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# Synthesis and characterization of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> based nanocomposites for binder-free sensor applications†

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This study presents the simultaneous exfoliation and modification of heterostructured copper oxide incorporated sulfur doped graphitic carbon nitride (CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>) nanocomposites (NCs) synthesized *via* chemical precipitation and pyrolysis techniques. The results revealed that the approach is feasible and highly efficient in producing 2-dimensional CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs. The findings also showed a promising technique for enhancing the optical and electrical properties of bulk g-C<sub>3</sub>N<sub>4</sub> by combining CuO nanoparticles (NPs) with S-doped g-C<sub>3</sub>N<sub>4</sub>. The crystallite and the average size of the NCs were validated using X-ray diffraction (XRD) studies. Incorporation of the cubical structured CuO on flower shaped S-doped-g-C<sub>3</sub>N<sub>4</sub> was visualized and characterized through XRD, HR-SEM/EDS/SED, FT-IR, BET, UV-Vis/DRS, PL, XPS and impedance spectroscopy. The agglomerated NCs had various pore sizes, shapes and nanosized crystals, while being photo-active in the UV-vis range. The synergistic effect of CuO and S-doped g-C<sub>3</sub>N<sub>4</sub> as co-modifiers greatly facilitates the electron transfer process between the electrolyte and the bare glassy carbon electrode. Specific surface areas of the NCs clearly revealed modification of bulk S-doped g-C<sub>3</sub>N<sub>4</sub> when CuO NPs are incorporated with S-doped g-C<sub>3</sub>N<sub>4</sub>, providing a suitable environment for the binder-free decorated electrode with sensing behavior for hazardous pollutants. This was tested for the preparation of a 4-nitrophenol sensor.

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## 1. Introduction

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a two-dimensional conjugated polymer with earth-abundant carbon and nitrogen elements, has been manufactured by replacing carbon atoms with nitrogen atoms.<sup>1</sup> For the production of g-C<sub>3</sub>N<sub>4</sub> based composites primarily two types of synthetic techniques were used. The first involves mixing of a substance with a carbon nitride precursor and then thermally condensing it at a desired temperature. The second involves post-treating a substance with as-formed g-C<sub>3</sub>N<sub>4</sub> by deposition or simply mixing.<sup>2</sup> In this regard, it is important to note that different synthetic

approaches have also been reported.<sup>3–6</sup> However, the yield of g-C<sub>3</sub>N<sub>4</sub> nanosheets is low, since g-C<sub>3</sub>N<sub>4</sub> is chemically stable and insoluble in common solvents, even at high temperatures and under intensive sonication. As a result, developing a more practical and dependable method for generating high-yield g-C<sub>3</sub>N<sub>4</sub> based hetero-structured NCs is still challenging. To solve this problem, researchers have put a lot of effort into adjusting the properties of g-C<sub>3</sub>N<sub>4</sub> based hybrid NCs *via* a variety of methods, such as pyrolysis at different temperatures,<sup>7</sup> and doping<sup>8</sup> with non-metals like boron,<sup>9</sup> nitrogen<sup>10,11</sup> or sulfur.<sup>12–14</sup> An alternative synthesis technique was also reported to adjust the structural and electrical properties of metals and metal oxides assembled on g-C<sub>3</sub>N<sub>4</sub> nanosheets. Examples are zirconia (ZrO<sub>2</sub>) for adsorption of molecules,<sup>12</sup> or copper oxide (CuO) for supercapacitors, synthesized by pyrolysis of C and N rich materials like urea and thiourea.<sup>15</sup> Scientific research to improve the structures, precursor effects, band gap, poor visible light absorption, high electron-hole pair recombination and low surface area of g-C<sub>3</sub>N<sub>4</sub> is ongoing.<sup>16–20</sup>

Up to date most groundbreaking research studies focused on modifying the inherent and morphological characteristics of g-C<sub>3</sub>N<sub>4</sub>-based nanomaterials in the context of powder suspensions for artificial photosynthesis and environmental remediation. However, a detailed study of the synergistic effect of g-C<sub>3</sub>N<sub>4</sub>

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and dopants (metals, nonmetals, and metal oxides), which is crucial for improving its activity, reveals its own challenge as visible-light-responsive photocatalyst. Finer details of the local structure, optical characteristics, and composition of the produced materials are not fully defined in many publications on g-C<sub>3</sub>N<sub>4</sub> based NCs and thus uncertainty prevails in many respects. Research into how internal van der Waals hetero-structures with spatially oriented charge flow may affect the geometric and electrical characteristics of metal oxides is still in its early stages.

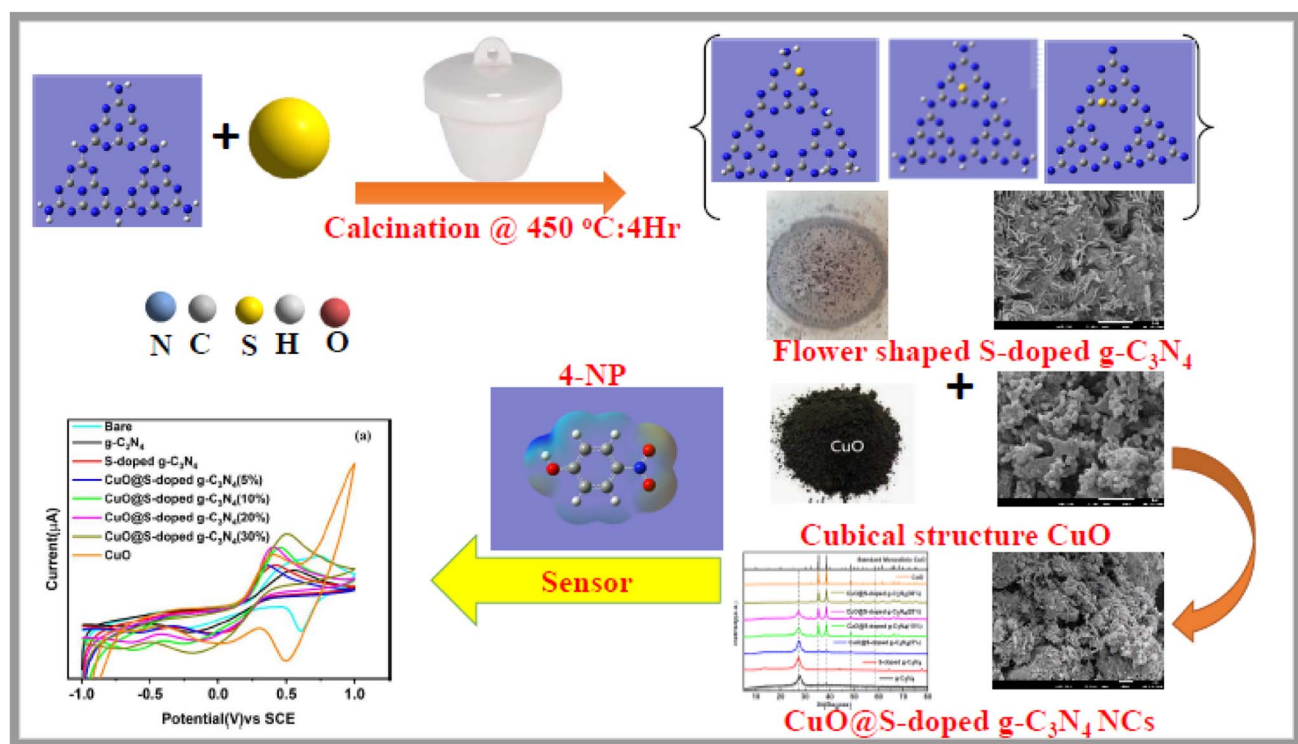
CuO is employed in g-C<sub>3</sub>N<sub>4</sub> heterojunction systems as a co-catalyst or co-photocatalyst to improve some of the shortcomings of pure g-C<sub>3</sub>N<sub>4</sub>. Thus, the goal of this study was to add previously unknown features to S-doped g-C<sub>3</sub>N<sub>4</sub>-based NCs by combining experimental and computational approaches. The research involved various properties of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> semiconducting hetero-structured materials as well as methods for incorporating CuO on S-doped g-C<sub>3</sub>N<sub>4</sub> based nanosheets. There are presently a number of DFT-based approaches for predicting structural characteristics, electronic excitation energies and wave functions in materials.<sup>21</sup> These followed two approaches; one is from the standpoint of material design, which offers important theoretical direction and prediction, while the other provides valuable information at the levels of atoms, molecules, and unit cells. First-principle calculations, on the other hand, reveal essential information, such as mechanical properties of S-doped g-C<sub>3</sub>N<sub>4</sub>, that is difficult to uncover during typical experimental procedures.<sup>22</sup> Thus computational techniques have been applied for the study of S-doped g-C<sub>3</sub>N<sub>4</sub><sup>14,23</sup> and P-doped g-C<sub>3</sub>N<sub>4</sub>.<sup>11,24</sup>

Even though there are ongoing efforts to enhance the performance of g-C<sub>3</sub>N<sub>4</sub> for multifunctional applications,<sup>19,20,25–28</sup> there is still a need for precise and reliable information on the full structural characterization, pore sizes, morphology, crystallinity, photoluminescence, formation energy, charge analysis, band gap, environmental applications and other features of S-doped g-C<sub>3</sub>N<sub>4</sub> based NCs. Therefore, we hereby report a straightforward procedure for producing CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> semiconducting hetero-structured NCs. We also lay the groundwork for future syntheses, clarifications, and potential uses of such semiconducting NCs utilizing a variety of experimental and computational methods. The overall schematic illustration is presented in Scheme 1.

## 2. Experimental

### 2.1 Chemicals and materials

The chemicals used in this study are urea (CO(NH<sub>2</sub>)<sub>2</sub>), ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sodium hydroxide (NaOH), copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), 4-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>), potassium ferric-hexa-cyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>), diethyl formamide (DMF) and alumina (Al<sub>2</sub>O<sub>3</sub>), all obtained from Sigma-Aldrich. Mono-sodium hydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) and disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) were obtained from Samir Tech-Chem, absolute ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) and NaOH from Labmark Chemicals, and KCl and HCl from Riedel-de Haen. All the reagents and chemicals were analytical-grade and used without further purification.



Scheme 1 A schematic illustration of the preparation of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs and its application for the detection of hazardous 4-NP.



