Facile synthesis of g-C$_3$N$_4$(0.94)/CeO$_2$(0.05)/Fe$_3$O$_4$(0.01) nanosheets for DFT supported visible photocatalysis of 2-Chlorophenol

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Visible light active g-C$_3$N$_4$(0.94)/CeO$_2$(0.05)/Fe$_3$O$_4$(0.01) ternary composite nanosheets were fabricated by facile co-precipitation routes. The density functional theory (DFT) computations investigated changes in geometry and electronic character of g-C$_3$N$_4$ with CeO$_2$ and Fe$_3$O$_4$ addition. Chemical and surface characterizations were explored with XRD, XPS, SEM, TEM, PL, DRS and Raman measurements. DRS and PL spectroscopy evidenced the energy band gap tailoring from 2.68 eV for bulk g-C$_3$N$_4$ and 2.92 eV for CeO$_2$ to 2.45 eV for the ternary nanocomposite. Efficient electron/hole pair separation, increase in red-ox species and high exploitation of solar spectrum due to band gap tailoring lead to higher degradation efficiency of g-C$_3$N$_4$(0.94)/CeO$_2$(0.05)/Fe$_3$O$_4$(0.01). Superior sun light photocatalytic breakdown of 2-Chlorophenol was observed with g-C$_3$N$_4$ having CeO$_2$ loading up to 5 wt%. In case of ternary nanocomposites deposition of 1 wt% Fe$_3$O$_4$ over g-C$_3$N$_4$/CeO$_2$ binary composite not only showed increment in visible light catalysis as predicted by the DFT studies, but also facilitated magnetic recovery. The g-C$_3$N$_4$(0.94)/CeO$_2$(0.05)/Fe$_3$O$_4$(0.01) nanosheets showed complete mineralization of 25 mg L$^{-1}$ 2-CP$_{\text{aq}}$ within 180 min exposure to visible portion of sun light and retained its high activity for 3 consecutive reuse cycles. The free radical scavenging showed superoxide ions and holes played a significant role compared to hydroxyl free radicals while chromatographic studies helped establish the 2-CP degradation mechanism. The kinetics investigations revealed 2.55 and 4.04 times increased rate of reactions compared to pristine Fe$_3$O$_4$ and CeO$_2$, showing highest rate constant value of 18.2 $\times$ 10$^{-3}$ min$^{-1}$ for the ternary nanocomposite. We present very persuasive results that can be beneficial for exploration of further potential of g-C$_3$N$_4$(0.94)/CeO$_2$(0.05)/Fe$_3$O$_4$(0.01) in advance wastewater treatment systems.

Energy, changing climate and water purification are becoming worldwide challenges to fulfill the demands of ever growing societies. In past few years water pollution has become an imperative problem for the environmental scientists across the globe. Wastewater is an essential by–product of modern industry and plays an important role as a pollution source in the environment. For instance, 2-Chlorophenol (2-CP) is an ubiquitous pollutant due to its widespread release into the environment as a by–product during the manufacturing of plastics, dyes, pulp and paper industry as well as petroleum refining$^1$. 2-CP possessing toxic natural properties, badly affects the biotic life forms along the food chain$^3$–$^5$. Moreover, it is difficult to remove 2-CP using conventional treatment
techniques because of their sensitivity to environmental factors, slow mode of action, high budgetary requirements and/or production of unwanted solid residues\textsuperscript{7–9}. Among the diverse sustainable developments of recent years, semiconductor photocatalysis for harnessing the virtually endless solar power resource has emerged as a technology with immense potential for power generation and environmental cleanup\textsuperscript{10}. Photocatalysis in particular, due to the non-selective behaviour toward organic contaminants is investigated as the most favourable technology for destructive removal of phenols and phenolic compounds from wastewater\textsuperscript{11,12}. For quite some years, the choice ultra violet (UV) and visible light (VL) active photocatalysts comprised of variants of semiconductors like TiO\textsubscript{2}, ZnS, Fe\textsubscript{2}O\textsubscript{3}, Cds, Bi\textsubscript{2}WO\textsubscript{6}, InVO\textsubscript{4}, Ta\textsubscript{3}N\textsubscript{5}, TaO\textsubscript{N}\textsuperscript{13,14}. While searching for vigorous and VL dynamic semiconductor photocatalysts g-C\textsubscript{3}N\textsubscript{4} has generated impression of enthusiasm among scientific societies as the next-generation photocatalyst, owing to its high physico-chemical stability, attractive optoelectronic properties, and tunable niche\textsuperscript{15–27}. The semiconductor catalyst can be synthesized by single step temperature controlled polymerization of low cost and readily available nitrogen rich precursor\textsuperscript{28–31}. Thus the surface chemistry of g-C\textsubscript{3}N\textsubscript{4} could be manipulated with ease through molecular level engineered surface designs. Furthermore, g-C\textsubscript{3}N\textsubscript{4} bears the lowest energy band gap among its seven polymeric phases, owing to sp\textsuperscript{2}-hybridized C and N having π-conjugated electronic systems. Compared to TiO\textsubscript{2}, g-C\textsubscript{3}N\textsubscript{4} band gap is considerably small i.e., 2.7–2.8 eV, responsible for absorption in 450–460 nm ranges of visible spectrum\textsuperscript{32}. Unfortunately pristine g-C\textsubscript{3}N\textsubscript{4} suffers from some limitations which hinder the wide scale use of g-C\textsubscript{3}N\textsubscript{4} involving slow efficiency of solar light utilization (>460 nm) and high electron/hole pair’s recombination following photo-excitation (in picoseconds). Furthermore, separation of non-magnetic photocatalyst from huge volumes of treated solutions also halts its practical implications at larger scale\textsuperscript{33,34}. The degradation potential of g-C\textsubscript{3}N\textsubscript{4} can also be enhanced significantly by pairing up with a variety of semiconductors like Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, AgI, InVO\textsubscript{4} and WO\textsubscript{3} due to efficient electron hole pair separation across the heterojunction between the semiconductors\textsuperscript{35–38}. Moreover, coupling with Fe\textsubscript{3}O\textsubscript{4} is explored owing to its stability, cost effectiveness and facile recovery of the resulting photocatalyst from the treated solution and absence of chemical and energy intensive post recovery activation procedures\textsuperscript{39,40}. Also recently, the simultaneous coupling of two kinds of semiconductors into g-C\textsubscript{3}N\textsubscript{4} has attracted considerable interest\textsuperscript{31,41}. To our literature survey, this is the first report on fabrication of g-C\textsubscript{3}N\textsubscript{4}(0.94)/CeO\textsubscript{2}(0.05)/Fe\textsubscript{3}O\textsubscript{4}(0.01) for applications in wastewater treatment yet. Hence, this investigation reports a novel g-C\textsubscript{3}N\textsubscript{4}(0.94)/CeO\textsubscript{2}(0.05)/Fe\textsubscript{3}O\textsubscript{4}(0.01) photocatalyst prepared by facile co-precipitation route. The nanocomposite showed remarkable photocatalytic performance in terms of 2-CP degradation under both visible and direct sunlight in versatile reaction conditions, thus advocating its use as an efficient and robust wastewater treatment candidate.

