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1. Introduction

Photocatalytic organic transformations through semiconductor-based nanocatalysts have recently gained much interest in the field of catalytic territory.¹⁻⁴ The photocatalytic hydroxylation of benzene to phenol is one of the most important reactions in this field. Benzene and phenol both act as very important intermediates in many chemical reactions.5 However, being a pollutant and carcinogen, the conversion of benzene to other valuable chemicals is necessary for environmental benefit. Moreover, phenol is a very important precursor or intermediate used for the synthesis of some pharmaceutical compounds, dyes, fibers, polymer resins, and plastics.^{6,7} Phenol can also be used as an intermediate in the synthesis of fungicides, and can be used as a preservative.^{8,9} Phenol is mainly prepared industrially from benzene via three-step cumene

^bAcademy of Scientific and Innovative Research, New Delhi, India

Efficient hydroxylation of benzene to phenol by H_2O_2 using Ni-doped CuWO₄ on carbon nitride as a catalyst under solar irradiation and its structure-activity correlation[†]

Purashri Basyach,^{ab} Ankur Kanti Guha, ^b ^c Sukanya Borthakur,^{ab} Lisamoni Kalita,^{ab} Pubali Chetia,^{ab} Karanika Sonowal^{ab} and Lakshi Saikia ^b ^{*ab}

A series of environmentally benign and highly efficient Z-scheme Ni-doped CuWO₄ nanoparticles on graphitic carbon nitride (g-C₃N₄) were synthesized. The Ni-CuWO₄ nanoparticles were prepared *via* the substitution of Ni²⁺ on a wolframite CuWO₄ crystal. The photocatalytic activity of these nanocomposites was investigated for the hydroxylation of benzene to phenol, considering the importance of phenol and carcinogenicity of benzene. An excellent benzene conversion of 98.5%, with 82.7% selectivity and 81.5% yield of phenol, was achieved over 0.2% Ni-CuWO₄/g-C₃N₄ in 15 minutes under sunlight using H₂O₂ as an oxidant in water, which is higher than those of pristine g-C₃N₄ and Ni-CuWO₄. The high yield of phenol is mainly attributed to the narrow band gap of the semiconductor and enhanced visible light absorption capacity over a specific range of wavelength by the introduction of g-C₃N₄, which minimized the rapid recombination of photogenerated holes and electrons. The computational study related to this work also implied the high optical property and stability of the photocatalyst.

process.^{10,11} However, the yield of phenol is very low (only 5%) under this process, which also requires high temperature and pressure in the presence of Lewis acid catalysts.^{12,13} These drawbacks lower the efficiency of the cumene process, so it is crucial to develop a new economical and environment-friendly process for the production of phenol from benzene with high yield using homogeneous and heterogeneous catalysts.¹⁴⁻¹⁶

The catalytic aerobic oxidation of benzene to phenol in the liquid phase can be performed by using molecular oxygen as an oxidant. However, the requirement of sacrificial reducing agents such as hydrogen, CO, ascorbic acid and NADH analogues are the main drawback of this process.^{17–21} Because of this, an oxidation system based on H_2O_2 as an oxidant has recently gained tremendous interest in the catalytic oxidative process, as this process is green, economical and environment-friendly, and produces only water or dioxygen as products.²²

The development of a photocatalytic process using visible light as a source of light for the efficient conversion of benzene to phenol has drawn more attention in the research field. Instead of using an artificial source of light, the use of natural sunlight as an active source has earned much attention in organic transformation reactions.²³ As most photocatalytic reactions are performed under conservative reaction conditions, the development of a suitable low-cost photocatalyst that can be used to conduct the reactions under controlled reaction conditions with high phenol yield is very challenging.^{24,25} Many reports have been found to be articulated on the visible light

^aAdvanced Materials Group, Materials Sciences & Technology Division, CSIR-North East Institute of Science and Technology, Jorhat-785006, Assam, India. E-mail: l. saikia@gamil.com/lsaikia@neist.res.in

^cDepartment of Chemistry, Cotton University, Panbazar, Guwahati-781001, India † Electronic supplementary information (ESI) available: XRD spectra of the Ni-CuWO₄/g-C₃N₄ composites having different mass ratios, XPS data and TEM images of the recovered catalyst 0.2 Ni-CuWO₄/g-C₃N₄; percent composition of the main metal elements (Cu, Ni and W) of the as-synthesised catalysts with different mass ratios, ¹H NMR and ¹³C NMR spectra of the products, GC graph of the products. See DOI: 10.1039/d0ta03729j

driven hydroxylation of benzene to phenol using H_2O_2 as an oxidant.²⁶⁻³¹ Recently, Hutchings and co-workers have reported the photocatalytic oxidation of benzene to phenol under UV light using titania-loaded monometallic Au and Pd as catalysts.³² In addition, Hosseini *et al.* have reported the visible light oxidation of benzene to phenol using a bimetallic AuPd@g- C_3N_4 photocatalyst.²² Zhao *et al.* have reported the g- C_3N_4 supported single metal atom catalyst for the oxidation of benzene to phenol using H₂O₂.³³

Metal tungstates, MWO_4 (M = Ni, Cu, Fe, Mg and others), with a wolframite-like structure, relatively high photocatalytic activity and good stability have recently attracted potential interest in photocatalytic reactions, such as CO₂ reduction, C-H activation and dye degradation.34-37 Recently, CuWO4, has gained more importance as a narrow band gap semiconductor because it can be used as a photocatalyst in many reactions.^{38,39} However the photocatalytic performance of CuWO₄ is not that satisfactory due to the rapid recombination of photogenerated holes and electrons. The incorporation of other metal ions into CuWO₄ may enhance its photocatalytic activity. As nickel salts are cost-effective and easily available, various forms of nickel can be used in many photocatalytic reactions. Considering its similar ionic radius with Cu²⁺, Ni²⁺ may easily replace the Cu²⁺ ion in the CuWO₄ crystal, thereby improving its photocatalytic activity. Therefore, the first aim of this study is to develop a metal tungstate-like CuWO₄ through the substitution of Ni²⁺ for better photocatalytic results.

Nowadays, graphitic carbon nitride (g- C_3N_4), a 2D layeredlike semiconductor, has attracted enormous interest in photocatalysts because of its suitable band gap (2.7 eV), electronic structure, superior visible light response, high thermal stability and non-toxicity.⁴⁰ However, like other photocatalysts, g- C_3N_4 has also encountered a high recombination of photogenerated holes and electrons, which diminishes its photoactivity. To avoid this circumstance, g- C_3N_4 has been blended with different narrow band gap materials to build a direct Z-scheme system for enhanced photocatalytic performance.⁴¹ Thus, the second aim of this work is to construct a novel g- C_3N_4 -supported CuWO₄ nanocomposite through the substitution of Ni²⁺ (simply denoted as Ni-CuWo₄/g- C_3N_4) for the efficient photocatalytic hydroxylation of benzene to phenol with high yield using natural sunlight as a promising source of light.

2. Experimental section

2.1 Materials

Urea (Himedia, 99.0%), CuCl₂·2H₂O (Sigma Aldrich, \geq 99.0%), NiCl₂ (anhydrous, Alfa Aesar, 98.0%), polyethylene glycol 4000 (SRL), benzene (LobaCheme, 99.5%), and phenol (Sigma Aldrich, \geq 99.0%) were used for this research purpose. All purchased chemicals were of analytical grade, and were used directly without further treatment.