## 2.2 Preparation of sulfur doped graphitic carbon nitride (S-doped g-C<sub>3</sub>N<sub>4</sub>) nanocomposite

The S-doped g-C<sub>3</sub>N<sub>4</sub> NCs were prepared by modifying an upgraded gas templating method.<sup>29</sup> Measured amounts of ammonium sulphate ((NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub>, 2 g) and urea (NH<sub>3</sub>)<sub>2</sub>CO, 8 g) were used *via* the following process. First, (NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> was placed at the bottom of a crucible and distributed uniformly (to be used as bed), then urea was laid over ammonium sulphate uniformly distributed on the upper surface. The crucible was then covered with alumina foil and placed in a muffle furnace at 550 °C with temperature rate of 15 °C min<sup>-1</sup> for 4 h. After cooling the furnace, the prepared bulk material was dissolved in 100 mL C<sub>2</sub>H<sub>5</sub>OH and sonicated (model; BANDELIN electronic Heinrichstrabe 2.4, 12 207 Berlin, Germany) for 2 h. To remove the unexfoliated impurities the obtained sulfur-doped graphitic carbon nitride was centrifuged at 4000 rpm. After filtering, the sample was dried at room temperature and collected. The exfoliated sample was abbreviated as S-doped g-C<sub>3</sub>N<sub>4</sub> sheets. For comparison, bare g-C<sub>3</sub>N<sub>4</sub> was prepared using pyrolysis of urea at the same heating temperature and time except exfoliation and absence of sulfur.

## 2.3 Synthesis of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs

The CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> heterostructured NCs were prepared by employing simple chemical precipitation and pyrolysis methods. Copper nitrate was used as precursor to produce CuO NPs. In a typical synthesis, a mixture of C<sub>2</sub>H<sub>5</sub>OH and S-doped g-C<sub>3</sub>N<sub>4</sub> was sonicated for 2 h, labeled as solution “A”. The desired amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was stirred by dropwise addition of 0.1 M of NaOH and also stirred while heating at 70 °C until a black precipitate formed, labeled as solution “B”. Solution B was then added to solution A and stirred for 4 h with addition of deionized water until the pH reached *ca* 10. The mixture was transferred to an oven to dry at 180 °C overnight. After grinding, the sample was placed into a muffle furnace at 500 °C, heating at a rate of 5 °C min<sup>-1</sup> for 3 h. After allowing the furnace to cool, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> hetero-structured NC, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (5%), CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (20%) and CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (30%) NCs were obtained. In addition, CuO NPs were also synthesized using chemical precipitation method.

## 2.4 Characterization techniques

Combining both the results of the characterization techniques and computational study provided a better understanding of doping efficiency into the host lattice. To observe the effects of combining CuO NPs with S-doped g-C<sub>3</sub>N<sub>4</sub> sheets, either being supported or as a support itself, characterization of the hetero-structured semiconducting materials has been undertaken. The phase structure of the samples was studied by powder X-ray diffraction (XRD) with X-ray tube Cu K $\alpha$  radiation target Cu, voltage = 40.0 (kV) current = 30.0 (mA) at a scanning speed of 3.0000 (deg/min) (SHIMADZU Corporation (Japan) Model XRD-7000X-RAY DIFFRACTOMETER). The phase purity of the materials was evaluated using Fourier transform infrared (FTIR, Frontier) measured using Spectrum 65 FT-IR (PerkinElmer) in

the range 4000–400 cm<sup>-1</sup> (resolution: 4 cm<sup>-1</sup>, number of scans: 4) in KBr pellets. Ultraviolet-visible (UV-vis) diffused reflectance (DRS) spectra were recorded using a scanning-type UV-Vis spectrometer (PerkinElmer, Lambda 950) with a BaSO<sub>4</sub>-based integrating sphere in the wavelength range of 200 to 800 nm. Thermal degradation and stability of the samples were measured using capillary tubes with a digital melting point apparatus. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed under a N<sub>2</sub> atmosphere (20 mL min<sup>-1</sup>) using a DTG-60H Shimadzu thermal analyzer. The rate of heating of the sample was set at 15 °C min<sup>-1</sup>; TGA/DTA techniques were performed with an NETZSCH STA 409 PC/PG, in which a heating rate of 15 °C min<sup>-1</sup> was applied between room temperature and 1000 °C. The steady photoluminescence (PL) spectra were carried out on a Cary Eclipse Fluorescence Spectrophotometer (Agilent, Malaysia) with excitation wavelength at 324 nm using a xenon (Xe) flash lamp as excitation source.

The morphologies of the prepared samples were visually characterized using high resolution scanning electron microscopy/Energy-dispersive X-ray spectroscopy/Secondary electrons diffraction (HR-SEM/EDS/SAED) HR-SEM: JEOL 7800F Field Emission SEM, with an Oxford EDS, EM: JEOL IT200 SEM, with a JEOL EDS. X-ray photoelectron spectroscopic (XPS) analysis (model PHI 5000 Versaprobe) was conducted to study chemical compositions of the prepared hetero-structured materials. A low energy Ar<sup>+</sup> ion gun and low energy neutralizer electron gun were used to minimize charging on the surface. A 100  $\mu$ m diameter monochromatic Al K $\alpha$  X-ray beam ( $h\nu$  = 1486.6 eV) generated by a 25 W, 15 kV electron beam was used to analyze the different binding energy peaks. Multipack version 9.8 software was utilized to analyze the spectra to identify the chemical compounds and their electronic states using Gaussian–Lorentz fits. Nitrogen adsorption–desorption isotherms and Brunauer–Emmett–Teller were applied for surface area and porosity measurements (isotherms) which were obtained with a Micrometrics ASAP 2020 surface area and porosity analyzer and ASAP 2020 v2.0 software. Data refinement was done with Microactive v1.01 software. Approximately 30 mg of samples were activated under vacuum at 150 °C for 16 h. Samples were cooled to room temperature and N<sub>2</sub> adsorption–desorption measurements were done at 77 K.

## 2.5 Preparation of 4-nitrophenol solution

0.5 mM stock solution of 4-nitrophenol (4-NP) was prepared by dissolving 70 mg 4-NP in 100 mL distilled water, and then filled to 1000 mL in volumetric flask. A series of 4-NP working solutions were freshly prepared from the stock solution by appropriate dilution of the stock solution with 10 mL phosphate buffer solution (PBS, pH = 7.0). All the solutions were prepared with doubly distilled water and all the measurements were carried out at room temperature (25  $\pm$  5 °C).

## 2.6 Electrochemical measurements

The voltammetric experiments were performed using Ivium Technologies B. V. De Zaal 11 5612 AJ Eindhoven, Netherlands,





coupled to a personal computer. A conventional three-electrode cell was used for the measurements with a bare glassy carbon electrode (GCE, with a diameter of 3 mm) and/or CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE as the working electrode, Ag/AgCl (3 M KCl) as reference electrode, and a platinum wire as counter electrode. The phosphate buffer (PBS, 0.1 M) electrolyte solutions were prepared using dibasic anhydrous sodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>) and monobasic anhydrous sodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>) salts with pH variation from 4 to 9, with the application of 0.1 M HCl or 0.1 M NaOH, using a pH meter.

Prior to modification, the bare GCE was polished using a polishing cloth with 0.05  $\mu$ m alumina slurry (Al<sub>2</sub>O<sub>3</sub>), washed successively with distilled water and absolute ethanol in an ultrasonic bath for 5 min and dried in air. Typically, to disperse the catalyst (CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>), 0.5% wt. solution of catalyst powder was prepared in DMF solvent and then mixed ultrasonically for 30 min to obtain a homogeneous suspension. The suspension of the catalyst was drop-casted on the well-polished GCE surfaces, and then the GCE surfaces were allowed to dry at room temperature. Afterwards, the dried CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC was gently washed with deionized water to remove the loosely attached CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs on the GCE surface. A similar procedure was followed to modify the other electrodes. Finally, the modified binder free electrodes were used for the electrochemical measurements.

## 2.7 Computational methods

In this study, we constructed s-triazine rings from heptazine units (C<sub>6</sub>N<sub>7</sub>), which consist of three fused s-triazine rings joined by nitrogen atoms. To mimic the doping of g-C<sub>3</sub>N<sub>4</sub> with sulfur, we investigated substitutions of N1, N2, and N3 with S, respectively, for the three different sites. The findings of geometric optimizations of pure g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, and CuO models were used as input. The results were visualized using Chemcraft 1.8 software. The ABAB-stacking order of s-triazine rings from heptazine units (C<sub>6</sub>N<sub>7</sub>) was assumed to ease DFT computations. The DFT method has been used to investigate natural bond orbitals (NBO) and electrostatic potential (ESP) analyses, such as electronic delocalization between donor and acceptor bonds. DFT simulations employing the Becke 3-Lee-Yang-Parr (B3LYP)<sup>30–32</sup> hybrid functional was used to estimate the electronic characteristics of the optimized geometries, wavefunctions, and energies of all structures. For all of the atoms, the B3LYP/6-31+G(d,p) method was employed in Gaussian 16.<sup>33</sup> Structural stability of the models was calculated using the energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO).

## 3. Results and discussion

To understand the key reaction parameters of converting ammonium sulphate and urea to S-doped g-C<sub>3</sub>N<sub>4</sub> sheets, we examined the retainability and delayed release impacts of the self-supporting environment formed by pyrolysis and the reaction temperature. A solid with pale yellow hue was produced on

the surface of a closed crucible when a specific quantity of ammonium sulphate was added. However, in an open crucible, all of the components were thermally destroyed and no solid precipitate was observed on the surface. According to studies on thermal decomposition of urea, when gas sources, like ammonium sulphate here, are placed at the bottom of urea, gas transfer from the bottom to the top of the crucible result in better utilization of decomposed gases and disruption of bulk g-C<sub>3</sub>N<sub>4</sub> growth. As a result of high-temperature self-polymerization of sulfur and graphitic carbon nitride, the yellow-colored g-C<sub>3</sub>N<sub>4</sub> phase was formed inside the crucible.<sup>29</sup>

### 3.1. XRD study

In order to verify phase and structural changes that occurred during integration of S and CuO to g-C<sub>3</sub>N<sub>4</sub>, the XRD spectra of pure g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub> and CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (5, 10, 20, and 30%) composites were recorded, as shown in Fig. 1. In the XRD analysis, two significant peaks for bulk g-C<sub>3</sub>N<sub>4</sub> and S-doped g-C<sub>3</sub>N<sub>4</sub> were observed. The low intensity peak at  $2\theta = 13.4^\circ$  and strong peak at  $26.99^\circ$  are attributed to (100) and (002) diffraction planes indicating the unique graphitic structure of pure g-C<sub>3</sub>N<sub>4</sub> respectively.<sup>34</sup> In comparison to bulk g-C<sub>3</sub>N<sub>4</sub>, the strong peak in S-doped g-C<sub>3</sub>N<sub>4</sub> is sharper and more intense, indicating crystallite nature. Moreover, the major peak for S-doped g-C<sub>3</sub>N<sub>4</sub> was found to have shifted negatively to  $2\theta = 26.99^\circ$ , which indicates the presence of impurities, in this case S in the precursor material substituting nitrogen atoms. Diffraction patterns reveal that there is no change in the basic structure of g-C<sub>3</sub>N<sub>4</sub> and S-doped g-C<sub>3</sub>N<sub>4</sub> sheets, which is in compliance with reported literature.<sup>35</sup>

The presence of Tenorite phase of monoclinic crystal CuO in the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC is confirmed by fundamental plane orientations at (110), (002), (111), and (202) of CuO (JCPDS card no. (05-0661)), which are assigned to the typical strong peaks at  $2\theta = (35.728^\circ, 38.940^\circ, 49.031^\circ)$  and  $(35.680^\circ, 38.791^\circ, 48.942^\circ)$  both in the synthesized and standard XRD

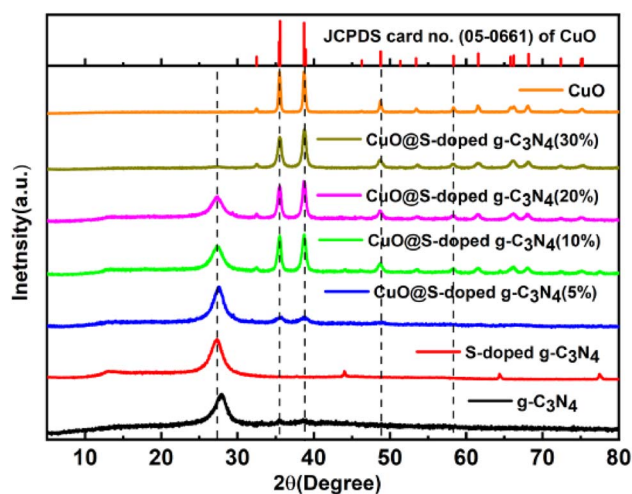


Fig. 1 XRD pattern of g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs and pure CuO.