Materials and Methods

Materials. Thiourea (SC(NH\textsubscript{2})\textsubscript{2}), ferric chloride hexahydrate (FeCl\textsubscript{3}.6H\textsubscript{2}O), ferrous chloride (FeCl\textsubscript{2}), cerium nitrate hexahydrate (Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O), potassium carbonate (K\textsubscript{2}CO\textsubscript{3}), sodium hydroxide (NaOH), ethanol (99.9%), ammonium hydroxide (NH\textsubscript{4}OH, 33%), hydrochloric acid (HCl, 37%) obtained from Sigma Aldrich (USA). 2-CP (Sigma Aldrich, USA) was used as pollutant in synthetic water.

Methods. Synthesis of g-C\textsubscript{3}N\textsubscript{4}(0.94)/CeO\textsubscript{2}(0.05)/Fe\textsubscript{3}O\textsubscript{4}(0.01) – g-C\textsubscript{3}N\textsubscript{4} was done according to the widely used protocol involving direct heating of SC(NH\textsubscript{2})\textsubscript{2} at 550 °C for 3 hours\textsuperscript{46,47}. CeO\textsubscript{2} was prepared by the precipitation of cerium nitrate hexahydrate with potassium carbonate solution at 60 °C and at constant pH = 9.0. The dried powder was calcined at 450 °C up to 3 h with a ramping rate of 5 °C min\textsuperscript{-1}. For the preparation of g-C\textsubscript{3}N\textsubscript{4}/CeO\textsubscript{2} binary composite, different weight percent of CeO\textsubscript{2} (3%, 5%, 7%) were mixed with g-C\textsubscript{3}N\textsubscript{4} in ethanol at 100 °C under constant stirring to uniformly distribute CeO\textsubscript{2} over g-C\textsubscript{3}N\textsubscript{4} surface. Ethyl alcohol was evaporated and slurry dried at 100 °C to obtain the nanocomposites labelled as GC3, GC5 and GC7. In order to synthesize ternary g-C\textsubscript{3}N\textsubscript{4}/CeO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} nanocomposite, 1.9 g of GC5 was dissolved in 50 ml of ethanol and water (volume ratio = 1:2) at constant stirring then 0.17 mM and 0.087 mM of FeCl\textsubscript{3}.6H\textsubscript{2}O and FeCl\textsubscript{2} were respectively mixed into the solution at 65 °C and the pH was adjusted at 10 with ammonia solution. Mixture was constantly stirred for another 30 mins (80 °C) and then cooled down at room temperature. Resulting nanocomposite was filtered, washed using ethanol and completely dried in oven at 80 °C\textsuperscript{49}. Based on the weight percent of Fe\textsubscript{3}O\textsubscript{4} i.e. 1%, 3%, 5%, 7% and 10% with respect to GC5, the prepared nanocomposites were labelled as GCF1, GCF3, GCF5, GCF7 and GCF10, respectively.