2.2 Catalyst preparation

2.2.1 Synthesis of g-C₃N₄. Bulk g-C₃N₄ was synthesized by the thermal polymerisation of urea, as reported earlier.⁴¹ Urea,

being less costly and readily available, can be used as the most valuable precursor for the synthesis of $g-C_3N_4$. In a typical process, 20 g urea taken in a silica crucible covered with a lid was calcined in a muffle furnace at 550 °C for 2 h with a heating rate of 5 °C min⁻¹ under an atmosphere of air. After cooling to room temperature, the yellow coloured bulk g-C₃N₄ was formed as the desired product.

2.2.2 Synthesis of Ni-CuWO₄ (NCW). The Ni-CuWO₄ nanocompound can be synthesized by the chemical precipitation method. In a typical synthesis, 1 mmol of $CuCl_2 \cdot 2H_2O$ was added to a solution of $Na_2WO_4 \cdot 2H_2O$ dissolved in 2% PEG-4000. A blue precipitate was observed. After sonication for half an hour, 1 mmol of NiCl₂ was added to it and mixed well. The blue precipitate turned bluish green after the addition of NiCl₂. The mixture was then sonicated again in an ultrasonicator bath for 2 h and stirred for 6 h. The obtained bluish green precipitate was filtered and washed with deionized water, followed by ethanol. The precipitate was dried under vacuum at 60 °C and finally calcined at 500 °C in a muffle furnace for 4 h to get the desired product.

2.2.3 Synthesis of Ni-CuWO₄/g-C₃N₄nanocomposite (NCWCN). For the synthesis of Ni-CuWO₄/g-C₃N₄ nanocomposite, the highly porous bulk g-C₃N₄ (340 mg) was first dispersed in 50 mL of methanol. Then, the solution of g-C₃N₄ was ultrasonicated for almost 10 h for exfoliation. Subsequently, a certain amount of as-prepared Ni-CuWO₄ (60 mg) was added to this solution, and was sonicated for almost 5 h. The solution was then kept stirring for about 24 h. The product obtained was filtered and washed with distilled water, followed by ethanol several times. Finally, the product was dried under vacuum at 60 °C. The products obtained were labelled as xNCWCN, where x was denoted as the value of the mass ratio of Ni-CuWO₄ and g-C₃N₄. Thus, the as-synthesized nanocomposite would contain a mass ratio of 0.2. In this manner, different mass ratios of Ni-CuWO₄/g-C₃N₄ nanocomposites, such as 0.05, 0.1, 0.3, 0.4, 0.5, were also synthesized. The percent composition of the main metal elements (Cu, Ni, W) in the catalysts with different mass ratios are included in ESI (Table S1[†]). The synthesis method is represented in Fig. 1.

2.3 Activity test

Catalytic experiments were done to investigate the activity of the photocatalysts for the conversion of benzene to phenol. In a typical procedure, 20 mg of prepared Ni-CuWO₄/g-C₃N₄ was taken into a 10 mL round bottom flask. To this, 1 mL benzene and 200 μ L distilled H₂O were added and the reaction mixture was stirred under dark conditions for half an hour to establish adsorption–desorption equilibrium. 500 μ L of 30% H₂O₂ was then added to the reaction mixture and was stirred in the presence of sunlight. The reaction was stopped after a certain period of time, and the catalyst was separated from the reaction mixture by centrifuge. The biphasic system appeared to be colourless before the reaction, and it changed to a light yellowish-like colour in a single phase at the end of the reaction. The reactions were carried out on sunny days from 10 am to 12 pm with an intensity of about 160 watt m⁻². The liquid products



were analysed by using a GC 700 series instrument (Thermo Scientific) equipped with an FID detector and capillary column (GC graph Fig. S5[†]). The GC oven temperature was set at 250 °C for this sample and it was run for 4 min. The required product was further confirmed by performing ¹H NMR and ¹³C-NMR spectroscopy in a 500 MHz FT-NMR spectrometer (Fig. S4⁺). The reaction was performed with a series of catalysts of Ni-CuWO₄/g-C₃N₄ having different mass ratios of Ni-CuWO₄. However, the 0.2 Ni-CuWO₄/g-C₃N₄ catalyst was found to give a better result for the photocatalytic hydroxylation of benzene to phenol. The reaction pathway is shown in Scheme 1. The effects of the reaction time, peroxide amount, and light were also studied for this photocatalytic hydroxylation reaction by varying these parameters and keeping the amount of benzene and aqueous medium constant. Some of the reactions were also carried out with molecular oxygen instead of H₂O₂ under the same reaction conditions to study their effects on the reaction by bubbling dioxygen (3 mL min^{-1}) to the bottom of the reaction mixture for 30 minutes before irradiation.

2.4 Catalyst characterisation

The synthesized catalysts were characterised by PXRD (Powder X-ray Diffractometer), UV-visible spectrophotometer, FTIR



Scheme 1 Reaction pathway for the photocatalytic hydroxylation of benzene to phenol.

spectrometer, SEM (Scanning Electron Microscope), TEM (Transmission Electron Microscope), BET adsorption isotherm, and other methods. The PXRD measurement was carried out on a Rigaku ultima IV X-ray diffractometer of 2θ range 2–80° using a Cu K α source of wavelength, $\lambda = 1.54$ Å. Nitrogen adsorption measurements were performed on an Autosorb-iQ (Quantachrome USA) adsorption analyser, which mechanically measures the adsorption isotherm, specific surface area, pore volume. The samples were degassed at 250 °C for 4 h. The FTIR spectra of the prepared catalysts were measured on a SHIMADZU IR Affinity-1 spectrometer in the frequency range of 4000-400 cm⁻¹ using the KBr pellet technique. The UV-visible spectra of the synthesized catalysts were recorded on a SHIMADZU UV-1800 spectrometer, and the fluorescence spectra were recorded on an Horiba Scientific Fluorolog 3 spectrometer to determine the optical properties. For analysing the surface, scanning electron microscopy images (SEM) were obtained using a Carl Zeiss SIGMA scanning electron microscope. The compositional analysis of the sample was performed by Energy Dispersive Xray spectroscopy on an Oxford EDS attached to the same instrument. TEM images were recorded on a JEOL, JEM-2100 Plus Electron Microscope. XPS analysis was performed on an X-ray Photoelectron Spectrometer (ESCALAB Xi+, Thermo Fischer Scientific Pvt. Ltd., UK) using monochromatised Al Ka radiation. The reaction products were analysed with a Trace GC 700 series GC system (Thermo Scientific) equipped with an FID detector and a capillary column. The products formed were further confirmed by ¹H and ¹³C NMR using a 500 MHz FT-NMR spectrometer.