**Table 1** Average crystallite sizes of S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> composites and CuO NPs

Material	2θ	FWHM	D (nm)
S-doped g-C <sub>3</sub> N <sub>4</sub>	23.984	0.642	13.23
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (5%)	33.857	0.935	9.28
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (10%)	31.914	1.270	6.80
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (20%)	33.846	0.931	9.32
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (30%)	26.509	1.551	6.50
Pure CuO NPs	40.987	0.285	30.09

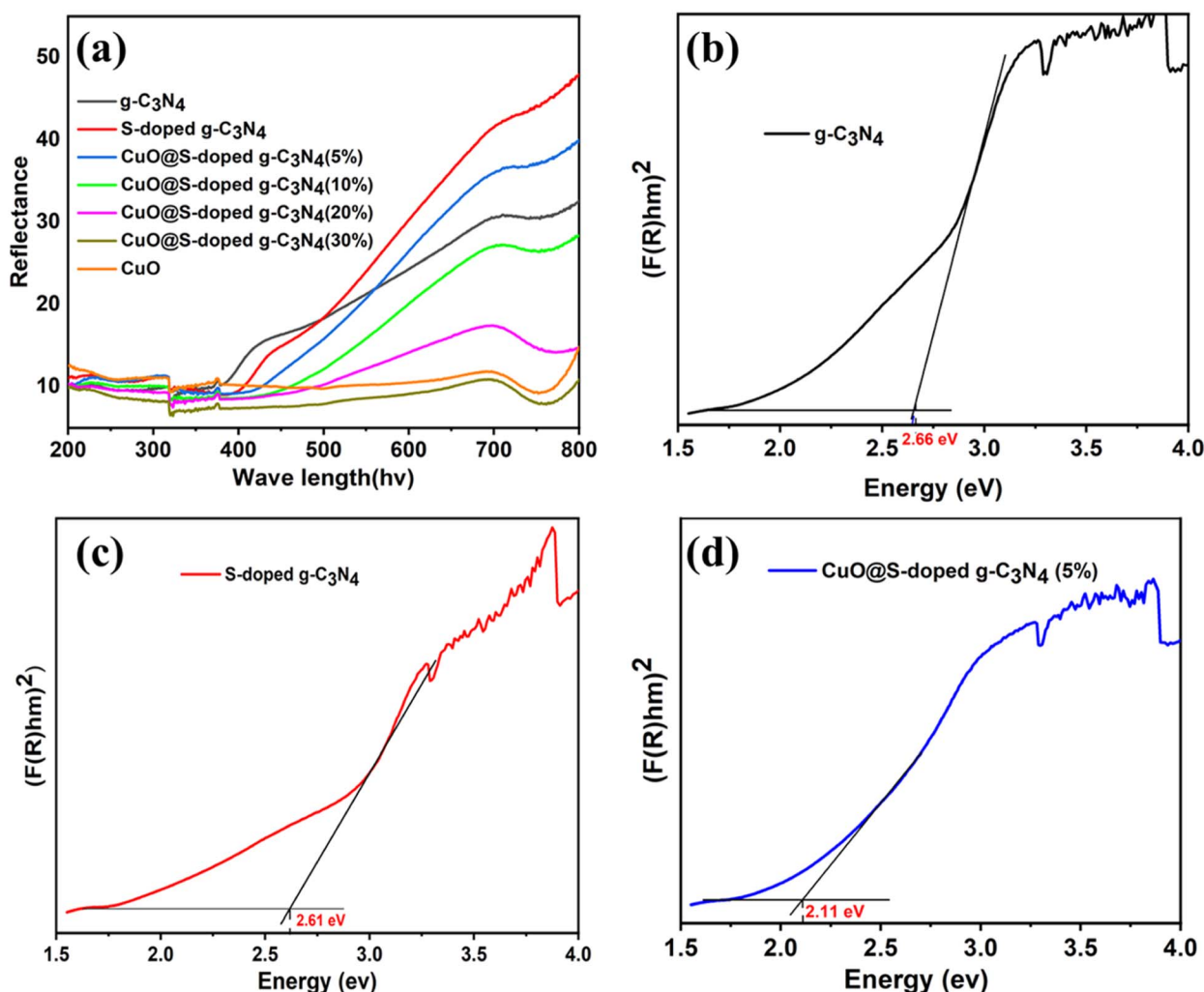
pattern shown in Fig. 1. The signals were found to rise as the amount of CuO in the NC increases, indicating the possibility of generating a metal–organic hybrid material or a coordination compound dominated by CuO NPs.<sup>36,37</sup> The average crystallite size of each catalyst was calculated using Scherrer's formula as given in eqn (1).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $\theta$  is the angle between the incident and diffracted beams (degree),  $\beta$  is the full width half-maximum (rad),  $D$  is the average particle size of the sample (nm) and  $\lambda$  is the wavelength of the X-rays. The average grain size of prepared S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (5, 10, 20 and 30%) NCs and pure CuO NPs were found to be 13.23, 9.28, 6.80, 9.32, 6.50 and 30.09 nm respectively, as presented in Table 1. All diffraction peaks of CuO are observed clearly for higher amount of CuO NPs. The diffraction peaks of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (CuO = 30%) are almost the same as those of CuO, probably because of the low content of S-doped g-C<sub>3</sub>N<sub>4</sub> in CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>. XRD peaks become gradually sharper with increasing amount of CuO, corroborating a possible increase in the average crystallite size.<sup>37</sup> CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs often emerge from agglomeration of tiny grains rather than particles due to processing kinetics.

### 3.2 Electronic structure analysis

UV-visible/DRS spectral studies of pure g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs and pure CuO NPs were conducted



**Fig. 2** Diffuse reflectance absorption spectra (a) and optical band gap plots transformed by Kubelka–Munk function (b–d) of bulk g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC, respectively.



at room temperature in the wavelength region between 200 and 800 nm. As shown in Fig. 2a, all hybrid composites exhibited a broad absorption band near 700 nm, showing an obvious red shift from 450 to 700 nm with the addition of S and CuO, as compared to bulk g-C<sub>3</sub>N<sub>4</sub>. It is worth noting that weak absorption tails were seen due to structural defects in hetero-structured samples, which may improve visible absorption of materials. This probably is attributed to structural defects formed in samples treated at a given temperature, showing doping of impurities in pure g-C<sub>3</sub>N<sub>4</sub>. The band gap energy ( $E_g$ ) of the synthesized materials was determined using the Kubelka-Munk formula as given in eqn (2).<sup>38</sup>

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where  $\alpha$  is the optical absorption coefficient of the semiconductor at a certain value of wavelength  $\lambda$ ,  $A$  is constant depending on transition probability that is related to effective masses associated with valence and conduction band,  $h$  is Planck's constant,  $\nu$  is the frequency of light,  $E_g$  is the gap between the bottom of the conduction band and the top of the valence band, and  $n$  is the power index that is related to the

optical absorption process which depends on the characteristics of the transition in the semiconductor. The  $n$ -value was chosen to be  $\frac{1}{2}$  and 2 for direct and indirect allowed transitions respectively.

As depicted in Fig. 2 and 3, it can be observed that the direct band gap ( $E_g$ ) values of the samples are between 2.66 eV for the bulk g-C<sub>3</sub>N<sub>4</sub> and 1.76 eV for pure CuO NPs, while the band gap of the quaternary NC was found to decrease as the amount of CuO increased (Table 2). This may be attributed to the shift to the visible range by doping-induced modification in the lattices and structure of the S-doped g-C<sub>3</sub>N<sub>4</sub> layers shift that are observed for CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> composites.<sup>39</sup>

### 3.3 Functional group studies

The chemical structure of bulk g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs and pure CuO NPs catalysts were investigated by FT-IR technique (Fig. 4). The intense band observed at 811 cm<sup>-1</sup> represents a typical bending vibration mode of the s-triazine ring (the out-of-plane bending vibration characteristic of heptazine rings).

The fingerprint region of 1200–1700 cm<sup>-1</sup> is dominated by C–N and C=N stretching vibrations of the tri-S-triazine rings.