Nanocomposite characterization. Investigation of crystalline nature of as synthesized materials was done using D8 Bruker X-ray Diffractometer varying the incident angle from 20° to 80° using Cu-Kα radiation (λ = 1.5418 nm). XPS measurements were performed in ultra-high vacuum conditions using standard Omicron system equipped with monochromatic Al Kα 1486.7 eV X-ray source operated at 15 kV at constant analyzer energy of 100 eV for survey scans and 20 eV for detailed scans. Morphology of fabricated photocatalysts was examined by scanning electron microscope (Hitachi S-4800 microscope operated at 20 kV) and JEOL-2100 TEM. The SEM was fitted with EDAX for elemental mapping of the synthesized materials. Raman spectroscopy was performed with a home-made confocal setup fitted with a 532 nm laser. The measurements were performed at 1 mW of excitation power and spectra recorded using an iHR550 imaging spectrometer (from Horiba Scientific). Surface area was calculated through nitrogen physisorption with Nova 2200e (Quantachrome). Diffuse reflectance was recorded in the wavelength ranging from 200 to 800 nm with PerkinElmer, Lambda 750 UV–Vis–NIR spectrophotometer, equipped with integrating sphere. Energy band gap of synthesized photocatalysts were calculated by Kubelka-Munk equation. Room Temperature PL spectra were measured with RF-5301 PC Fluorescence Spectrofluorophotometer (Shimadzu, Japan).
Computational study. In this study, the spin-polarized density functional theory (DFT) was performed using the Vienna ab initio simulation package (VASP)\textsuperscript{49-51}. Exchange correlation interaction energy was calculated by using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional\textsuperscript{52}. Projector augmented wave (PAW) pseudopotentials were used to explain the interaction between the valence and core electrons\textsuperscript{41}. Valence electrons are described by $4f^1 5d^1 6s^2$ for Ce, $3d^6 6s^2$ for Fe, $2s^2 2p^4$ for O, $2s^2 2p^3$ for N and $2s^2 2p^2$ for C. Energy cutoff of 450 eV was employed for treatment of valence electrons. g-C$_3$N$_4$ was modeled with a super cell consisting of 27 Carbon atoms and 36 Nitrogen atoms. A vacuum space of 15 Å was used to avoid interaction in the complex and its periodic system. The Fully optimized structure of g-C$_3$N$_4$ is shown in Fig. 1(a,b). For geometry optimizations the Brillouin zone integration was calculated with $5 \times 5 \times 1$ $k$ sampling point to gain accuracy. We have used the $5 \times 5 \times 1$ point sampling for PDOS calculation to gain accuracy for interaction of atomic orbitals near the Fermi Level. All the ions were allowed relaxing till maximum force on any ion is less than 0.02 eV/Å.

Photocatalytic experiments. In a typical experiment, 100 ml of 2-CP solution (25 mg L$^{-1}$) was taken into 8 inches diameter Pyrex reaction flasks and catalyst was added in the order of 1 g L$^{-1}$. The suspension was placed in dark for 30 min to equilibrate 2-CP molecules over photocatalyst surface, later the reaction mixture was exposed to direct sun light. During the experiments, reaction vessels were covered with glass covers to ensure only visible light degradation of 2-CP. 5 ml aliquots were sampled after 30 min time intervals and filtered with 0.22 μm syringe filters. Residual concentrations of 2-CP were examined with UV-Vis spectrophotometer at $\lambda = 274$ nm. Percentage degradation efficiency (DE %) was determined using Eq. 1:

$$\text{DE} \% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$  

(1)

Here $C_o$ = initial pollutant concentration and $C_t$ = pollutant concentration at time 't' (min). Influence of different reaction conditions as catalyst dose, $C_0$, pH of solution and reusability studies were also conducted on the selected best photocatalyst. For better insight into the degradation mechanism and to assess the active degrading species separate experiments were designed in lines with the optimal photocatalytic experiments with active species trapping agents. In these experiments t-butanol, p-benzoquinone (BQ) and ethylenediaminetetraacetic acid (EDTA) were used as hydroxyl radical (•OH), superoxide radicals (•O$_2^-$) and holes (h$^+$) scavengers, respectively.

Gas chromatography (GC). For GC analysis of 25 mg L$^{-1}$ 2-CP, degraded with 1 g L$^{-1}$ GCF1 under visible light, 5 mL aliquots were taken at specified intervals, filtered through 0.22 μm membrane filters and analyzed for the residual 2-CP concentration using GC. To determine the intermediate products, each test sample (0, 30, 90, 150 min) was extracted thrice using 25 mL of Dichloromethane (DCM). Extract thus obtained was dried using anhydrous Na$_2$SO$_4$. Samples were subjected to the GC (QP2010 ultra, Shimadzu) having a DB-5ms capillary column using He as carrier. Initial column temperature for 3 min was maintained at 50 °C followed by a gradual temperature increase at 5 °C min$^{-1}$ up to 250 °C. Injector and detector temperatures were fixed at 200 and 260 °C, respectively.
Results and Discussions

Structural characterization. Figure 2a shows the XRD of synthesized components and binary nanocomposites. In pure g-C₃N₄, a strong typical peak appears at 27.30° which has an interlayer distance of 0.33 nm is assigned to (002) plane of g-C₃N₄, indicating presence of interplaner stacking carbon nitride units. Another diffraction peak with very small intensity at around 13.10° is indexed to (100) and represents tri-s-triazine structure (JCPDS No. 21-1272& 87-1526). The CeO₂ diffraction peaks ascribed to the planes of CeO₂ including main peak (111) and three sister peaks (200), (220) and (311) corresponding to the pure cubic structure of CeO₂ (JCPDS No. 043-1002& 34-0394). In case of binary nanocomposites g-C₃N₄/CeO₂ clear indication of sister diffracted planes of CeO₂ appears (200), (220) and (311). But the main (111) diffracted peak of CeO₂ at ~28.60° might have been overlapped with the strong plane (002) of g-C₃N₄. We noticed the overall intensity of binary nanocomposite g-C₃N₄/CeO₂ has enhanced as we increase the content of CeO₂ from 3% (GC3), 5% (GC5) and 7% (GC7). Moreover the (100) plane in binary nanocomposite system disappeared which could be the result of CeO₂ attachment to g-C₃N₄ as reported earlier. The XRD patterns of Iron oxide have been presented in Fig. 2(b). The diffracted peaks reflect the mix phase of Fe₃O₄ and Fe₂O₃ have been observed in pristine iron oxide system. These planes are perfectly corresponding to the cubic spinel Fe₃O₄ (JCPDS No. 19-0629, 65-3107, 77-1545 & 3-0863). But interestingly, in all ternary composites of g-C₃N₄/CeO₂/Fe₃O₄ nanosheet samples only the diffracted peaks introduced due to Fe₃O₄ phase were noted. The main intense diffracted peak is the combination of (002) from g-C₃N₄ and (111) and from CeO₂ in all samples.

