 µmol g$^{-1}$ H$_2$ respectively. These results when compared and evaluated on basis of our study on the aNi-MOF/ g-C$_3$N$_4$ systems, indicate that primarily a metal- nitrogen bonding (M-N) is essential in contributing to improved photocatalytic hydrogen production in any MOF/ g-C$_3$N$_4$ system. This study further confirms our hypothesis and thus, it can be confirmed that introducing vacancy defects in g-C$_3$N$_4$ and further integrating them into the extended frameworks of MOF can be an effectual approach in delineating the charge transfer mechanism involved in the photoreactivity of any MOF/ g-C$_3$N$_4$ complex system.

**Conclusion**

In summary, different vacancy defective (carbon (C$_v$CN) and nitrogen (N$_v$CN)) g-C$_3$N$_4$ systems were coordinatively integrated to an amorphous nickel imidazole framework (aNi-MOF) to understand the interactive mechanism between a MOF and g-C$_3$N$_4$ system. The introduced vacancy defects effectively vary the bonding between MOF and g-C$_3$N$_4$ and thus the photocatalytic hydrogen evolution by the g-C$_3$N$_4$/ aNi-MOF systems. The C-defective g-C$_3$N$_4$/ aNi-MOF system (C$_v$CN/aNi) proved to be a potential candidate to improve the hydrogen production with 3922.01 µmol g$^{-1}$ for 3 hours which is over 3900 times better hydrogen production than aNi-MOF. Together with the experimental and theoretical studies, the coordination of Ni$^{2+}$ from the aNi-MOF to N in the g-C$_3$N$_4$ is imperative in a g-C$_3$N$_4$/ aNi-MOF system. Therefore, the present work shows that defect engineering on g-C$_3$N$_4$ can be used as an approach to study the interactive reaction mechanism to improve the photocatalytic water splitting performance of g-C$_3$N$_4$/ MOF systems.

**Acknowledgements**

The authors thank the Department of Science and Technology- Water Technology Initiative (DST-WTI) [DST/TMD/EWO/WTI/2K19/EWFH/2019/169] and Department of Science and Technology-Promotion of University Research and Scientific Excellence (DST-PURSE) [File No: SR/PURSE/2021/65] for financial support. SK thanks Climate Compatible Growth programme, which is funded by UK aid from the UK government.
Supporting Information

Characterization studies including XRD Patterns, XPS spectra, FE-SEM and TEM images, XPS Survey spectra, UV-DRS Tauc Plot, Hydrogen production data, Photoluminescence (PL) Spectra

References