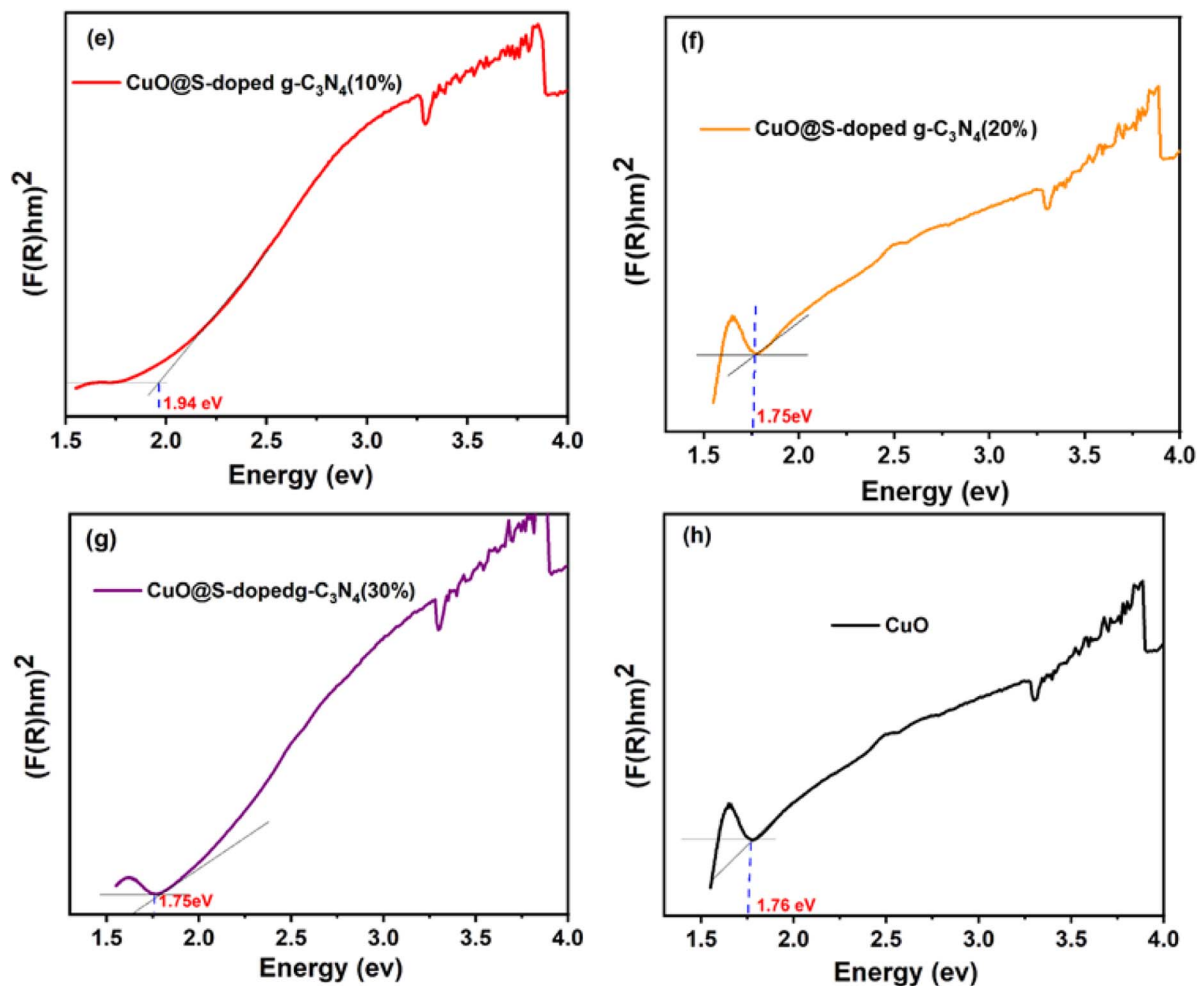


Fig. 3 Optical band gap plot transformed by Kubelka–Munk function (e–h) of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs and pure CuO.



**Table 2** Experimental  $E_g$  values of different synthesized polymeric semiconductors

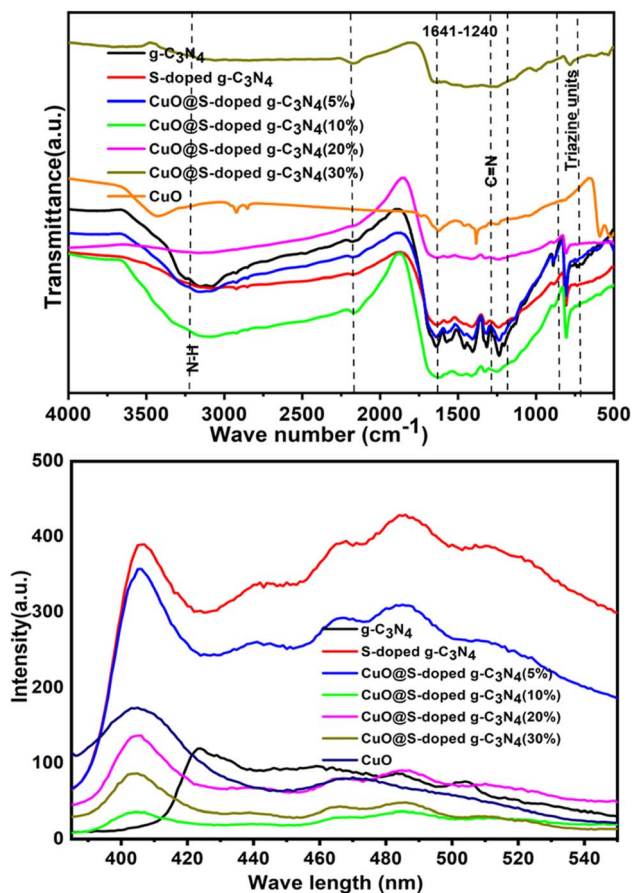
Samples	Band gap ( $E_g$ eV <sup>-1</sup> ) ( $F(R)h\nu$ ) <sup>1/2</sup>
Pure g-C <sub>3</sub> N <sub>4</sub>	2.66
S-doped g-C <sub>3</sub> N <sub>4</sub>	2.61
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (CuO = 5%)	2.11
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (CuO = 10%)	1.94
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (CuO = 20%)	1.75
CuO@S-doped g-C <sub>3</sub> N <sub>4</sub> (CuO = 30%)	1.75
Pure CuO	1.76

The prominent bands in the region of the wide absorption at band 3000–3500 cm<sup>-1</sup> are attributed to the stretching modes of terminal –NH groups and C–N of the terminal amino groups by incomplete condensation in g-C<sub>3</sub>N<sub>4</sub>. The weak peak of the S–C bond appeared around 710 cm<sup>-1</sup> in the FTIR spectrum of S-doped g-C<sub>3</sub>N<sub>4</sub>—it corroborates successful incorporation of sulfur into the g-C<sub>3</sub>N<sub>4</sub> structure. S-doped g-C<sub>3</sub>N<sub>4</sub> had similar properties to g-C<sub>3</sub>N<sub>4</sub>, however sulfur doping induced a minor change in the band position for the tri-substituted tri-S-triazine ring, indicating that S-doped g-C<sub>3</sub>N<sub>4</sub> was successfully

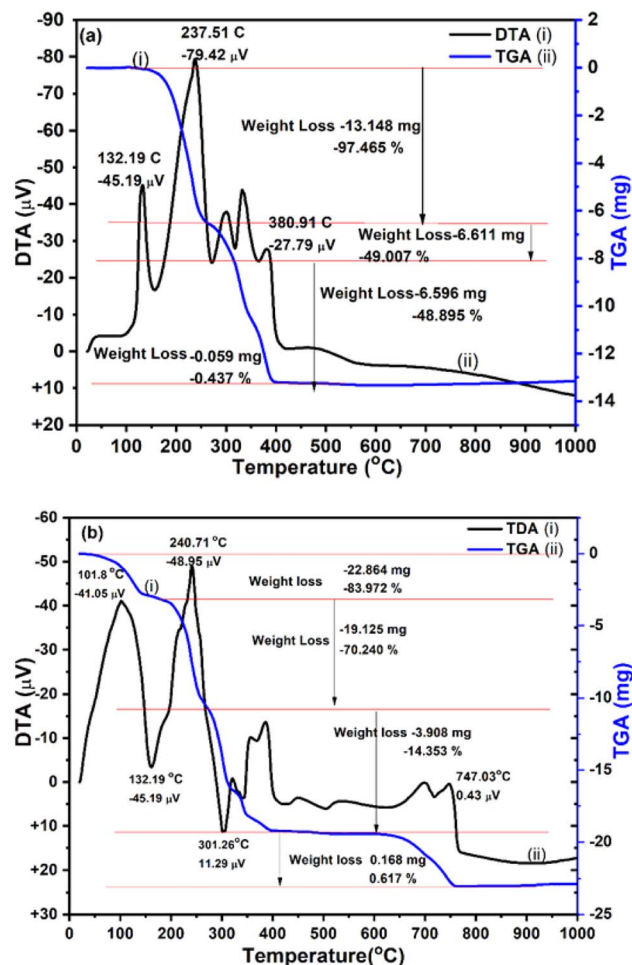
formed.<sup>29,40</sup> The absence of visible new bands shows that sulfur vacancies had no effect on the overall framework structure of g-C<sub>3</sub>N<sub>4</sub>.<sup>41</sup>

### 3.4 Photoluminescence (PL) analysis

By observing the buildup of electrons on the conduction band, PL is an effective technique for determining the rate at which photogenerated electrons and holes recombine in catalysts. It is generally accepted that photogenerated carriers separate faster at lower fluorescence intensity.<sup>42</sup> As shown in Fig. 5, PL peak intensities of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> (5, 20 and 30% CuO) catalysts at 442 nm were found to be in between S-doped g-C<sub>3</sub>N<sub>4</sub> and bulk g-C<sub>3</sub>N<sub>4</sub>, which indicates that CuO deficiencies inhibit the recombination rate of photogenerated carriers in the catalyst and are beneficial to improve photocatalytic and sensor activities. The PL spectrum of the g-C<sub>3</sub>N<sub>4</sub> shows a major characteristic peak at 423.67 nm (Fig. 5). The S-doped g-C<sub>3</sub>N<sub>4</sub> at 406.13 nm had a band that was identical to the quenched PL emission peak at around 485.54 nm, which supports the UV-Vis/DRS. This shows that, in contrast to pristine g-C<sub>3</sub>N<sub>4</sub> sheets, the recombination of photogenerated charge carriers caused by mixing CuO NPs in g-



**Fig. 4** FTIR spectra (top) and PL spectra (bottom) for g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs, and pure CuO.



**Fig. 5** TGA/DTA thermogram for (a) S-doped g-C<sub>3</sub>N<sub>4</sub> NC and (b) CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs.





$\text{C}_3\text{N}_4$  was inhibited. For the  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  NCs a wide peak lies between 406.13 and 560.00 nm, and pure  $\text{CuO}$  NPs at 403.63 nm. The intermediate intensity peak was observed for  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  ( $\text{CuO} = 5, 20$  and  $30\%$ ) NCs between  $S$ -doped  $g\text{-C}_3\text{N}_4$ , and  $g\text{-C}_3\text{N}_4$  sheets suggest intermediate electron recombination. This dramatic change in PL intensity magnifies the synergistic effect due to incorporation of  $\text{CuO}$  NPs into the NCs, which is due to charge transfer at the interfaces of  $g\text{-C}_3\text{N}_4$ ,  $S$ -doped  $g\text{-C}_3\text{N}_4$  and  $\text{CuO}$  NPs. The lower recombination rate of photogenerated electron and hole pairs of  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  ( $\text{CuO} = 10\%$ ) may be due to structural defects.<sup>40,43</sup>

### 3.5 Thermal stability

To elucidate the contents in  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  NCs and their thermal stabilities, TGA was used from room temperature to  $1000^\circ\text{C}$  at a heating rate of  $15^\circ\text{C min}^{-1}$  (Fig. 5). The TGA/DTA thermogram shows change in sample weight as a function of temperature under controlled gas atmosphere ( $\text{N}_2$ ) and temperature. From DTA (Fig. 5, black line) the dynamic relationship between temperature with change in physical or chemical processes and percentage weight change (gain or lose) over a programmed temperature range, was observed.