Morphological and compositional analysis. The morphological properties of the synthesized material were investigating by using SEM and TEM imaging. The SEM images of g-C₃N₄, CeO₂, Fe₂O₃, GC5 and GCF1 are displayed in Fig. 3(a,c,e,g,i), respectively. For better elucidation of the particle dimensions and morphology of the synthesized nanocomposites TEM images of g-C₃N₄, CeO₂, Fe₂O₃, GC5 and GCF1 are provided in Fig. 3(b,d,f,h,j), respectively. The surface morphology of g-C₃N₄ appeared to be composed of a large number of irregular sheets having sufficient small pores which may be due to the discharge volatiles from thiourea decomposition. Such morphology of g-C₃N₄ could be due to the aggregation of the sheets of the synthesized samples. The CeO₂ exhibited very thin flakes like structures with a relatively rough surface while the Fe₂O₃ consisted of spheres with the size of ~10–20 nm as reported in similar studies. In case of the nanocomposites, the TEM images clearly indicate that the sheets of g-C₃N₄ covered with the CeO₂ flakes and Fe₂O₃ nanoparticles.

The elemental composition and distribution in the prepared samples were also investigated to confirm the morphology of the synthesized materials. Elemental mapping of the samples is presented in Fig. 4. The high purity of g-C₃N₄, CeO₂ and Fe₂O₃ nanoparticles was confirmed in the respective samples. Similar results were found in the case of GC5 and GCF1 which not only displayed the high purity but also showed the homogeneous distribution of elements within the composites. The surface area determinations of the nanocomposite
photocatalysts exhibited a higher surface area for bulk g-C3N4 i.e., 17.421 m²·g⁻¹, CeO2, and 5% CeO2 exhibited surface area of 30.229 and 29.444 m²·g⁻¹, respectively confirming the incorporation of CeO2 within the g-C3N4 matrix.

The amplified Raman spectra of the synthesized nanocomposite series is provided in Fig. 5. The peak located 1485 cm⁻¹ arises from the vibration modes of CN clearly visible in all the composite samples including GC and GCF (1–10), signifying that there was no phase change during the composite formation might be due to CeO2 and Fe₃O₄ which is in complete agreement with the XRD results. A series of modes could be detected in the amplified Raman spectrum of GCF1 including the D and G band located around 1405 cm⁻¹ and 1570 cm⁻¹ respectively. The peaks corresponding to the CH₃ bending (scissor deformation, 1449 cm⁻¹) from amide δ N–H deformation (1544 cm⁻¹), and amide 1 C=O stretching (1646 cm⁻¹) are characteristic of g-C₃N₄.

**Chemical characterization.** High resolution (HR) XPS investigations identified the oxidation states of complete series of samples. To understand the photocatalytic activity, here we have presented the XPS data of GCF1 and GCF5 samples. The atomic percentage of C (38.92%), O (7.69%), Ce (0.76%), N (50.69%), Fe (1.94%) were obtained from XPS measurement. Similarly the measured atomic parentage values of C (35.57%), O (19.72%), Ce (1.09%), N (34.79%), Fe (8.84%) were obtained for GCF5 sample. The presence of higher oxygen content may be due to the surface oxidation by adsorption of environmental oxygen species on the surface of samples. The Fig. 6(a,b) presented C-1s HR-XPS for GCF1 and GCF5 composites nanosheets, respectively. We found a higher intensity peak located at 288.18 eV corresponds to sp²-bonded carbon (C-N-C) in GCF1 surface of samples. The peaks corresponding to the CH₃ bending (scissor deformation, 1449 cm⁻¹) from amide 2 N–H deformation (1544 cm⁻¹), and amide 1 C=O stretching (1646 cm⁻¹) are characteristic of g-C₃N₄.

**Diffuse reflectance and photoluminescence studies.** Figure 7(a) shows the DRS of g-C₃N₄, CeO₂, GC5 and GCF1. For band gap calculation \((F(R) \propto hν)^2\) and \((F(R) \propto hν)^{1/2}\) vs. \(hν\) were plotted the indirect energy band gaps of g-C₃N₄, CeO₂, GC5 and GCF1. From the plot the band gap energy \(E_g\) was determined from the linear region of the plot on x-axis. The inset shows the reflectance band edges corresponding to band gap energies of 2.68 eV, 2.82 eV, 2.62 eV and 2.45 eV for g-C₃N₄, CeO₂, GC5 and GCF1, respectively. The second band edge in GCF1 corresponding to \(E_g\) 1.84 eV may represent Fe₃O₄ as reported in literature. These results suggest that GCF1 is an indirect band gap semiconductor. The RT-PL spectra (@ λ = 325 nm) for the pristine g-C₃N₄,
Figure 4. Elemental mapping of prepared pristine and nanocomposite photocatalysts.

Figure 5. Resolved Raman Spectra of –gC₃N₄ nanosheets composite series.
binary GC5 and ternary GCF1 nanosheet samples are presented in Fig. 7(b–e), respectively. We noticed that bare g-C3N4 and hybrid nanosheets exhibit intense emission PL spectra as compared to pristine CeO2 nanosheets. The diminishing in emission peak strength for binary and ternary nanocomposites is due to restrained e−/h+ recombination within the g-C3N4/CeO2 and g-C3N4/CeO2/Fe3O4 heterojunctions, which further indicate a successful charge separation. The FWHM of binary nanocomposite samples was less than pure g-C3N4 while the ternary nanocomposite samples the case was reverse. The variation in the values of FWHM may be due to the variable defects concentration in each sample. Consequently, the data was deconvoluted into three fitted peaks for bare, binary and ternary nanosheets samples. These fitted peaks with varied peak positions were assigned names peak-1, peak-2 and peak-3 as illustrated in Fig. 7(b,d,e). Gaussian fitting of PL emission bands reflects the different type of possible defects in each sample. Figure 7(b) evidenced for the line profile investigation of the g-C3N4 sample, which includes the emission center peak-1 (454 nm, 2.73 eV), peak-2 (500 nm, 2.48 eV) and peak-3 (542 nm, 2.28 eV). Similarly, the central emission of peak-1 for binary sample (442 nm, 2.80 eV) and ternary sample (436 nm, 2.84 eV) indicates clearer variation in band gap.