2.5 Computational study

 $3 \times \sqrt{3}$ and $\sqrt{3} \times 3$ single g-C₃N₄ layers containing 18 carbon and 24 nitrogen atoms were used to match a (3 × 2) twelve atomic layer stoichiometric CuWO₄ (010) surface slab containing 108 atoms of W, Cu and O atoms. Density functional calculations using the hybrid functional PBE0 with the relativistic small-core effective core-potential basis set of Stuttgart/ Dresden (SDD) were used for all atoms with the periodic boundary condition as implemented in the GAUSSIAN16 suite of programs.⁴²⁻⁴⁴ The projected density of states (PDOS) were calculated on the optimized geometries using 128 *k*-spaces for the Brillouin zone interaction. Plots of the PDOS were obtained using a broadening energy parameter of 0.1 eV and the Multiwfn program code.⁴⁵

3. Results and discussion

3.1 Catalyst characterisation

The purity of the phase and crystal structures of the assynthesized samples were analysed by the powder XRD technique, as shown in Fig. 2. Two well-defined diffraction peaks were found in the samples, which are the characteristic peaks of typical $g-C_3N_4$. The strongest peak at around 27.4° depicts a characteristic interlayer stacking structure of the conjugated aromatic system triazine ring, and indexes as the (002) crystal plane of the graphitic materials.⁴⁶ The small peak at 13.2°



Fig. 2 PXRD pattern of the as-synthesized catalysts.

reflects the (100) plane of g-C₃N₄. In addition, the observed diffraction peaks at 15.4°, 19°, 28.7°, 30.1°, and 31.5° corresponding to the planes (010), (100), (-1-11), (111), (020), respectively, show the crystalline nature of the CuWO₄ nanocompound, confirming the formation of the triclinic phase of CuWO₄ (JCPDS no. 01-070-1732).⁴⁷ After the addition of the Ni²⁺ species, the intensity of the major diffraction peaks of CuWO₄ underwent a slight weakening and broadening due to the incorporation of the Ni²⁺ ion into the CuWO₄ crystal, replacing some of the Cu2+ ions during the synthesis process. This implied that there was a close interaction between the Ni²⁺ species and CuWO₄. The lattice parameters of the composite 0.2 Ni-CuWO₄/g-C₃N₄ were also found to be less than that of 0.2 CuWO₄/g-C₃N₄, which may be due to the substitution effect of Ni²⁺ into CuWO₄.⁴⁸ With the increase in the mass ratio of Ni-CuWO₄/g-C₃N₄, the intensities of the major diffraction peaks of g-C₃N₄ were also found to be diminished, depicting the formation of the nanocomposite with $g-C_3N_4$ (Fig. S1[†]).

For further confirmation of the formation of the nanocomposite, FTIR spectra of $g-C_3N_4$, pure Ni-CuWO₄ and Ni-



Fig. 3 FTIR spectra of the as-synthesized catalysts.

CuWO₄/g-C₃N₄ were studied and are depicted in Fig. 3. The intense band within 1230–1650 cm⁻¹ corresponds to the typical stretching vibrational mode of the carbon nitride heterocycles.49 The peak at 809 cm⁻¹ is associated with the characteristic mode of the triazine unit, indicating the presence of a typical structure of g-C₃N₄. The broad bands at 3020–3660 cm⁻¹ provide evidence of the presence of NH or NH₂ groups. For pure Ni-CuWO₄, the absorption band below 600 cm⁻¹ indicates the deformation modes of the W-O-W bridges or W-O in the WO₄ tetrahedra.⁵⁰ The band appearing at around 1400 cm^{-1} is associated with the δ (OH) mode or v_{W-O} bond.⁵¹ The bands around 700–800 cm⁻¹ can be attributed to the stretching of the Cu–O bond.⁵⁰ From the figure, it was seen that the intensity slightly decreased for the FTIR spectrum of the as-synthesized Ni-CuWO₄/g-C₃N₄ compared to that of pure $g-C_3N_4$, which confirmed that the Ni-CuWO₄ nanocompound was chemically coordinated to the g- C_3N_4 support.

The BET adsorption isotherm of the pure g- C_3N_4 , 0.2 Ni-CuWO₄/g- C_3N_4 and 0.2 CuWO₄/g- C_3N_4 catalysts are shown in Fig. 4. It was observed that the pure g- C_3N_4 catalyst has a Brunauer–Emmet–Teller (BET) surface area of 50 m² g⁻¹ and a pore volume of 0.18 cm³ g⁻¹, while the BET surface areas of 0.2 Ni-CuWO₄/g- C_3N_4 and 0.2 CuWO₄/g- C_3N_4 were found to be 103.2 m² g⁻¹ and 81.6 m² g⁻¹ with pore volumes of 0.66 cm³ g⁻¹ and 0.42 cm³ g⁻¹, respectively (Table 1). The surface area of Ni-CuWO₄/g- C_3N_4 was found to be higher compared to CuWO₄/g-C₃N₄ and pure g- C_3N_4 , implying that the incorporation of Ni²⁺ into CuWO₄ led to an increase in the surface area of Ni-CuWO₄.



Fig. 4 Nitrogen adsorption-desorption isotherms of the as-prepared samples.

Catalyst	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore radius (nm)
$g-C_3N_4$	50.2	0.18	1.8
0.2 CuWO ₄ /g-C ₃ N ₄ 0.2 Ni-CuWO ₄ /g-C ₃ N ₄	81.6 103.2	0.42 0.66	1.9 1.9

The increase in the surface area of Ni-CuWO₄/g-C₃N₄ with respect to the bare support is due to the doping effect and the creation of new pores from the effective diffusion of Ni-CuWO₄ species in the g-C₃N₄ support during the preparation method, which caused an increase in the surface roughness without clogging the pores.⁵²

Fig. 5a illustrates the UV-visible absorption abilities of the pure g-C₃N₄, 0.2 NiWO₄/g-C₃N₄, 0.2 CuWO₄/g-C₃N₄, pure Ni-CuWO₄ and 0.2 Ni-CuWO₄/g-C₃N₄ composites. From Fig. 5a, it was observed that pure g-C₃N₄ possessed a blue-shifted absorption edge at around 450 nm, which is associated with the n- π * electronic transition of the lone pair electrons of the N-atoms.³⁵ It was observed that the UV-visible absorption capacity of the as-prepared composites was higher than that of pure g-C₃N₄. The energy band gaps of the synthesized materials estimated *via* Tauc plots (based on the UV-visible absorption results) are shown in Fig. 5b. The Tauc plot is based on the following formula:

$$\alpha h v = A (h v - E_{\rm g})^{n/2}$$

where α is the absorption coefficient, *h* is Planck's constant, *A* is a constant, *v* is the frequency of light, E_g is the band gap energy, and the *n* value is determined by the type of optical transition of the semiconductor (n = 1 and 4) with direct or indirect band characteristics.⁵³ The energy gap of the composite Ni-CuWO₄/g-C₃N₄ (2.2 eV) was found to be narrower than that of the composite CuWO₄/g-C₃N₄ (2.5 eV), as evident from Fig. 5b. The incorporation of the Ni²⁺ ion into the CuWO₄ crystal may affect the band edge positions of CuWO₄. The top of CB and bottom of VB help in generating an intermediary level between CB and VB of CuWO₄/g-C₃N₄, which causes a decrease in the band gap of Ni-CuWO₄/g-C₃N₄ and enhances its visible light absorption capacity.⁵⁴ Owing to the narrow band gap energy, the photocatalysts Ni-CuWO₄ and g-C₃N₄ absorb incident visible light upon sunlight irradiation, which helps in the transfer of an electron from VB to CB, creating holes in its VB. As a Z-scheme material, the photoinduced electrons in the CB of Ni-CuWO₄ tend to recombine with the photogenerated holes in the VB of g-C₃N₄, maintaining an electron in the CB of g-C₃N₄ and holes in the VB of Ni-CuWO₄. This process helps in minimizing the fast recombination of the electron and hole pairs, which intensifies the optical property of Z-scheme narrow band gap semiconductor composites like Ni-CuWO₄/g-C₃N₄.