From the DTA curve, endothermic transformations were observed at  $132.19, 237.51$  and  $300.91^\circ\text{C}$ . The increase in the rate of weight loss that rises to its maximum and occurs during isomerization is evidence of the breakdown reaction of urea and ammonium sulphate, which results in gases that escape and remove heat from the system.<sup>9</sup> The weight loss and endothermic effect may be caused by pyrolysis of urea into  $g\text{-C}_3\text{N}_4$  and decomposition of  $\text{NO}_3$  from ammonium sulfate to form  $S$ -doped  $g\text{-C}_3\text{N}_4$  during the heating process.

Two heat absorption peaks observed during the first stage of mass loss are apparent from the DTA, providing evidence for endothermic events: first the slow melting of the sample between  $22.27$  and  $132.9^\circ\text{C}$  (representing melting rather than decomposition by the absence of any detected mass loss) and the first stage decomposition reaction up to  $385^\circ\text{C}$  endothermic transformations. The weight loss and endothermic peaks may be caused by pyrolysis of urea. The second peak located between  $200$  and  $385^\circ\text{C}$  (about  $97.465\text{ wt\%}$  weight loss) observed in the TGA curve corresponds to further decomposition of urea and ammonium sulphate to form  $S$ -doped  $g\text{-C}_3\text{N}_4$  during the heating process. Afterwards, the remaining portions of urea and ammonium sulphate are decomposed very slowly up to  $400^\circ\text{C}$  and become stable. TGA (blue line) plots of  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  NC (Fig. 5) showed behavior that is similar to that of pure  $S$ -doped  $g\text{-C}_3\text{N}_4$  sample, with significant continuous weight losses in the region  $400\text{--}615^\circ\text{C}$ . This confirms that no  $\text{CuO}$  phase is found in the prepared hybrids. It was also found that the composite that includes  $\text{CuO}$  starts to burn at a lower temperature, with decomposition of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  being complete at  $700^\circ\text{C}$ , as shown in Fig. 5.

### 3.6 Morphology and composition analysis

The HR-SEM/EDS technique was used to add understanding of the morphological and elemental composition in the inner and outer surfaces of features of the prepared  $g\text{-C}_3\text{N}_4$ ,  $S$ -doped  $g\text{-C}_3\text{N}_4$  and  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  heterostructured NCs (Fig. 6). In this technique, the magnified images of the size, shape, elemental composition, crystallography, and other physical and chemical properties were investigated. The samples were subjected to HR-SEM investigation of the bulk  $g\text{-C}_3\text{N}_4$ ,  $S$ -doped  $g\text{-C}_3\text{N}_4$

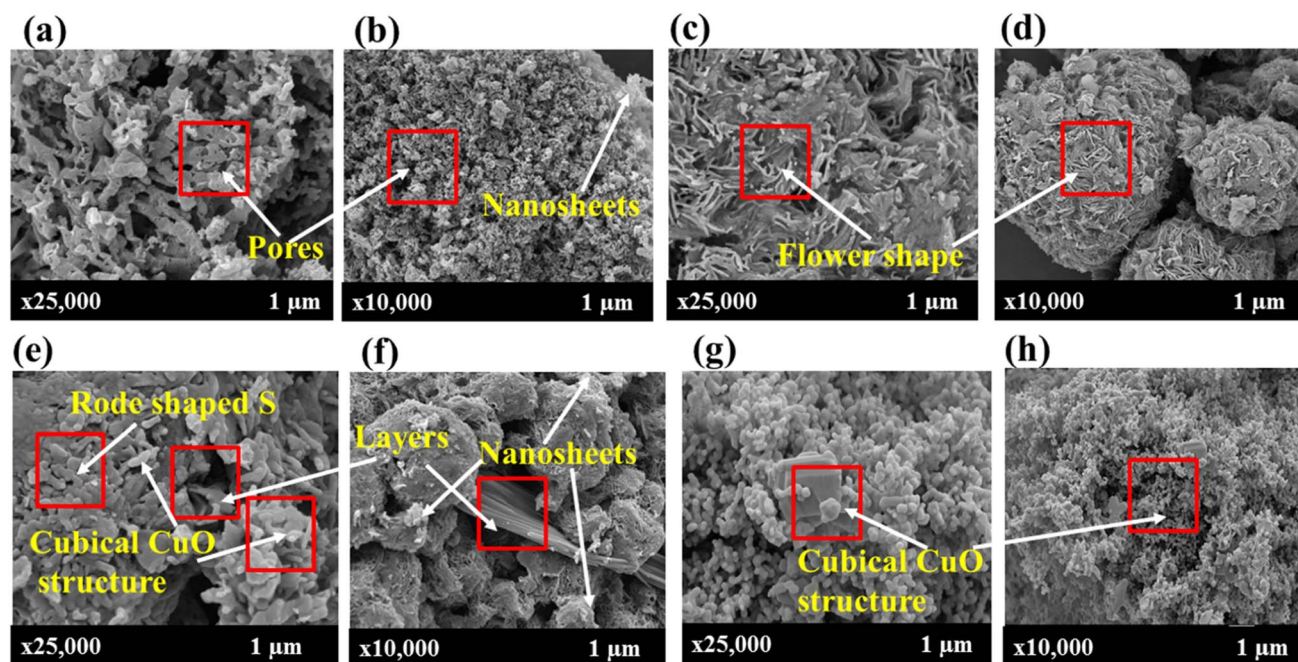


Fig. 6 HR-SEM image of (a and b) bulk  $g\text{-C}_3\text{N}_4$ , (c and d)  $S$ -doped  $g\text{-C}_3\text{N}_4$ , (e and f)  $\text{CuO}@S$ -doped  $g\text{-C}_3\text{N}_4$  composites, and (g and h) cubic shaped  $\text{CuO}$  NPs at different magnifications.





C<sub>3</sub>N<sub>4</sub> and CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>, which showed agglomerated particles with irregular shape and variable packing density. The HR-SEM image of the bulk g-C<sub>3</sub>N<sub>4</sub> at different magnification (Fig. 6) shows highest porosity with specific surface area value (Table 2), an irregular shape and desultorily assembled together with the microspheres morphology of typical g-C<sub>3</sub>N<sub>4</sub> particles, similar to observations in other reports.<sup>44</sup> CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC is composed of three types of morphology microspheres (Fig. 6): a thin straight bar, *i.e.* rod-shaped S, flower-shaped microsphere S-doped g-C<sub>3</sub>N<sub>4</sub> (Fig. 6), and sphere and cubic-shaped CuO NPs. These results corroborate the successful formation of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC. This kind of hybrid heterostructured composite is believed to enhance the accumulation of electrons on the conduction band to maintain electron flow and reduce the electron-hole recombination rate which can improve the photocatalytic efficiency of the material.<sup>45</sup> The aggregated particles' dimensions were found to be substantially greater than what were found in the XRD results. The difference between calculated and observed sizes in the HRSEM micrograph is ascribed to the calculated size being that of a single crystallite, whilst the observed size is that of an agglomeration made up of numerous synthesized crystallites.

From the HR-SEM image (Fig. 6), quantitative analysis of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs (CuO = 29%) reveals atomic weight percentages of N, C, S, Cu and O elements as 35.7, 29.3, 0.1, 17.6 and 11.4 wt%, respectively. These values are close to the theoretical percentage of CuO (30%). This indicated that Cu and O atoms were distributed in the entire host of the S-doped g-C<sub>3</sub>N<sub>4</sub> NC. Where Cu and O were present in the form of CuO, these analyses revealed CuO to be integrated firmly with S-doped g-C<sub>3</sub>N<sub>4</sub> NCs, creating hybrid structures.

Distribution of the elements in the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC was further inspected using elemental mapping images of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> from HR-SEM/EDS (Fig. 7). The outcome

confirmed a considerable amount of C, N, S, Cu and O elements homogeneously distributed in the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC and only a very small amount of impurity on the upper surface of the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC. In CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs, cubic CuO NPs aggregation on the surface of S-doped g-C<sub>3</sub>N<sub>4</sub> is clearly visible. On the surface of the bulk g-C<sub>3</sub>N<sub>4</sub>, on the other hand, S was sparsely scattered.

From the above HR-SEM/EDS analyses, it was observed that the C/N ratio varies from 0.75 to 0.83 in bulk g-C<sub>3</sub>N<sub>4</sub> and S-doped g-C<sub>3</sub>N<sub>4</sub>, giving average molecular formula's, C<sub>3.5</sub>N<sub>4</sub> and C<sub>3.7</sub>N<sub>3.8</sub>, respectively. The C/N ratio in the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs is 0.82, which is higher than the theoretical values of 0.75<sup>46,47</sup> and reported C/N = 0.67 corresponds to the composition of melon annealing at 600 °C.<sup>48</sup>

### 3.7 Surface area analysis

Nitrogen adsorption isotherms of pure g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, and CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> samples were measured to gain information about the specific surface area, as shown in Fig. 8. We examined the surface features of synthesized semi-conducting NCs by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC shows remarkable properties in *S*<sub>BET</sub> and pore features. The pore size distribution of the samples shows that most of the pores fall into a size range of 2 to 50 nm. Adsorption isotherms are type IV and type H3 hysteresis loops.

For pure g-C<sub>3</sub>N<sub>4</sub>, the larger adsorption capacity is found in the high pressure range (*P*/*P*<sup>0</sup> > 0.2), indicating that it has mainly mesopores, while the other NCs achieve most of their N<sub>2</sub> adsorption before *P*/*P*<sup>0</sup> = 0.2, an indication of microporosity.<sup>49</sup> The specific surface areas of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> for (5, 10, 20, and 30% of CuO) NCs and pure CuO NPs were calculated to be 30.7, 28.6, 26.6, 22.9 and 28.2 m<sup>2</sup> g<sup>-1</sup>, respectively.