DFT- geometry and electronic structure of binary and ternary nanocomposites. Geometry and electronic structure of Ce- g/C3N4 monolayer. The optimized geometry of Ce- g/C3N4 monolayer shown in the Fig. 8(a). It is found that the Ce atom preferred to locate on Hollow site of g-C3N4 monolayer is bonded with three Nitrogen atom with the bond distance of Fe-N (2.23 Å) and (2.21 Å), respectively. The Fig. 8i(b) shows the charge density differences of Ce-g-C3N4 monolayer, which shows the significant charge density accumulation and depletion region between the Ce atom and its neighboring nitrogen atoms. To clearly understand the electronic

Figure 6. High resolution XPS spectra of GCF1 vs GCF5 (a,b) C-1s, (c,d) N-1s, (e,f) Ce-3d, and (g,h) Fe-2p peaks.
structure, Fig. 8i(c) demonstrates the partial density of states (PDOS) of Ce-g-C3N4 monolayer. Figure 8i(a) also depicts that strong interaction between Ce and N atoms. Further confirmed by overlapping peaks of Ce-4f, 6s and N-2p orbitals near to the fermi level suggests, higher reactivity of Ce-g/C3N4 monolayer.

Geometry and electronic structure of CeO2 doped on g/C3N4 monolayer.

Figure 8ii(a) illustrates the most energetically preferred adsorption complex of CeO2 on g-C3N4 monolayer. The bond distance between the Ce-O is 2.00 Å and 1.97 Å respectively. The bond distance of O-O is slightly elongated from 1.23 (Free O2) to 1.48 Å due to the charge transfer from Ce to O2 and activate the O2 molecule. The Fig. 8ii(b) shows the charge density differences of CeO2 doped on graphitic carbon nitride (g/C3N4) monolayer. The charge density transfers occur from the Ce 4f, 6s orbitals to 2π* antibonding orbitals of O. The Fig. 8ii(c) displays the PDOS curves of the CeO2 adsorption on the g-C3N4 monolayer. The strong mixing observed between 4f and 6s orbitals of Ce and 2π* orbitals of O and N near to the fermi level can be clearly seen, which is the significant wreaking of the O-O bond distance and strong binding of CeO2 with g-C3N4.

Geometry and electronic structure of Fe3O4 doped on Ce-g-C3N4 monolayer.

The most stable adsorption configuration of Fe3O4 doped on Ce-g-C3N4 monolayer shown in Fig. 8iii(a). The observed Ce-O bond length is (2.02 Å and 2.02 Å) and the O-Fe is (1.83 Å, 1.83 Å and 1.62 Å) respectively. The Fig. 8iii(b) shows the charge density differences of Fe3O4 doped on Ce-graphitic carbon nitride (g/C3N4) monolayer. The charge density transfers occur from the Ce 4f, 6s orbitals to 2π* antibonding orbitals of O. Figure shows the charge density accumulation and depletion region between the Ce atom and its neighboring oxygen atoms. The Fig. 8iii(c) shows the partial density of state (PDOS) curves of the Fe3O4 doped on Ce-g-C3N4 monolayer. The strong mixing observed between the 3d orbitals of Fe, 4f and 6s orbitals of Ce and 2π* orbitals of O near to the fermi level can be clearly seen. Furthermore, the strong interaction between the Fe, Ce and O atoms are confirmed by the overlapping peaks near to the fermi level. The fermi level is set to be zero.

Photocatalysis of 2-CP.

The photocatalytic degradation of 2-CP under direct sunlight using pristine and modified binary and ternary nanocomposite photocatalysts was investigated as shown in Fig. 9. The photocatalytic experiments evidenced rapid increase in the degradation of 2-CP by using 5% g-C3N4/CeO2 (GC5) as compare to other pristine components and binary nanocomposites. Further increase in the CeO2 content up to 7%, manifested lowering the photocatalytic degradation efficiency signifying light absorption hindrance effect due to excessive CeO2 content. Excessive CeO2 content was also harmful for the efficient electron hole separation.
Figure 8. (i) Single Ce atom, (ii) CeO₂ and (iii) Fe₃O₄ doped on graphitic carbon nitride (g/C₃N₄) monolayer. (a) Optimized geometry. (b) Charge density differences, for the contour plots, the charge accumulation regions are rendered in green. The contour value of the charge difference density is ±0.05 a.u. and (c) The spin-polarized partial density of states (PDOS) projected on TDOS (black), C-2s (black) and C-2p (red), N-2s (black) and N-2p (red), Ce-6s (black) and Ce-4f (cyan), O-2s (black) and O-2p (red) and Fe-4s (black), Fe-4p (red) and Fe-3d (blue) states. The Fermi level is set to zero.

Figure 9. Photocatalytic 2-CP degradation using pristine and modified nanomaterials.
and decreased the active sites on the nanocomposite. Therefore, further catalyst modifications with Fe₃O₄ were carried upon GC₅.