The photoluminescence property of the synthesized materials g-C₃N₄, 0.2 NiWO₄/g-C₃N₄, 0.2 CuWO₄/g-C₃N₄ and 0.2 Ni-CuWO₄/g-C₃N₄ composites are shown in Fig. 5c. A compound having a lower PL intensity helps in attaining a better charge separation of photoinduced holes and electrons, which was observed in Fig. 5c.³⁵ The g-C₃N₄ material had a strong emission peak at around 450 nm, indicating that there was a fast recombination of the photogenerated holes and electron pairs in g-C₃N₄, which lowered its photoactivity to some extent. On the other hand, it can be said that the combination of g-C₃N₄ with other materials (via formation of a heterojunction) helps in enhancing the charge separation efficiency of the photogenerated holes and electrons. In addition, the PL intensity of the composite 0.2 Ni-CuWO₄/g-C₃N₄ was found to be the least amongst all composites like 0.2 CuWO₄/g-C₃N₄ and 0.2 NiWO₄/ g-C₃N₄. This may be due to the substitution of Ni^{2+} into CuWO₄, which helps in creating an intermediary level between CB and VB of CuWO₄, thus minimizing the recombination process of



Fig. 5 (a) UV-DRS spectra, (b) Tauc plot, (c) PL spectra and (d) lifetime spectra of the as-synthesised catalysts.

the electron and hole pairs of the material $Ni-CuWO_4/g-C_3N_4$ and enhanced its photocatalytic activity.

To further investigate the charge transfer properties of the as-synthesized materials, time-resolved PL spectra of pure g-C₃N₄ and the composite 0.2 Ni-CuWO₄/g-C₃N₄ were performed, and are depicted in Fig. 5d. Generally, a shorter lifetime corresponds to a faster recombination of the photogenerated electron and hole pairs. On the contrary, a longer lifetime is associated with a lower recombination, *i.e.*, fast separation of the electron-hole pairs.55 It was observed from the decay curves that the composite 0.2 Ni-CuWO₄/g-C₃N₄ had a longer life-time compared to its support g-C₃N₄. The reason for the prolonged life-time of the composite may be due to an interfacial electron transfer with $g-C_3N_4$, indicating the formation of



Fig. 6 $\,$ TGA curves of pure $g\text{-}C_3N_4$ and the composite 0.2 Ni-CuWO_4/ $g\text{-}C_3N_4.$

a heterojunction with g- C_3N_4 and thereby improving its photocatalytic activity.

The thermal stability of the synthesized materials g-C₃N₄ and 0.2 Ni-CuWO₄/g-C₃N₄ was examined by thermogravimetric analysis (TGA) under N₂ atmosphere with a heating rate of 10 °C min⁻¹ in the temperature range of ambient to 800 °C (Fig. 6). The g-C₃N₄ material was stable up to 550 °C under N₂ atmosphere, and a rapid weight loss of the material was observed at 550 °C, which can be attributed to the decomposition of g-C₃N₄. On the other hand, the composite 0.2 Ni-CuWO₄/ g-C₃N₄ showed its thermal stability up to 490 °C, which is lower than that of pure g-C₃N₄. The initial decomposition of the composite started at 490 °C. The complete decomposition occurred at 615 °C, indicating the combustion of g-C₃N₄ in the composite under N₂ atmosphere. The residual content of Ni-CuWO₄ in the composite Ni-CuWO₄/g-C₃N₄ could be easily calculated from the remaining weight after heating the sample up to 800 °C, and was found to be \sim 9.8%. This may be due to the absorption and activation of atmospheric oxygen on the catalyst, considering the oxidative property of the material.56

The as-synthesized 0.2 Ni-CuWO₄/g-C₃N₄ was further investigated by XPS analysis, which is shown in Fig. 7. The XPS data shows the presence of C, N, O, Cu, Ni and W on the surface of the catalyst and their concentrations were 42.1%, 41.8%, 11.5%, 1.7%, 1.1% and 1.8%, respectively. The photoelectron peaks of these elements were distinctly observed from the XPS spectra at binding energies of 286.9 eV (C 1s), 398.1 eV (N 1s), 530.2 eV (O 1s), 935.1 eV (Cu 2p), 874.8 eV (Ni 2p) and 35.4 eV (W 4f), respectively (Fig. 7a). The high-resolution C 1s spectra (Fig. 7b) were fitted into several C species with different binding energies of 283.7 eV and 287.1 eV, corresponding to graphitic carbon (C– C) and sp²-bonded carbon (N–C==N), respectively.⁵⁷ The highresolution N 1s spectra (Fig. 7c) for 0.2 Ni-CuWO₄/g-C₃N₄



Fig. 7 (a) XPS survey, (b) C 1s XPS spectra, (c) N 1s XPS spectra, (d) O 1s XPS spectra, (e) Cu 2p XPS spectra, (f) Ni 2p XPS spectra and (g) W 4f XPS spectra of the catalyst 0.2 Ni-CuWO₄/g-C₃N₄.

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exhibited three N states, including triazine rings, C=N-C (397.5 eV), tertiary nitrogen, N-(C)₃ (399.3 eV) and the amino functions, N-H (402.8 eV), which are the three units that constituted

the heptazine ring of $g-C_3N_4$.⁵⁸ It could be inferred that the framework of $g-C_3N_4$ was not altered with the loading of Cu, Ni and the tungsten species. There were two main peaks of O 1s



Fig. 8 (a and b) FESEM images of $g-C_3N_4$ and Ni-CuWO₄, respectively. (c) EDX pattern of the composite 0.2 NCWCN. (d and e) TEM images of $g-C_3N_4$ and the composite 0.2 NCWCN, respectively. (f and g) HRTEM images of 0.2 NCWCN and 0.2 CWCN, respectively. (h) STEM image of the composite 0.2 Ni-CuWO₄/g-C₃N₄.

with binding energies of 529.5 eV, 531.4 eV and 533.1 eV, as shown in Fig. 7d. The peak at 529.5 eV was assigned to the lattice oxygen of Ni-CuWO₄. Another peak at 531.4 eV indicated the presence of oxygen vacancies in the photocatalyst. The peak at 533.1 eV corresponded to the oxygen of -OH in water molecules, which might be due to loosely bound moisture on the surface of the solid.⁵⁹ The higher resolution Cu 2p XPS spectra are shown in Fig. 7e. The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ were observed at 933.4 eV and 953.2 eV, respectively, and these doublet peaks occurred with a ratio of 1 : 2 due to spin orbit coupling. Because of the inelastic scattering of the core level electrons, strong shake-up peaks were observed at 940.1 eV and 942.4 eV for Cu $2p_{3/2}$ and another one at 962.0 eV for Cu $2p_{1/2}$, implying the presence of the Cu²⁺ species in the composite.⁶⁰ As shown in Fig. 7f, the Ni 2p spectra mainly depicted the peaks of the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ orbits, owing to spin orbit coupling at binding energies of 855.2 eV and 873.4 eV, respectively. In addition, the appearance of two shake-up satellite peaks mainly indicate the presence of the Ni²⁺ species.⁶¹ The deconvoluted highresolution XPS spectra of W 4f (Fig. 7g) showed two main peaks of W 4f at 34.5 eV and 36.4 eV, corresponding to W 4f_{7/2} and W 4f_{5/2}, respectively. In addition, two satellite peaks appeared at 35.4 eV for W $4f_{7/2}$ orbit and 37.5 eV for W $4f_{5/2}$, confirming the presence of tungsten in the W⁶⁺ state.⁶²