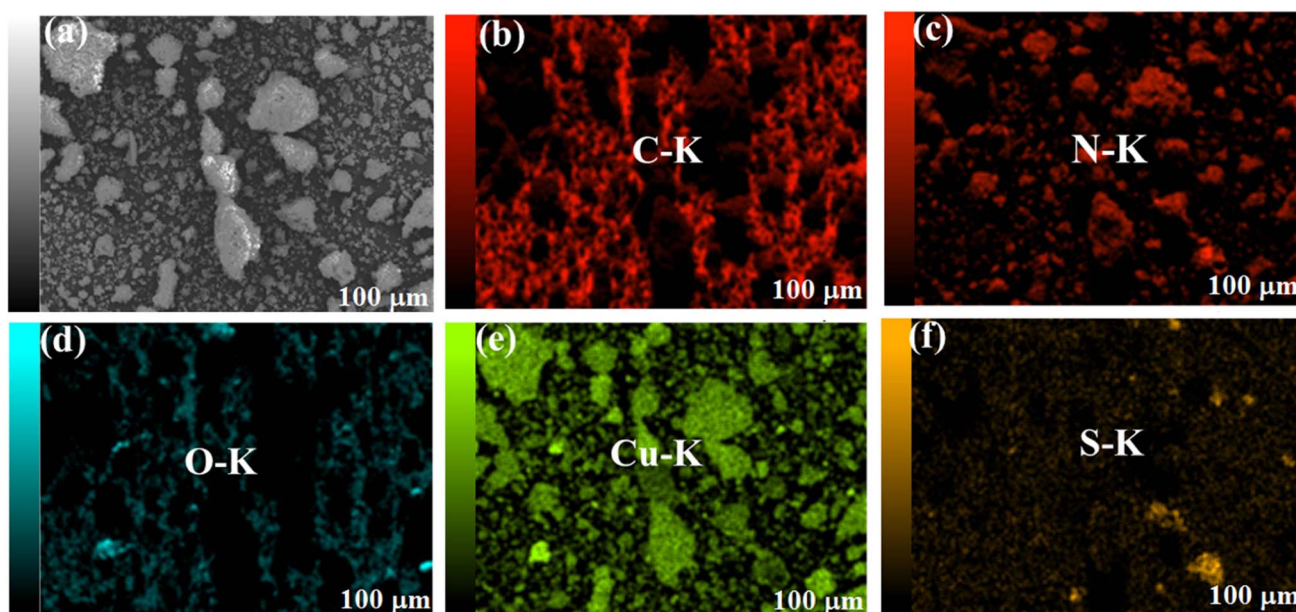


Fig. 7 HRSEM/EDS mapping for different elements and in the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs.

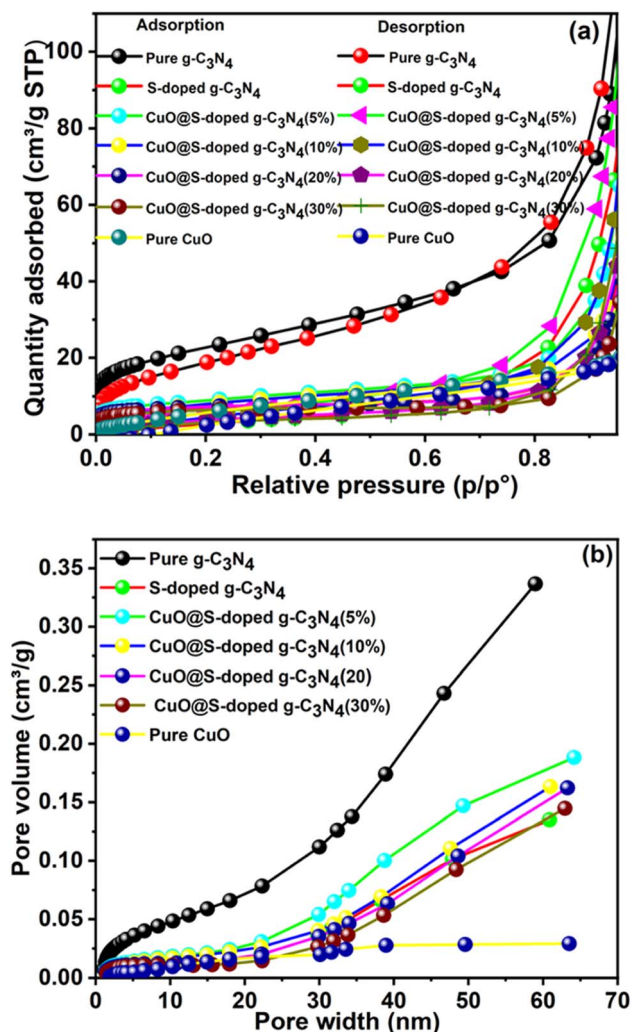


Fig. 8 (a)  $N_2$  adsorption-desorption BET isotherms, and (b) pore size distribution curves of pure  $g\text{-C}_3\text{N}_4$ , S-doped  $g\text{-C}_3\text{N}_4$ , CuO@S-doped  $g\text{-C}_3\text{N}_4$  NCs, and pure CuO, measured at 77 K.

The surface specific area of NC was found to be lower than that of pure  $g\text{-C}_3\text{N}_4$  ( $81.6 \text{ m}^2 \text{ g}^{-1}$ ), but higher than that of the S-doped  $g\text{-C}_3\text{N}_4$  ( $24.4 \text{ m}^2 \text{ g}^{-1}$ ). The decreased surface area after doping by S is attributed to disappearance of the small pores, but was gradually enhanced by the appearing of additional small pores when CuO was confined within the NC. This is

confirmed by the pore size distribution, shown in Table 3 and Fig. 8b. At the same time, the BJH pore size and volume of CuO@S-doped  $g\text{-C}_3\text{N}_4$  NC semiconductors were also increased, implying cavities or tunnels developing in CuO@S-doped  $g\text{-C}_3\text{N}_4$  NCs. Therefore, CuO@S-doped  $g\text{-C}_3\text{N}_4$  NC has appealing features such as a large specific surface area and a mesoporous structure, allowing for higher degree of absorption, which may be beneficial for aqueous penetration in the photocatalytic reaction. In general, the  $S_{\text{BET}}$  results illustrate that enhanced photocatalytic performance is not only due to improved electron-hole recombination rate, but also the result of changes in BET surface areas of the samples.

### 3.8 XPS analysis

The surface chemical compositions of the CuO@S-doped  $g\text{-C}_3\text{N}_4$  nanocomposite were investigated by using X-ray photoelectron spectroscopy (Fig. 9). The survey spectrum of  $g\text{-C}_3\text{N}_4$  (Fig. 9a) clearly shows that  $g\text{-C}_3\text{N}_4$  is composed of only C and N, which is consistent with the chemical analysis. The C 1s and N 1s peaks situated at 288.1 eV and 398.7 eV correlates well with reported values in the  $g\text{-C}_3\text{N}_4$  bond.<sup>50</sup> The S-doped  $g\text{-C}_3\text{N}_4$  (Fig. 9b) sample also reveals prominent peaks for C 1s and N 1s at the same binding energy positions as in Fig. 9a. It is important to note that S was not detected, since the S concentration was below the detection limit of the instrument. High-resolution XPS for C 1s, N 1s, O 1s and S 2p are presented in the SI. The N 1s peak around 397.2 eV was attributed to deprotonated N atoms of  $\text{C}=\text{N}-\text{C}$  bonds,<sup>51,52</sup> whereas the peak around 398 eV was assigned to the  $\text{C}=\text{N}-\text{C}$  bonds of the melon structure of the graphitic carbon nitride.<sup>51,52</sup> In the XPS spectra of S-doped  $g\text{-C}_3\text{N}_4$  for S 2p (Fig. S1f†), a peak located around 164.2 eV was assigned to C-S.<sup>40,53</sup> The peak around 283.7 eV in the C 1s spectrum (Fig. S1c†) was also assigned to the C-S bond of S- $g\text{-C}_3\text{N}_4$ , whereas the peak around 286.6 eV was assigned to the  $\text{N}=\text{C}-\text{N}$  bond.<sup>54,55</sup> This overall analysis is in line with previous reports.<sup>19,40,51–53</sup>

Cu 2p, 3s and 3p peaks were clearly detected for the CuO@S-doped  $g\text{-C}_3\text{N}_4$  NC and pure CuO samples in Fig. 9c and d. O 1s was detected in the CuO sample (Fig. 9d) at 529.6 eV and this correlated well with the binding energy value of O 1s in CuO.<sup>56</sup> In Fig. 9d, C 1s was detected, which is ascribed to an impurity. High-resolution peaks for Cu 2p were recorded in order to investigate the bonding environment in the CuO@S-doped  $g\text{-C}_3\text{N}_4$  NC and pure CuO matrix. In CuO@S- $g\text{-C}_3\text{N}_4$  NC (Fig. 10a)

Table 3 BET surface areas, pore sizes and pore volumes in the prepared samples

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	Pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )		Pore size (nm)	
		BJH adsorption	BJH desorption	BJH adsorption	BJH desorption
$g\text{-C}_3\text{N}_4$	81.6	0.33	3.74	12.7	35.9
S-doped $g\text{-C}_3\text{N}_4$	24.4	0.13	0.75	15.1	23.5
CuO@S-doped $g\text{-C}_3\text{N}_4$ (5%)	30.7	0.19	0.23	15.9	21.2
CuO@S-doped $g\text{-C}_3\text{N}_4$ (10%)	28.6	0.16	0.22	14.4	27.0
CuO@S-doped $g\text{-C}_3\text{N}_4$ (20%)	26.6	0.16	0.26	16.6	45.5
CuO@S-doped $g\text{-C}_3\text{N}_4$ (30%)	22.9	0.14	0.26	15.4	41.6
Pure CuO	28.2	0.04	0.06	4.1	10.0