Figure 9 also showed that among all the ternary nanocomposites, highest degradation of 2-CP was achieved upon using g-C₃N₄(0.94)/CeO₂(0.05)/Fe₃O₄(0.01 i.e., GCF₁ and the degradation efficiency decreased as the Fe₃O₄ percentage increased from 1–10%. Increased amount of Fe₃O₄ might have acted as a recombination centre for the photo-generated e⁻/h⁺ which ultimately decreased the photocatalytic efficiency of the nanocomposites. Enhanced photocatalysis of pristine g-C₃N₄ by modifying its surface with CeO₂ and Fe₃O₄ can be explained firstly as the addition of CeO₂ and Fe₃O₄ leads to modify the colour of this material, leading to the improved harvesting of visible light region as shown in UV-Vis DRS. Secondly, formation of semiconductor-semiconductor heterojunction of g-C₃N₄ with other semiconductors components resulted in effective electron hole separation in the nanocomposite and increased generation of oxidant species for the degradation of 2-CP.

Figure 10(a) shows the results in terms of 2-CP degradation as a function of irradiation time. Degradation efficiency showed considerable decline with increasing 2-CP concentration up to 75 mg L⁻¹. Highest degradation at 25 mg L⁻¹ was achieved due to availability of higher surface area per unit 2-CP molecules at lower pollutant concentration. Upon increase in 2-CP concentration the number of pollutant molecules increased while the number of catalyst active sits for pollutant attachment remained constant thus decreasing the overall degradation efficiency. Increase in pollutant concentration not only decreased the surface area of photocatalyst but also restrained the light utilization by the photocatalyst for the generation of reactive species like hydroxyl radicals. Catalyst dose is one of the most important factors which significantly affects the degradation efficiency of photocatalytic process. A series of experiments were conducted by using varied amounts of GCF₁ (from 0.5–2 g.L⁻¹) over constant 2-CP concentration of 50 mg.L⁻¹. From Fig. 10(b), it is evident that enhanced photocatalytic activity was achieved with increase in catalyst dose from 0.5–1.5 g.L⁻¹ as increased catalyst dose enhances the number of active sit which results in generation of more reactive red-ox species. But as we move from 1.5–2 g.L⁻¹ catalyst dose, the degradation efficiency clearly decreased owing to the light screening effect of the additional catalyst dose which reduces the surface area of photocatalyst for light illumination, in turn reducing the degradation efficiency of the photocatalyst. Figure 10(c) illustrates reduction in GCF₁ photocatalysis of 50 mg.L⁻¹ 2-CP with increase in pH. The degradation rate at pH 3 and 4 was low due to the competition between the 2-CP molecules and excess Cl⁻ ions (from HCl used to adjust the pH). On the contrary, lower degradation rate at basic conditions could be the result of electrostatic repulsion between the negatively charge GCF₁ (pHzpc = 6.9) and phenolate ions. This decreases the adsorption of 2-CP molecules on the surface of the catalyst and negatively affects the degradation rate. To evaluate stability of nanocomposites additional runs of 2-CP degradation (25 mg.L⁻¹)
were conducted at optimum conditions. Figure 10(d) illustrates the degradation efficiency of reused catalyst in three successive runs. The photocatalytic degradation efficiency of GCF1 declined ordinarily after the second and third reuse of the photocatalyst with only 8% reduction in the photocatalytic efficiency. However, only 8% loss in activity after three time use and in absence of any regeneration procedure is a testament of catalyst stability and retention of high catalytic activity.

Photocatalytic degradation of 2-CP is evaluated with first order, second order and zero order reaction kinetics.60,61. Basic relationships of these equations are given below in respective order:

\[ \ln \left( \frac{C_0}{C} \right) = kt \]  

(2)

\[ \frac{1}{C} = \frac{1}{C_0} + kt \]

(3)

\[ C_0 - C = kt \]

(4)

Here, \( C_0 \) = 2-CP (initial concentration), \( C \) = 2-CP (residual concentration after solar exposure time ‘t’ (min)) while k is rate constant (min\(^{-1}\)) of respective equations.

Kinetic plot for first order ('ln (C_0/C)' vs time), second order equation (1/C vs time) and zero order equations (C_0-C vs time) at variable reaction parameters demonstrated that the ternary nanocomposite followed pseudo first-order reaction kinetics with 2.55 and 4.04 times increased rate of reactions compared to pristine Fe\(_3\)O\(_4\) and CeO\(_2\), with highest rate constant value of 18.2 min\(^{-1}\).

Table 1. Kinetic constant values explaining the effect of catalyst dose, pH and 2-CP concentration over ternary nanocomposite GCF1. *(Catalyst dosage: 1 g L\(^{-1}\), Solution pH = 5). *(2-CP initial concentration: 50 mg L\(^{-1}\); Catalyst dosage: 1 g L\(^{-1}\)). *(2-CP = 50 mg L\(^{-1}\), pH = 5).
can react with the ubiquitous molecular oxygen to form the superoxide radical $\cdot O_2^-$, which can contribute to the decomposition of 2-CP while the photo generated $h^+$ oxidize $H_2O$ and $OH^-$ ion into free $•OH$ radicals\textsuperscript{41,42}. Finally, 2-CP molecules are degraded by the holes, superoxide radicals and hydroxyl radicals.

The gas chromatographic analysis of optimized photocatalytic study complementing our findings are provided in Fig. 11(c). The degradation of 2-CP can be clearly visualized through decline in the GC peak intensity at retention time 8.31 min. From the results it can be seen that phenol, catechol and hydroquinone were formed as intermediate products during the degradation process by hydroxylation and de-halogenations mechanisms proposed in similar studies\textsuperscript{63-65}. However at later stages of the photocatalytic process (at time 150 min) the intermediate species disappear indicating their mineralization along with 2-CP and complete mineralization at 180 min.