The morphological structures of pure $g-C_3N_4$ and 0.2 Ni-CuWO₄/ $g-C_3N_4$ were further verified by SEM, TEM and HRTEM analysis. The SEM image of the pure $g-C_3N_4$ sample showed the closely arranged staking of the conjugated aromatic system with some small scattered particles at the surface, which is depicted in the inset of Fig. 8a. The reason may be due to the light layer crack during the crystal growth.⁶³ Fig. 8b shows that the Ni-CuWO₄ particles appeared as clusters with polyhedral shapes. The elemental composition of this nanocomposite was obtained from the EDX pattern of 0.2 Ni-CuWO₄/ $g-C_3N_4$, which confirmed the presence of C, N, O, Cu, Ni and W in the compound (Fig. 8c). The TEM and HRTEM images of the pure g C_3N_4 and synthesized 0.2 Ni-CuWO₄/g- C_3N_4 are shown in Fig. 8d-f. Fig. 8d shows a TEM image of the synthesized pure g-C₃N₄ nanosheets. It was observed that the TEM image showed freestanding nanosheets with diameters of a few nanometres. Fig. 8e shows an enlarged image of the composite 0.2 Ni-CuWO₄/g-C₃N₄. A uniform distribution of the supported Ni-CuWO₄ nanoparticles having polyhedral morphology was seen in the TEM image. The HRTEM images of Ni-CuWO₄/g-C₃N₄, along with pure CuWO₄/g-C₃N₄, are also depicted in Fig. 8f and g. It can be observed from the HRTEM images that the lattice spacing of the (010) plane of CuWO₄ in the Ni-CuWO₄/g-C₃N₄ nanocomposite is somewhat different from that of pure $CuWO_4/g-C_3N_4$. This is because of the incorporation of Ni²⁺ into the CuWO₄ crystal, leading to disorder in the crystal. Besides this, the HRTEM images also revealed an integration heterojunction of Ni-CuWO₄/g-C₃N₄ or CuWO₄/g-C₃N₄. This enabled the formation of the Z-direct scheme, enhancing the photocatalytic performance by preventing the charge recombination of these materials. Furthermore, the selected area electron diffraction (SAED) pattern is also shown in the inset of Fig. 8f. The diffused rings in the SAED pattern implied the formation of crystalline phases over the support due to the interaction of the Ni-CuWO₄ nanoparticles with the g-C₃N₄ support. The STEM image of the composite 0.2 Ni-CuWO₄/g-C₃N₄ is also shown in Fig. 8h, and the EDX mapping images of composite 0.2 Ni-CuWO₄/g-C₃N₄ are depicted in Fig. 9a-f, which also confirmed the existence of C, N, O, Cu, Ni and W elements in the composite. The presence of the lower content of Cu, Ni and W elements in the composite can be ensured from the low intensity signal of these elements.

3.2. Catalyst screening for the photocatalytic hydroxylation of benzene to phenol

3.2.1 Effect of metal loading. The activities of the assynthesized catalysts were investigated for the photocatalytic



Fig. 9 (a-f) Elemental mapping of the composite 0.2 Ni-CuWO₄@g-C₃N₄.

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Table 2 Photocatalytic hydroxylation of benzene to phenol with various catalysts⁴

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		Benzene conversion	Phenol selectivity	Phenol yield
Entry	Catalyst	(%)	(%)	(%)
1	No catalyst	0	0	0
2	0.05 NCWCN	68.7	70.2	48.2
3	0.1 NCWCN	82.6	75.3	62.2
4	0.2 NCWCN	98.5	82.7	81.5
5	0.3 NCWCN	>99	74.5	73.2
6	0.4 NCWCN	>99	60.6	60.3
7	Ni-CuWO ₄	25.8	62.5	16.1
8	0.2 NWCN	30.2	54.5	16.5
9	0.2 CWCN	32.5	56.3	18.3
10	$g-C_3N_4$	≈2	<1	_
11^b	0.2 NCWCN	16.8	94.3	15.8
12^b	Ni-CuWO ₄	4.8	95.2	4.5
13^b	g-C ₃ N ₄	≈1	_	—

^{*a*} Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 (0.5 mL), reaction time (15 min), sunlight. ^{*b*} reactions performed with molecular oxygen.

hydroxylation of benzene to phenol under sunlight irradiation using H_2O_2 (30% V/V) as an oxidant in aqueous medium. The results are summarized in Table 2. The amount of benzene was kept constant for all reactions.

As predicted, no benzene conversion was observed when the reaction was carried out without any catalyst (entry 1). With pristine Ni-CuWO₄ (NCW), 25.8% benzene conversion was observed (entry 7). In addition, with pure $g-C_3N_4$, a very poor conversion of benzene was obtained with a low yield of phenol (entry 10). In contrast, when the hydroxylation reaction was conducted with g-C₃N₄ supported Ni-CuWO₄ (Ni-CuWO₄/g-C₃N₄) having a different mass ratio of Ni-CuWO₄/g-C₃N₄, an increase in the conversion of benzene was observed (entries 2-6). With 0.05 Ni-CuWO₄/g-C₃N₄, 68.7% conversion of benzene was obtained with 70.2% selectivity of phenol. However, the yield of phenol was not satisfactory (48.2%). The low yield of phenol was observed because of the lower conversion of benzene. This may be due to the presence of fewer active catalytic sites in the 0.05 mass ratio of Ni-CuWO₄/g-C₃N₄. However, it was observed that the conversion of benzene was also found to be enhanced from 82.6% to >99% with the increase in the mass ratio of Ni-CuWO₄/g-C₃N₄ from 0.1 to 0.4 (Table 1, entries 3-6).

The best result was observed with 0.2 Ni-CuWO₄/g-C₃N₄, which provided 98.5% conversion of benzene with 82.7% selectivity and 81.5% yield of phenol for 15 minutes of reaction under sunlight, and is worth mentioning. However, with the increase in the mass ratio of the composite Ni-CuWO₄/g-C₃N₄ up to 0.4, a decrease in the selectivity and yield of phenol was attained (entries 5, 6). This may be due to the increase in the active catalytic sites (from the increase in the mass ratio of Ni-CuWO₄/g-C₃N₄) producing more hydroxyl radicals. This enables more benzene conversion and produced phenol, but the presence of an excess amount of hydroxyl radicals further oxidizes phenol and produces other products like *p*-benzoquinone. Furthermore, with individual NiWO₄/g-C₃N₄ (0.2 NWCN) and CuWO₄/g-C₃N₄ (0.2 CWCN), a lower benzene conversion with a low phenol yield was obtained (entries 8, 9). Thus, Ni-CuWO₄/ $g-C_3N_4$ (0.2 mass ratio of Ni-CuWO₄/ $g-C_3N_4$) was found to be the best catalyst for the conversion of benzene to phenol with a high yield, and this may be due to the incorporation of Ni²⁺ ions into the CuWO₄ crystal, which leads to an increase in the active catalytic sites in the composites for photocatalytic performance.