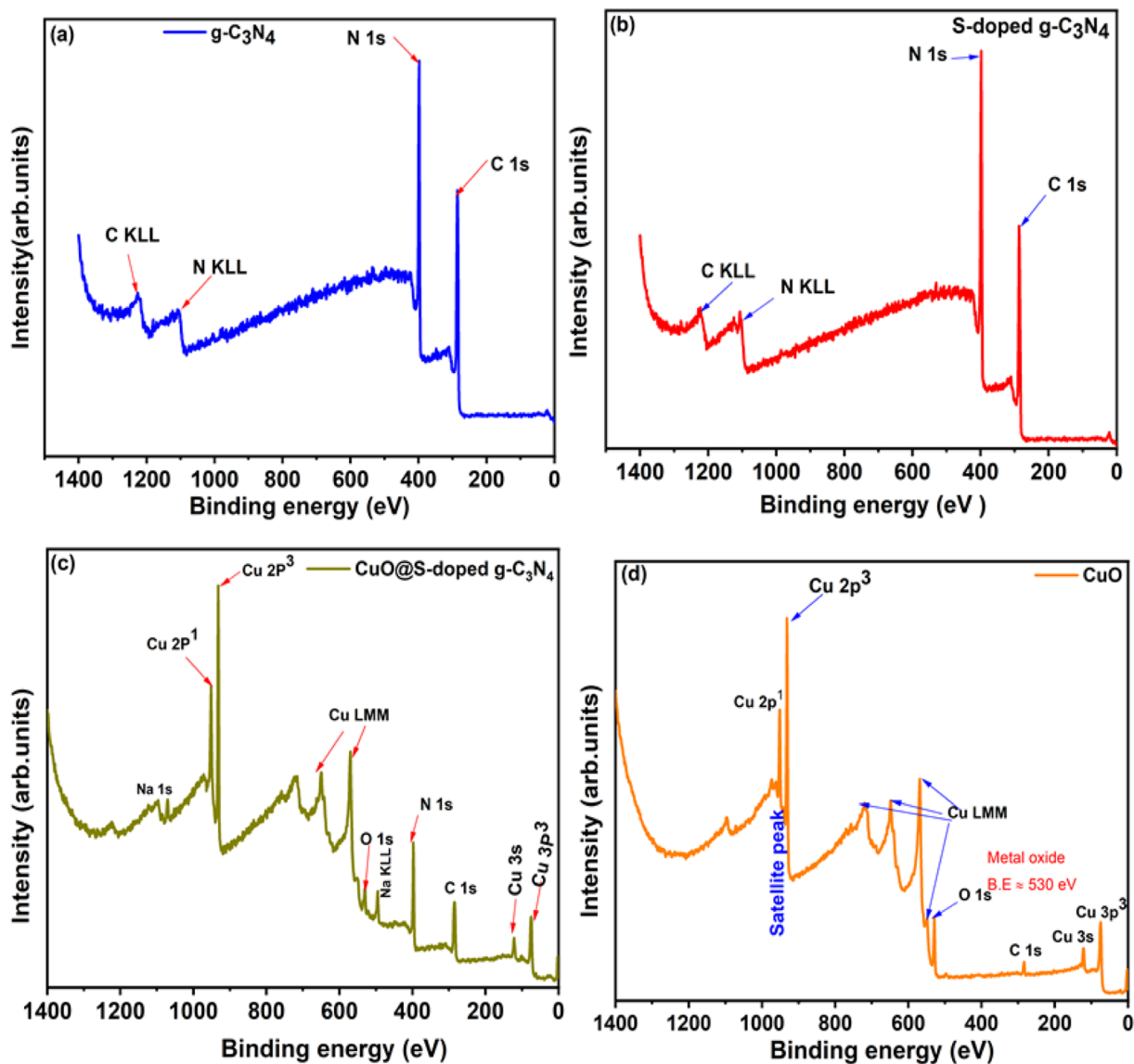


Fig. 9 XPS survey spectra for (a) pure  $\text{g-C}_3\text{N}_4$ , (b) S-doped  $\text{g-C}_3\text{N}_4$ , (c)  $\text{CuO@S-g-C}_3\text{N}_4$  NCs and (d) pure  $\text{CuO}$ .

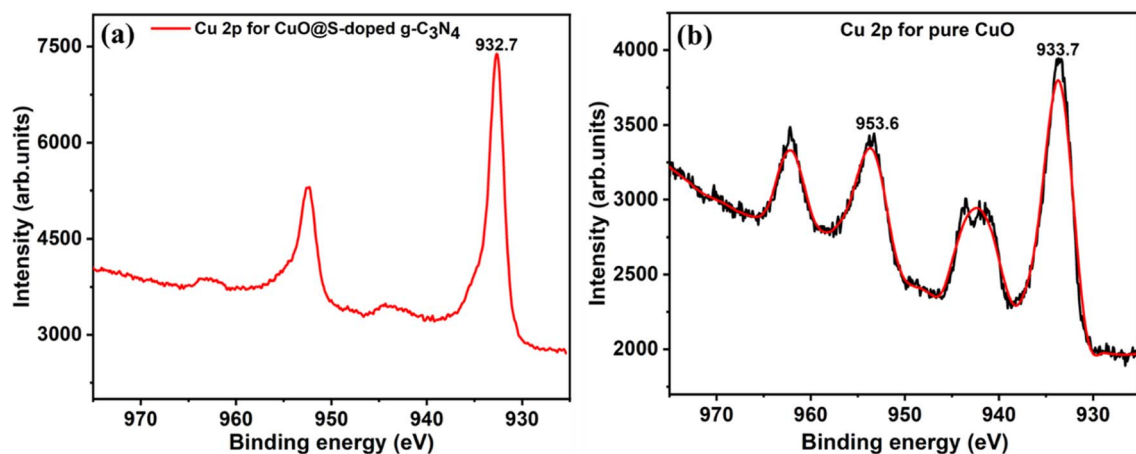


Fig. 10 XPS high resolution spectra of (a) Cu 2p peaks for  $\text{CuO@S-doped g-C}_3\text{N}_4$ , and (b) Cu 2p peaks for pure  $\text{CuO}$  NP.



the two peaks at 932.7 and 952.3 eV were assigned to the Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> spin orbit splitting peaks of Cu.<sup>56</sup> Fig. 10b shows the Cu 2p peak for pure CuO NPs. The Cu 2p<sub>3/2</sub> peak is seen at 933.7 eV and this together with the peak shape clearly indicates the CuO bond. The O 1s peak in the CuO sample (Fig. 9d) is situated at 529.6 eV, which correlates well with O 1s in CuO.<sup>56</sup> Fig. 10b suggests that Cu is in the 2+ oxidation state, while Fig. 10a suggests a metallic state of Cu. The reason for this may be due to thermal decomposition of CuO at elevated temperatures during the pyrolysis process.

### 3.9. Electrochemical characterizations of the modified electrodes

CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE was characterized by cyclic voltammetry in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> redox probe electrolyte solution containing 0.1 M KCl as shown in Fig. 11a, in the range, -0.8 to 1.0 V, at a scan rate of 50 mV s<sup>-1</sup>. The modified CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE electrode (CuO = 30%) results exhibit a well-defined

redox peak with high electron transfer capability when compared to g-C<sub>3</sub>N<sub>4</sub>/GCE, S-doped g-C<sub>3</sub>N<sub>4</sub>/CPE, CuO/CPE and bare GCE. Herein, S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE shows low electron transfer when compared to other electrodes, which is ascribed to its low electrical conductivity that restricts the electron transfer probe [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> along the surface of the GCE. When the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE electrode was introduced, electrical conductivity was enhanced and peak-to-peak separation (reversible process) was reduced due to the large surface area provided by g-C<sub>3</sub>N<sub>4</sub>. The redox process probed by the electrode at scan rates varying from 20 to 100 mV s<sup>-1</sup> was shown to be enhanced in the cyclic voltammetry results. The electron transfer mechanism between the electrolyte and the bare glassy carbon electrode is substantially facilitated by the synergistic impact of CuO and S-doped g-C<sub>3</sub>N<sub>4</sub> as co-modifiers, as shown in Fig. 11a. The NC with 30% CuO performed better in terms of sensing than the others. According to Table 3, bulk g-C<sub>3</sub>N<sub>4</sub> has a surface area of 81.6 m<sup>2</sup> g<sup>-1</sup>. The surface area reduced to 24.4

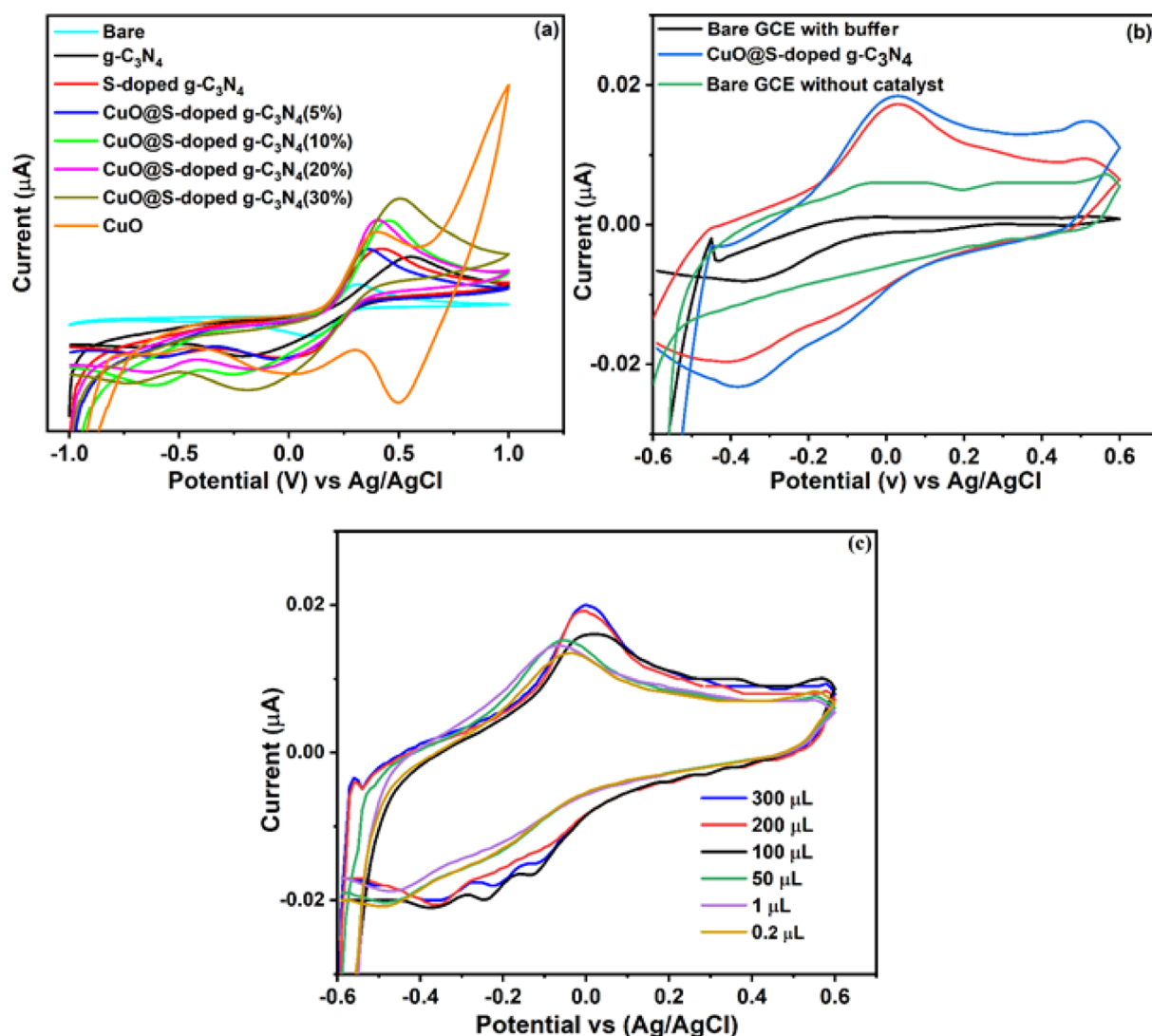


Fig. 11 Cyclic voltammetry scans for (a) bare and modified GCEs in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 M KCl, (b) bare and modified GCEs for 4-NP in 0.1 M BPS and 0.05 mM of 4-NP at pH = 7, and (c) illustration of the effect of different concentrations.



$\text{m}^2 \text{g}^{-1}$  after sulfur doping and further decreased to  $22.9 \text{ m}^2 \text{g}^{-1}$  after adding CuO. This amply demonstrated the alteration of the S-doped  $\text{g-C}_3\text{N}_4$  and offers a favorable environment for the binder-free decorated electrode with hazardous pollutant sensing behavior. We tested the modified electrode to sense 4-nitrophenol in order to verify such an observation.