Conclusions

Novel g-C$_3$N$_4$ based magnetically separable and visible light active ternary composite nanosheets for photocatalysis of 2-CP polluted water is reported. TEM imaging showed that the GCF nanocomposite exhibited high purity and crystallinity with uniform dispersion of CeO$_2$ and Fe$_3$O$_4$ nanoparticles over g-C$_3$N$_4$ nanosheets. The DFT predicted charge density transfers occur from the Ce 4f, 5s orbitals to 2$\pi^*$ antibonding orbitals of O and N. The PDOS curves of Fe$_3$O$_4$ doped on g-C$_3$N$_4$/CeO$_2$ monolayer suggested strong interaction between Fe, Ce and O atoms confirmed by the overlapping peaks near to the fermi level which favor the photocatalytic reactions over the nanocomposite. The XRD and XPS determinations supported the existence of Fe$_3$O$_4$ in the composite as the dominant crystalline structure and the obtained GCF1 nanocomposite showed excellent visible light photocatalytic activity towards 2-CP breakdown at concentrations from 25–75 mg.L$^{-1}$. Complete mineralization was observed within 180 min of sun light exposure with highest rate constant value of $18.2 \times 10^{-3}$ min$^{-1}$. The catalyst showed high stability over extreme pH conditions and repeatability test showed that GCF1 retained 92.5% activity after three times reuse confirming the robustness of the photocatalysts system. In comparison, pristine g-C$_3$N$_4$, CeO$_2$, Fe$_3$O$_4$ and all other binary and ternary nanocomposites synthesized, best photocatalytic performance was obtained by using GCF1. The GCF1 catalyst also exhibited very swift reaction rate with rate constant value of $60 \times 10^{-4}$ min$^{-1}$ and regression co-efficient value of 0.9991 at pH 5. This study describes an easy fabrication of novel ternary composite and provides an innovative solution for the treatment of 2-CP contaminated wastewater with an additional advantage of easy recovery and reusability simply through applying a weak external magnetic field.