3.2.2 Effect of the catalyst amount. The effect of the 0.2 Ni-CuWO₄/g-C₃N₄ catalyst amounts on the sunlight-driven hydroxylation of benzene to phenol was also surveyed, and the results are depicted in Fig. 10a. When the reaction was carried out with 10 mg of catalyst, a 72.4% conversion of benzene with 92.5% selectivity and 67% yield of phenol were found to be observed. With the increase of the catalyst amount up to 30 mg, a gradual increment in the conversion of benzene was observed. With 20 mg of catalyst, the reaction showed its best result of 98.5% conversion of benzene and 81.5% yield of phenol. However, further increasing the catalyst amount up to 30 mg resulted in a decrease in the yield of phenol. This is because of the formation of other products (like p-benzoquinone) from the over-oxidation of phenol. It can be said that an increase in the catalyst amount in the reaction mixture would lead to an increase in the active catalytic sites, which produced more hydroxyl radicals. This enhances the conversion of benzene molecules and produces phenol, but the presence of an excess amount of hydroxyl radicals accelerates the overoxidation of phenol and produces other products like p-benzoquinone. Thus, 20 mg of the catalyst amount was found to be the appropriate amount for the production of a high yield of phenol.

3.2.3 Effect of the reaction time. The reaction time has a significant influence on the photocatalytic hydroxylation of benzene to phenol, and this is depicted in Fig. 10b. It is clear from the figure that a lower benzene conversion of 25.6% was observed with a high selectivity of phenol (95.2%) when the reaction was carried out for five minutes under natural sunlight. The low conversion also affects the yield of phenol, and was found to be a bit low (24.3%). However, with the subsequent increase in time from 10 minutes to 60 minutes, the conversion of benzene was also found to be boosted from 60.2% to >99%



Fig. 10 (a) Effect of the catalyst amount in the photocatalytic hydroxylation of benzene to phenol under sunlight irradiation. Reaction conditions: catalyst from 10 mg to 30 mg, benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 (0.5 mL), reaction time (15 min), sunlight. (b) Effect of the catalyst amount in the photocatalytic hydroxylation of benzene to phenol under sunlight irradiation. Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 (0.5 mL), reaction time (15 min), sunlight, irradiation. Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 (0.5 mL), reaction time from 5 to 60 minutes, sunlight. (c) Effect of the peroxide amount in the photocatalytic hydroxylation of benzene to phenol under sunlight irradiation. Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 from 0.1 mL to 1 mL, reaction time (15 min), sunlight.

with an increase in the phenol yield up to 15 minutes. However, the selectivity of phenol was observed to be low and the reaction reached its optimization condition with 98.5% conversion of benzene, 82.7% selectivity, and 81.5% yield of phenol after 15 minutes of reaction. It was observed that with the gradual increase in time, the yield of phenol was also found to be diminished. This is due to more exposure to sunlight with increasing time, which caused more H_2O_2 decomposition and produced more hydroxyl radicals. In addition, because of the surplus amount of hydroxyl radicals, some of the phenol produced in the reaction became over-oxidized and produced other hydroxylated benzene products. Thus, these results indicate that phenol is more stable under our optimized reaction condition, *i.e.*, for 15 minutes of reaction.

3.2.4 Effect of H₂O₂ and molecular oxygen. The effect of H₂O₂ in the hydroxylation of benzene to phenol was also studied, and this is summarized in Fig. 10c. It was observed that no benzene conversion occurred within 15 minutes without H_2O_2 . With a lower amount of H_2O_2 (30% v/v) such as 100 µL, a very low conversion of benzene (15%) was observed with 95% selectivity of phenol. However, the yield of phenol was not convincing (only 14.2%). When the reaction was carried out for 1 h, the conversion was increased to around 80.5% with a phenol yield of 67.2%. With the increase in the peroxide amount from 200 µL to 1000 µL, a gradual enhancement in the conversion of benzene was marked up to >99%, but with a decrease in the selectivity from 92.5% to 55.6%. The reaction showed a better result with 500 μ L of H₂O₂, and was found to be optimized with 98.5% conversion of benzene and 81.5% phenol yield. The increase in the phenol yield with the increase in the amount of peroxide up to 500 µL indicated the presence of more hydroxyl radicals in the reaction mixture. These hydroxyl radicals led to greater benzene conversion by attacking the benzene rings, and the production of more hydroxylated species of benzene-like phenol. However, although the conversion of benzene was remarkably high, a decline in the yield of phenol was observed when the peroxide amount was increased up to 1000 µL. This is because of the formation of the other hydroxvlated product *p*-benzoquinone due to the over-oxidation of phenol. Thus, it is worth mentioning that H₂O₂ has significant effects on the hydroxylation of benzene to phenol. The results of the reactions carried out with molecular oxygen (dioxygen, O_2) are illustrated in Table 2 (entries 11-13). It was observed from the results that there was about 16.8% conversion of benzene with the 0.2 NCWCN photocatalyst for 15 minutes of reaction (Table 2, entry 11), and the phenol yield was also on the lower side. This can be explained on the basis of the oxidising property of molecular oxygen. Molecular oxygen is not as strong as H2O2 as an oxidising agent because of its lower reduction potential, as compared to H2O2. Additionally, molecular oxygen needs to first form H₂O₂ to achieve the desired product phenol by capturing an electron from the photocatalyst in a prolonged way, as discussed in the reaction mechanism (Fig. 11b), thereby explaining the role of oxygen in this photocatalytic hydroxylation.

3.2.5 Effect of light. To study the effects of light, some of the reactions were executed under dark conditions along with



Fig. 11 (a) Photocatalytic hydroxylation of benzene to phenol with or without scavengers. ^aReaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H_2O (0.2 mL), H_2O_2 (0.5 mL), reaction time (15 min), scavengers (20 mmol). (b) Plausible mechanism of the photocatalytic hydroxylation of benzene to phenol.

sunlight irradiation. From the GC results, no noticeable conversion of benzene or phenol yield was obtained when the reactions were performed under dark conditions (Table 3, entries 1–5). The catalytic activity was found to be remarkably intensified with exposure to sunlight. It was also found from the results that under dark conditions, only 2.4% conversion of benzene was obtained with the catalyst 0.2 Ni-CuWO₄/g-C₃N₄

under optimised reaction conditions (entry 3). The hydroxylation process seemed to be enhanced with 98.5% conversion of benzene when the reaction was performed in the presence of sunlight irradiation. Under sunlight irradiation, the catalysts adsorbed sunlight and stimulated the decomposition of H_2O_2 . Consequently, a large number of hydroxyl radicals were generated, which attacked benzene molecules and converted them to

	able 3 Effect of light in the photocalarytic hydroxylation of benzene to phenol over various catalysts					
Entry	Catalyst	In sunlight		Under dark		
		Benzene conversion (%)	Phenol yield (%)	Benzene conversion (%)	Phenol yield (%)	
1	$g-C_3N_4$	≈2	_	<1		
2	Ni-CuWO ₄	25.8	16.1	<1		
3	0.2 NCWCN	98.5	81.5	≈2.4		
4	0.2 CWCN	32.5	18.3	<2		
5	0.2 NWCN	30.2	16.5	≈1		

 Table 3
 Effect of light in the photocatalytic hydroxylation of benzene to phenol over various catalysts^a

^{*a*} Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H₂O (0.2 mL), H₂O₂ (0.5 mL), reaction time (15 min), reactions were performed under both sunlight and dark.

phenol and other hydroxylated products. Thus, it can be implied that light has a compelling influence on this hydroxylation reaction.