### 3.10. Electrochemical behavior of 4-NP at the modified electrode

Cyclic voltammetry was used to study electrochemical characteristics of CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$ , bulk  $\text{g-C}_3\text{N}_4/\text{GCE}$ , S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$ , and CuO/GCE in 0.1 M  $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$  buffer solution of pH = 7 at a scan rate of  $50 \text{ mV s}^{-1}$  (Fig. 11a). Using bare GCE, no oxidation peak was observed, however, CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$  (20 and 30% of CuO) and pure S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$  exhibits oxidation of 4-NP when using the 30% CuO electrode in the composite. The oxidation peak in Fig. 11b is that of 4-NP. At +0.030 V, the oxidation peak current,  $I_{\text{pa}} = -4.85 \times 10^{-6} \text{ A}$ , is recorded for the bare GCE. The 4-NP oxidation peak current,  $I_{\text{pa}} = 1.78 \times 10^{-5} \text{ A}$ , increased with negatively shifted peak potential to  $-0.020 \text{ V}$  at CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$ , indicating that the electrochemical oxidation of 4-NP was significantly improved. This demonstrates that

CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$  has a greater redox peak current than the other modified electrodes. This high oxidation peak current when using CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$ , is attributed to the production of a synergistic effect due to CuO. There are two reasons for this improvement. Firstly, the BET analyses showed that CuO@S-doped  $\text{g-C}_3\text{N}_4$  has a large surface area, which allows for abundant active sites. Secondly, CuO@S-doped  $\text{g-C}_3\text{N}_4$  NC has electron-rich O and N atoms that could interact with 4-NP. CuO@S-doped  $\text{g-C}_3\text{N}_4$  NC allows for a strong electrocatalytic mediation effect, which significantly increased the current ( $-4.85 \times 10^{-6} \text{ A}$  to  $1.78 \times 10^{-5} \text{ A}$ ). Therefore, CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$  was considered as the working electrode.

### 3.11. Effect of pH

The influence of pH when using a 0.1 M phosphate buffer solution (0.1 M  $\text{Na}_2\text{HPO}_4 - 0.1 \text{ M NaH}_2\text{PO}_4$ ) (PBS) on the electrode reaction of  $100 \mu\text{M}$  of 4-NP was recorded at pH 5, 7 and 9 at the favored scan rate of  $50 \text{ mVs}^{-1}$ . The effect of pH on the oxidation of  $100 \mu\text{M}$  4-NP at CuO@S-doped  $\text{g-C}_3\text{N}_4/\text{GCE}$  was investigated using cyclic voltammetry at a pH range 3 to 9, also at  $50 \text{ mVs}^{-1}$ . As shown in Fig. 11c, the oxidation peak current of 4-NP gradually shifted to the right when increasing pH from 4 to 9, however, maximum current was achieved at pH 7 with

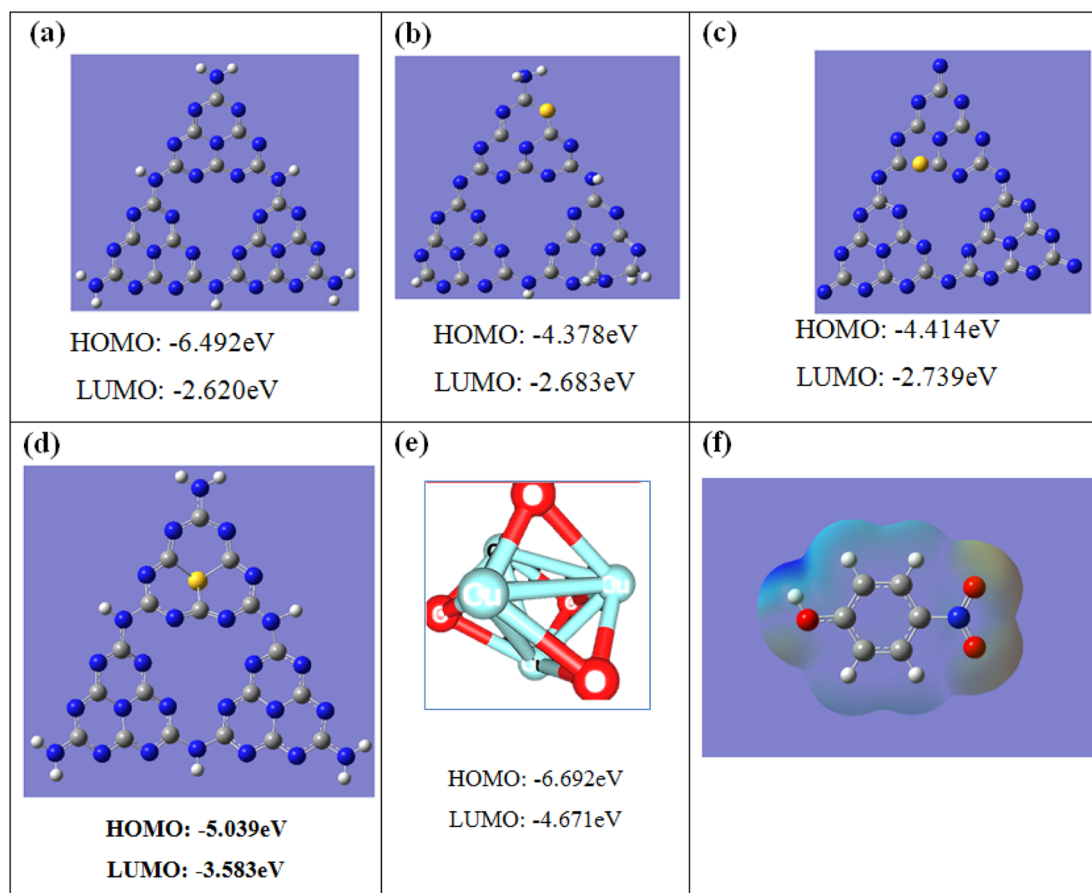


Fig. 12 Molecular orbital energies and structures of: (a) pure  $\text{g-C}_3\text{N}_4$ , (b) S-doped  $\text{g-C}_3\text{N}_4$  with nitrogen (N1) substituted by sulfur at site 1, (c) S-doped  $\text{g-C}_3\text{N}_4$  with nitrogen (N2) substituted by sulfur at site 2, (d) S-doped  $\text{g-C}_3\text{N}_4$  with nitrogen (N3) substituted by sulfur at site 3, (e) pure CuO, and (f) ESP mapping of the optimized 4-NP. Color coding: gray C, blue N, yellow S, red oxygen, and white hydrogen.

**Table 4** Band gap energy (eV) calculated for different S positions in S-doping configurations

Sample	Band gap ( $E_g$ ) (eV)	
	DFT	Experimental
Pure g-C <sub>3</sub> N <sub>4</sub>	3.87	2.61
S-center out	1.66	2.63
S-in-between	1.46	—
S-outside	1.70	—

oxidation peak shift towards negative potentials. Thus, pH 7 was chosen for the subsequent analytical experiments.

### 3.12. Effect of concentration

The sensing behavior of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE was also investigated by cyclic voltammetry at diverse concentrations of 4-NP varying from 0.1 to 300  $\mu$ M in the presence of 0.1 M PBS (pH = 7) and scan rate of 50 mV s<sup>-1</sup>, see Fig. 11c. It is seen that the oxidation peak current response of 4-NP was gradually increased when the concentration of 4-NP was increased from 0.02 to 300  $\mu$ M. When a concentration of 0.1  $\mu$ M was reached, the peak shift occurred. These observations suggest that the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>/GCE modified electrode has an excellent detection activity at lower concentrations of 4-NP.<sup>57</sup>

### 3.13. Computational results

Since the exact position for S and CuO substitution cannot be identified experimentally, we did DFT calculations to elucidate the electronic structure of CuO@S-doped C<sub>3</sub>N<sub>4</sub>. Geometric optimizations of pure g-C<sub>3</sub>N<sub>4</sub>, S-doped g-C<sub>3</sub>N<sub>4</sub>, and CuO models were performed with the DFT/B3LYP/6-31+G(d,p) method. An atomic structure model of pure g-C<sub>3</sub>N<sub>4</sub> composed of melon units (S-triazine) was constructed as shown in Fig. 12. In this model, three types of periodic N atoms exist in the melon system, indicated as N<sub>1</sub>, N<sub>2</sub>, and N<sub>3</sub> numbered based on their positions for S substitution. The DFT-calculated band gap of S-doped g-C<sub>3</sub>N<sub>4</sub> is slightly underestimated. Although  $E_g$  results are found to depend on the doping condition and type of basis set, the overall DFT result is that all considered doping scenarios are unfavorable; hence all calculated values presented in Table 4 are lower than the corresponding experimental values. It is nevertheless seen that the gap narrows down to ~1.5 eV upon doping compared to experimental value. It is worth mentioning that DFT calculations show narrowing of the band gap upon doping. Since S is a much larger atom than N and C, it was found that for the optimized geometries, substitution of N with S caused a significant lattice distortion, which in turn changed the  $E_g$  values, while in all the other cases of substitution of N with S, the structure kept a planar geometry, in agreement with a previous study.<sup>8</sup>

## 4. Conclusions

In this study, pyrolysis and elementary chemical techniques were used to successfully produce CuO@S-doped g-C<sub>3</sub>N<sub>4</sub>

nanocomposites. The structural characterization, pore sizes, morphology, crystallinity, photoluminescence, formation energy, charge analysis, and band gap data for CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs were examined using a variety of experimental and computational techniques. The outcomes confirmed the successful formation of CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs. The HR-SEM/EDS investigations revealed that the C/N ratio in both bulk and S-doped g-C<sub>3</sub>N<sub>4</sub> ranges from 0.75 to 0.83. Additionally, it was discovered that the CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NC had desirable qualities, such as a sizable specific surface area and a mesoporous structure that permits a higher degree of absorption, which may be advantageous for aqueous penetration during photocatalytic processes. From the electrochemical studies, it was observed that the electron transfer mechanism between the electrolyte and the bare glassy carbon electrode is substantially facilitated by the synergistic impact of CuO and S-doped g-C<sub>3</sub>N<sub>4</sub> as co-modifiers. BET results demonstrated alteration of S-doped g-C<sub>3</sub>N<sub>4</sub>, which offers a favorable environment for the binder-free decorated electrode with hazardous pollutant sensing behavior. As a result, the synthesized NCs were used to detect 4-nitrophenol, a recognized environmental pollutant. CuO@S-doped g-C<sub>3</sub>N<sub>4</sub> NCs were demonstrated as promising candidates for binder-free electrode materials that may be manufactured for the purpose of monitoring environmental pollutants and for a variety of electrochemical applications employing low-cost cyclic voltammetry techniques.

## Conflicts of interest

The authors have no conflicts of interest to declare.

## Author contributions

NA, HCAM, BA and TBD designed and run the experiments, analyzed the data and wrote the original draft; NA, KGvE, EHGL and LCH run the characterization experiments; HCAM, BA and TBD supervised the work, and all authors reviewed and edited the article.

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