Figure 11. (a) UV-Visible absorption spectra of 2-CP degradation over GCF1. (b) Influence of reactive species scavenging on photocatalytic activity; (c) GC Analysis results.
42. Gea, W. et al. Graphene oxide template-confined fabrication of hierarchical porous carbons derived from lignin for ultrahigh-efficiency and fast removal of ciprofloxacin. J. Ind. Eng. Chem. 66, 456–467 (2018).
43. Akhundi, M. & Yangjeh, A. H. Ternary magnetic g-C3N4/Fe3O4/Ag nanocomposites: Novel recyclable photocatalysts with enhanced activity in degradation of different pollutants under visible light. Mater. Chem. Phys. 174, 59–69 (2016).
44. Yangjeh, A. H. & Akhundi, M. A. Novel ternary g-C3N4/Fe3O4/Ag, CrO3 nanocomposites: magnetically separable and visible-light driven photocatalysts for degradation of water pollutants. J. Mol. Catal. A-Chem. 415, 122–130 (2016).
45. Moussavi, M. & Yangjeh, A. H. Magnetically separable ternary g-C3N4/Fe3O4/BiO3 nanocomposites: novel visible-light-driven photocatalysts based on graphic carbon nitride. J. Colloid. Interf. Sci. 465, 83–92 (2016).
46. Zhang, L. et al. Facile synthesis of phosphorus doped graphic carbon nitride polymers with enhanced visible-light photocatalytic activity. Mater. Res. Bull. 48, 3485–3491 (2013).
47. Zhang, W., Zhang, Q., Dong, F. & Zhao, Z. The multiple effects of precursors on the properties of polymeric carbon nitride. Int. J. Photoenergy 2013, 685038 (2013).
48. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. B. 38, 7657–7677 (1988).
49. Ou, M., Zhong, Q., Zhang, S. & Yu, L. Ultrasound assisted synthesis of heterogeneous g-C3N4/BiVO4 composites and their visible-light-driven photocatalytic activity. J. Photochem. Photobiol. A-Chem. 309, 34–40 (2016).
50. Hu, X. Y., Fan, J., Zhang, K. L. & Wang, J. J. Photocatalytic removal of organic pollutants in aqueous solution by Bi4NbxTa (1-x)O3, J. Alloy. Compd. 626, 401–409 (2015).
51. Huang, L. et al. Synthesis and characterization of g-C3N4/Fe3O4/SiO2 nanocatalyst with enhanced visible-light photoactivity. Appl. Surf. Sci. 283, 25–32 (2013).
52. Dong, G., Zhang, Y., Pan, Q. & Qiu, J. A fantastic graphic carbon nitride (g-C3N4) material: electronic structure, photocatalytic and photoelectronic properties. J. Photoch. Photobiol. 20, 33–50 (2014).
53. Yuan, X. et al. Facile Synthesis of g-C3N4/Ni3O4 nanocomposites with enhanced photocatalytic activity in reduction of aqueous chromium(VI) under visible light. Nanomaterials 6, 173 (2016).
54. Tang, X., Nia, L., Han, J. & Wang, Y. Preparation and characterization of ternary magnetic g-C3N4 composite photocatalysts for removal of tetracycline under visible light. Chinese J. Catal. 38, 447–457 (2017).
55. Zhong, P., Ma, W. & Li, W. Construction of a magnetic Z-scheme photocatalyst with enhanced oxidation/reduction abilities and recyclability for the degradation of tetracycline. RSC Adv. 115, 114374–114382 (2016).
56. Hsu, L. J., Lee, L. T. & Lin, C. C. Adsorption and photocatalytic degradation of polyvinyl alcohol in aqueous solutions using P-25 TiO2, Chem. Eng. J. 173, 698–705 (2011).
57. Hu, X. Y., Fan, J., Zhang, K. L. & Wang, J. J. Photocatalytic removal of organic pollutants in aqueous solution by Bi4NbxTa (1-x)O3, Sci. Total Environ. 87, 1155–1160 (2012).
58. Rashid, J., Barakat, M. A., Ruzmanova, Y. & Chianese, A. Facile Synthesis of g-C3N4/Ni3O4 Nanosheets/ZnO nanocomposites for photocatalytic degradation of 2-Chlorophenol in simulated wastewater. Environ. Sci. Pollut. R. 22, 3149–3157 (2015).
59. Gao, D., Liu, Y., Liu, P., Si, M. & Xu, D. Atomically thin B doped g-C3N4 Nanosheets: high-temperature ferromagnetism and calculated half-metallicity. Sci. Rep. 6, 35768 (2016).
60. Gea, W. et al. Graphene oxide template-confined fabrication of hierarchical porous carbons derived from lignin for ultrahigh-efficiency and fast removal of ciprofloxacin. J. Ind. Eng. Chem. 66, 456–467 (2018).
61. Akhundi, M. & Yangjeh, A. H. Ternary magnetic g-C3N4/Fe3O4/Ag nanocomposites: Novel recyclable photocatalysts with enhanced activity in degradation of different pollutants under visible light. Mater. Chem. Phys. 174, 59–69 (2016).
62. Zhang, W., Zhang, Q., Dong, F. & Zhao, Z. The multiple effects of precursors on the properties of polymeric carbon nitride. Int. J. Photoenergy 2013, 685038 (2013).
63. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. B. 38, 3686–3688 (1996).
64. Ou, M., Zhong, Q., Zhang, S. & Yu, L. Ultrasound assisted synthesis of heterogeneous g-C3N4/BiVO4 composites and their visible-light-induced photocatalytic oxidation of NO in gas phase. J. Alloy. Compd. 626, 401–409 (2015).
65. Huang, L. et al. Synthesis and characterization of g-C3N4/Fe3O4 photocatalyst with improved visible-light photoactivity. Appl. Surf. Sci. 283, 25–32 (2013).
66. Dong, G., Zhang, Y., Pan, Q. & Qiu, J. A fantastic graphic carbon nitride (g-C3N4) material: electronic structure, photocatalytic and photoelectronic properties. J. Photoch. Photobiol. 20, 33–50 (2014).
67. Yuan, X. et al. Facile Synthesis of g-C3N4/Ni3O4 Nanosheets/ZnO nanocomposites with enhanced photocatalytic activity in reduction of aqueous chromium(VI) under visible light. Nanomaterials 6, 173 (2016).
68. Tang, X., Nia, L., Han, J. & Wang, Y. Preparation and characterization of ternary magnetic g-C3N4 composite photocatalysts for removal of tetracycline under visible light. Chinese J. Catal. 38, 447–457 (2017).
69. Zhong, P., Ma, W. & Li, W. Construction of a magnetic Z-scheme photocatalyst with enhanced oxidation/reduction abilities and recyclability for the degradation of tetracycline. RSC Adv. 115, 114374–114382 (2016).
70. Hsu, L. J., Lee, L. T. & Lin, C. C. Adsorption and photocatalytic degradation of polyvinyl alcohol in aqueous solutions using P-25 TiO2, Chem. Eng. J. 173, 698–705 (2011).
71. Hu, X. Y., Fan, J., Zhang, K. L. & Wang, J. J. Photocatalytic removal of organic pollutants in aqueous solution by Bi4NbxTa (1-x)O3, Chem. Phys. Lett. 87, 1155–1160 (2012).
72. Rashid, J., Barakat, M. A., Ruzmanova, Y. & Chianese, A. Facile Synthesis of g-C3N4/Ni3O4 Nanosheets/ZnO nanocomposites for photocatalytic degradation of 2-Chlorophenol in simulated wastewater. Environ. Sci. Pollut. R. 22, 3149–3157 (2015).
73. Gao, D., Liu, Y., Liu, P., Si, M. & Xu, D. Atomically thin B doped g-C3N4 Nanosheets: high-temperature ferromagnetism and calculated half-metallicity. Sci. Rep. 6, 35768 (2016).
74. Gaya, U. I., Abdullah, A. H., Zainal, Z. & Hussein, M. Z. Photocatalytic treatment of 4-chlorophenol in aqueous ZnO suspensions: Intermediates, influence of dosage and inorganic anions. J. Hazard. Mater. 166, 57–63 (2009).
75. Shen, Q. et al. Facile synthesis of catalytically active CeO2 for soot combustion. Catal. Sci. Technol. 5, 1941–1952 (2015).
76. Qiao, F., Wang, J., Ai, S. & Li, J. A new peroxidase mimetics: The synthesis of selenium doped graphic carbon nitride nanosheets and applications on colorimetric detection of H2O2 and xanthine. Sensor. Actuat. B-Chem. 216, 418–427 (2015).

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Author Contributions
Jamshaid Rashid: Supervised, advised lab work, analyzed the data and wrote the manuscript. Nadia Parveen: Performed the synthesis and lab work with data analyses. Aneela Iqbal: performed data analysis and wrote the manuscript. Saif Ullah Awan and Naseem Iqbal: performed G.C., S.E.M. and E.D.A.X. analysis. Shamraiz Hussain Talib: performed the DFT measurements. Naveed Hussain: performed the XPS analysis. Bilal Akram: performed TEM analysis. Ata Ullahq and Bilal Ahmed: performed the Raman spectroscopy. Ming Xu co-advised the characterization and data analysis.

Additional Information
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