3.2.6 Plausible reaction mechanism. For the mechanistic investigation, a series of trapping experiments were performed to explore the effects of active species (including \cdot OH, h⁺ and e⁻) in the photocatalytic process. Therefore, three different chemicals were chosen as scavengers for these trapping experiments: isopropanol for \cdot OH, EDTA for h⁺ and K₂Cr₂O₇ for e⁻.

From the results depicted in Fig. 11a, it was observed that significant quenching in the photocatalytic activity occurred when isopropanol and EDTA were used in the reaction system, indicating that \cdot OH and h⁺ were the main active species. Thus, comparing the conversion of benzene after the inclusion of these scavengers, the significance of these three types of species follows a trend of \cdot OH > h⁺ > e⁻.

Based on these results, a Z-scheme photocatalytic mechanism for the Ni-CuWO₄/g-C₃N₄ nanocomposite can be proposed, and is schematically depicted in Fig. 11b. Under sunlight irradiation, both Ni-CuWO₄ and g-C₃N₄ are excited, and the photoinduced holes and electrons are in their respective valance band (VB) and conduction band (CB). The energy band positions of the valence band (VB) and conduction band (CB) can be calculated by the following equations:

$$E_{\rm CB} = \chi - E_{\rm e} - \frac{1}{2} E_{\rm g}$$
$$E_{\rm VB} = E_{\rm CB} + E_{\rm g}$$

where χ is the absolute electronegativity of the semiconductor, $E_{\rm g}$ is the energy of the free electrons on the hydrogen scale (4.5 eV), and $E_{\rm g}$ is the band gap of the semiconductor.⁶⁴ According to this equation and the DRS analysis, the CB and VB potentials of g-C₃N₄ can be calculated to be -1.13 eV and 1.57 eV. Similarly, the CB and VB potentials of the compound Ni-CuWO₄ were found to be 0.51 eV and 2.41 eV, respectively. It is seen from Fig. 11b that the CB and VB of Ni-CuWO4 were lower than that of g-C₃N₄. In addition, the energy difference between the CB of Ni-CuWO₄ and the VB of g-C₃N₄ is not too much. So, upon excitation, the photoinduced electrons transferred from the CB of Ni-CuWO₄ to the VB of g-C₃N₄, following a Z-scheme pathway, thereby improving the separation process for the photoinduced electron-hole pairs. The photogenerated electrons on the CB of g-C₃N₄ can cause a decomposition of H₂O₂ under sunlight irradiation, and produce OH⁻ and the ·OH radical. Besides this, the electrons stored in the CB of g-C₃N₄ were captured by the dissolved O_2 molecules and produced O_2 .⁻ radicals, which again reacted with H⁺ from the surface water to form H₂O₂ and subsequently produce ·OH radicals.65 Furthermore, the photoinduced holes in the VB of Ni-CuWO4 also reacted with the adsorbed water molecules to generate ·OH radicals. The generated ·OH radicals further attacked the benzene molecules, and thereby produced the hydroxylated benzene species in radical form. Upon further attack by a ·OH radical, the hydroxylated benzene radical was converted to our desired product phenol with H₂O as the only byproduct. There is supposed to be another minor route where the surface holes



Fig. 12 Model for simulating the interface between the $g-C_3N_4-CuWO_4$ heterojunction for geometry optimization: (a) before optimization, (b) after optimization.

react with the benzene molecule to form the corresponding intermediate, which upon further reaction with the dissolved oxygen molecule, produces our required product phenol.⁶⁵

3.2.7 Structure-activity correlation. From the geometry optimization, the g-C₃N₄ surface showed distortion due to the interaction of the g-C₃N₄ surface with the CuWO₄ (010) surface (Fig. 12). The equilibrium distance between the g-C₃N₄ surface and the top of the CuWO₄ (010) surface is 2.215 Å. The calculated equilibrium adhesion energy per formula unit of CuWO₄ was -0.801 eV, as obtained from eqn (1). The negative value of the adhesion energy suggests that the interaction of the g-C₃N₄ surface with the CuWO₄ (010) surface is stabilizing.

$$E_{\rm ad} = E_{\rm comp} - E_{\rm g-C3N4} - E_{\rm CuWO4\ (010)} \tag{1}$$

To have a better understanding of the interaction of $g-C_3N_4$ with the CuWO₄ surface, it is important to study the electronic



Fig. 13 Projected density of states (PDOS) of the (a) pure $g-C_3N_4$ surface and (b) $g-C_3N_4-CuWO_4$ heterojunction surface. The dotted line represents the Fermi level.

structure of the interface. Fig. 13 shows the projected density of states (PDOS) of the pure g-C₃N₄ surface, g-C₃N₄-CuWO₄ heterojunction surface and Ni-doped g-C3N4-CuWO4 heterojunction surface. The valence band maximum (VBM) of pure g-C₃N₄ is mainly composed of N 2p states, while the conduction band maximum (CBM) has contributions from the C 2p and N 2p hybridized state. In the case of the g-C₃N₄-CuWO₄ heterojunction, the VBM is composed of the N 2p and O 2p hybridized state, while the CBM is mainly composed of the W 5d state. The involvement of the W 5d state in the CBM of the g-C₃N₄-CuWO₄ heterojunction may be the electronic factor towards the stability of the heterojunction. Moreover, there is a decrease in the band gap in the g-C₃N₄-CuWO₄ heterojunction compared to the pure g-C₃N₄ surface. The decrease in the band gap is greater in the Ni-doped heterojunction (Fig. 13c), which is expected to increase the optical activity of the heterojunction. This decrease in the band gap may play a key role in the optical excitation.

We have also calculated the highest occupied surface crystal orbital (HOSCO), HOSCO-1, HOSCO-2, and the lowest unoccupied surface crystal orbital (LUSCO, LUSCO+1 and LUSCO+2) at the Γ -point to further understand the origin of the visible light absorption. Fig. 14 shows the respective orbitals. The HOSCO is mainly composed of the N 2p orbital, in agreement with the PDOS analysis. HOSCO-1 has contributions from the N 2p and O 2p orbitals. The contribution of the electron density of g-C₃N₄ vanishes at HOSCO-2. The LUSCO is mainly composed of W 5d orbitals. The normal photoexcitation of CuWO₄ takes place from the O 2p orbital (HOSCO) to the W 5d states. However, upon the composite formation with g-C₃N₄, some low energy gap bands form, which may enhance the electron-hole pair separation, leading to higher photocatalytic activity of the heterojunction. This was also confirmed from the

optical studies like UV-DRS analysis, Tauc plot and PL spectroscopic analysis. Thus, our theoretical calculations provided a rationale at the microscopic level towards an understanding of the mechanism of charge transfer and higher photocatalytic ability of the prepared composites.

3.2.8 Comparative study. A comparative study of the optimised catalyst 0.2 Ni-CuWO₄/g-C₃N₄ was surveyed with other previously reported catalysts for the photocatalytic hydroxylation of benzene to phenol, which is shown in Table 4.

3.2.9 Catalyst recyclability. Apart from the high catalytic activity, the stability of the catalyst is also a very important factor for heterogeneous catalysis. To study the stability, recyclability of the 0.2 Ni-CuWO₄/g-C₃N₄ catalyst was performed. The reusability of the photocatalyst in the hydroxylation of benzene to phenol was evaluated under optimized reaction conditions (20 mg catalyst, 1 mL benzene, 0.2 mL H₂O, 0.5 mL H₂O₂) in the presence of sunlight. Being heterogeneous in nature, the catalyst could be easily separated from the reaction mixture after each run by centrifugation. The recovered catalyst was then directly used in the next catalytic run after washing and drying under the same reaction conditions. The results in Fig. 15a demonstrates that the conversion of benzene only slightly decreases through five consecutive runs, resulting in 95.2% conversion of benzene with 78.1% selectivity and 74.3% yield of phenol in the fifth run. As there is no massive change in the conversion of benzene in all catalytic cycles, so it can be emphasized that the photocatalytic activity was almost kept stable during the recyclability experiment.

The recycled catalyst was also characterised by XPS and TEM analysis, and the details of these experiments are included in ESI (Fig. S2 and S3[†]). The XPS analysis showed that there was no significant change in the signal peak positions. From the TEM



Fig. 14 Γ -point orbital-isoamplitude surfaces of the respective orbitals.

Table 4 Comparative study of different reported catalysts with our catalyst

Catalyst	Benzene conversion	Phenol yield	Reaction conditions	References
Cu ^{II} -based MOF	27.9%	27.1%	Catalyst – 10 mg, benzene – 1 mmol, H ₂ O, H ₂ O ₂ (30%) – 1.25 mmol, 60 °C, 6 h, 40 W	5
Ferrocene modified carbon nitride	Not known	14.4%	LED bulb Catalyst – 50 mg, benzene – 0.8 mL (9 mmol), H ₂ O – 4 mL, CH ₃ CN – 4 mL, H ₂ O ₂ (30%) – 0.51 mL (5 mmol),	6
Au-Pd/g-C ₃ N ₄	24%	23.52%	4 h, 300 W xenon lamp Catalyst – 10 mg, $CH_3CN - 5$ mL, H_2O_2 (25%) – 2 mL, 2 h, 100 W mercury lamp	22
Au@g-C ₃ N ₄	6%	3.42%	Catalyst – 10 mg, CH ₃ CN – 5 mL, H ₂ O ₂ (25%) – 2 mL, 2 h, 100 W mercury lamp	22
Fe-g-C ₃ N ₄	4.8%	0.39%	Catalyst – 50 mg, benzene – 0.8 mL (9 mmol), $H_2O - 4$ mL, $CH_3CN - 4$ mL, H_2O_2 (30%) – 0.51 mL (5 mmol), 4 b 500 W yenon lamp	31
Fe-g-C ₃ N ₄ /SBA-15	11.9%	2.46%	Catalyst – 50 mg, benzene – 0.8 mL (9 mmol), $H_2O - 4$ mL, CH ₃ CN – 4 mL, H_2O_2 (30%) – 0.51 mL (5 mmol), 4 b 500 W xenon lamp	31
BCW-4	5.8%	5.75%	Catalyst – 50 mg, benzene – 0.5 mmol), H ₂ O – 0.1 mL, CH ₃ CN – 3 mL, O ₂ – 3 mL min ⁻¹ , 3 h, 300 W xenon	65
Cu ₂ O-8/dG	30.18%	19.30%	Catalyst – 5 mg, benzene – 1 mmol, H_2O – 5 mL, CH_3CN – 5 mL, H_2O_2 (30%) – 1 mmol, 16 h, white LED here (120 mW + m ²)	66
Au/dG	30.06%	0.46%	Catalyst - 5 mg, benzene - 1 mmol, H_2O - 5 mL, CH_3CN - 5 mL, H_2O_2 (30%) - 1 mmol, 16 h, white LED	66
CuAg@g-C ₃ N ₄	99%	Not known	$(130 \text{ mW} \times \text{cm})$ Catalyst – 25 mg, benzene – 1 mmol, CH ₃ CH ₂ OH – 5 mL, CH ₃ CN – 5 mL, H ₂ O ₂ (30%) – 1.1 mmol, 30 min, 20 W	67
g-C ₃ N ₄ /Cu/Pd	98.1%	87.8%	Catalyst – 20 mg, benzene – 0.5 mL, CH ₃ CN : H ₂ O – 1 : 1, H ₂ O ₂ (30%) – 5 mmol, 1.5 h, solar simulator	68
Ni-CuWO ₄ /g-C ₃ N ₄ (0.2)	98.5%	81.5%	Catalyst – 20 mg, benzene – 1 mL (11.3 mmol), $H_2O = 0.2$ mL, H_2O_2 (30%) – 0.50 mL (4.5 mmol), 15 min, natural sunlight	This work

analysis, the morphology was also found to be the same as that of the fresh catalyst.

To confirm the heterogeneous catalytic nature of the catalyst during the reaction, a filtration reaction was conducted. In this case after 10 minutes of the reaction, the solid catalyst was removed from the reaction mixture by centrifuge, and the reaction solution was subsequently allowed to react for another 50 minutes under the same reaction conditions. As shown in Fig. 15b, no further conversion of benzene was observed in the absence of the catalyst. Therefore, it can be demonstrated that there is no leaching of metal during the reaction, which confirms the heterogeneous nature of the catalyst.



Fig. 15 (a) Recyclability of 0.2 Ni-CuWO₄/g-C₃N₄ in the photocatalytic hydroxylation of benzene to phenol, (b) leaching experiment. Reaction conditions: catalyst (20 mg), benzene (1 mL, 11.3 mmol), H₂O (0.2 mL), H₂O₂ (0.5 mL), reaction time (15 min), sunlight.

4. Conclusion

In conclusion, an inexpensive and environmentally benign nanocomposite of Ni²⁺-substituted CuWO₄ crystal on graphitic carbon nitride was successfully synthesized to inhibit the rapid recombination of photoinduced holes and electrons. The wellcharacterized catalysts by different physico-chemical, spectroscopic and microscopic techniques were found to be highly efficient for the photocatalytic hydroxylation of benzene to phenol under natural sunlight using H₂O₂ as an oxidant in the presence of water. A high benzene conversion of 98.5% with 82.7% selectivity and 81.5% phenol yield were obtained after only 15 minutes of reaction in aqueous medium, which was very efficient. The photocatalyst could also be reused under the optimized reaction conditions without a significant diminution in photocatalytic activity. We performed a theoretical study on the highest occupied surface crystal orbital and the lowest unoccupied surface crystal orbital at the Γ -point to further understand the origin of visible light absorption. This study supports the experimental results on the photocatalytic hydroxylation of benzene to produce phenol. Thus, the research emphasizes that a cost-effective and efficient novel g- C_3N_4 -supported Ni-CuWO₄ photocatalyst can be easily synthesized. This catalyst provides a new outlook for green and potential applications towards photocatalysis for energy efficient processes.

Conflicts of interest

There is no conflicts to declare.

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