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Investigation of heterojunction between α -Fe₂O₃/V₂O₅ and g-C₃N₄ ternary nanocomposites for upgraded photo-degradation performance of mixed pollutants: Efficient dual Z-scheme mechanism

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Abstract

In this present work, a g-C₃N₄ decorated dual Z-scheme α -Fe₂O₃ and V₂O₅ heterojunction of magnetically recoverable GFV (g-C₃N₄/ α -Fe₂O₃/V₂O₅) composite was rationally synthesized using facile calcination and hydrothermal approach. The crystal structure, surface morphology, chemical composition and optical properties of the as-obtained composite photocatalysts (PCs) were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra high-resolution scanning electron microscopy (HR-SEM, high-resolution transmission electron microscopy (HR-TEM), X-ray

photoelectron spectroscopy (XPS) measurement, UV-Vis diffuse reflectance spectra (DRS) and photoluminescence (PL) analyses respectively. Benefiting from these structural and compositional features, the optimum GFV heterostructured PCs sample revealed that the superior photo-degradation performance of methyl yellow (MY) and methylene blue (MB) mixed dye under visible-light, while the degradation rates were 93.4 % for MY and 87.5 % for MB dye at 90 min, respectively. Moreover, the enhanced photo-degradation performance of GFV composite PCs displayed an extended visible-light fascination due to lower bandgap, reduced recombination rates, high charge separation and good charge transfer capacity with the efficient dual Z-scheme heterojunction. Meanwhile, high photo-degradation stability is continued after five successive reusability tests. A possible photo-degradation mechanism of dual Z-scheme charge transfer paths was also been proposed. This study is also capable of emerging visible-light active facile heterojunction photocatalysts for various organic pollutants removal with great efficiency.

Keywords: g-C₃N₄/α-Fe₂O₃/V₂O₅; Nanocomposites; Visible-light; Mixed dye; Magnetic separable; Z-Scheme;

1. Introduction

The fast industrialization and anthropogenic activities have caused negative impacts on the ecosystem by severe environmental pollution. With continuing water quality weakening, several renewable and greener approach for the effective removal of emergent toxic impurities has been explored by various researchers. Industrial wastewater regularly comprises abundant organic contaminants and heavy metals, while has become a threat to the environment [1]. It was assessed that about 10-15 % carcinogenic and mutagenic dye molecules are released into the aquatic system from various industries, which are liable for producing serious human illnesses such as cancer, lung diseases etc., [2] Since, a wide array of bright shades as well as the strong ability to bind with cloths fabrics, the azo dyes consuming a toxic azo group (-N=N-) are broadly used in these various industries [3]. Among these several approaches, the promising semiconductor-based green photocatalytic technology utilizing sun-light and/or visible-light energy has wide prospects for resolving the above problems and environmental crisis, which is essential for practical and large-scale utilization [4]. However, the UV region signifies only 4-6 % of the solar-light spectrum, whereas the visible-light region occupies up to ~45 % of the entire solar spectrum region [5]. Exclusively, the application of photocatalytic technology in photo-oxidation for various industrial dyes will convey more positive suggestions to ecological refinement [6].

Graphitic carbon nitride (g-C₃N₄) as a metal-free conjugated polymer has been described as the most common photocatalyst for environmental cleaning and energy-related application. It has a great semiconductor with a suitable optical energy bandgap (E_g) of ~2.7 eV which displays excellent properties due to its good thermal-chemical stability, optical and electronic features as of tri-s-triazine based structure blocks and is used as visible-light reactive photocatalyst [7,8]. In contrast, the many drawbacks, with speed charge recombination rate and poor visible-light fascination ability, while the limit of its photocatalytic better performance. Still, single-phase semiconductor photocatalysts (PCs) suffer from severe limits on their photocatalytic performance, including limited sun-light as well as visible-light utilization, with low quantum yield and high charge carrier recombination rate [9] respectively. These limits have been efficiently addressed by the formation of heterojunction structures by different semiconductors (SCs) with optimal bandgap and electronic band alignment for supreme optical absorption and energetic electronic interfaces [10]. Effective metal-oxides as α -Fe₂O₃ have been united to form Fe₂O₃/g-C₃N₄ nanostructures with rapid photo-excited charge transfer, less recombination rates and strong redox ability [11]. Owing to its narrow-bandgap (~2.0 eV), good stability, outstanding visible-light absorbing ability, promising magnetism, low-cost, non-toxicity and simply recovered by external magnetic field over the resultant photocatalyst from the treated solution [12,13]. Various Z-scheme heterojunctions utilizing g-C₃N₄ such as g-C₃N₄/LaFeO₃ [9], Ag₃PO₄/p-g-C₃N₄ [14,15], MoO₃/g-C₃N₄ [16], g-C₃N₄/MnO₂ [7], g-C₃N₄/CoFe₂O₄ [17], CaTiO₃/g-C₃N₄/AgBr [8], g-C₃N₄/rGO/Bi₂WO₆ [18], CeO₂/g-C₃N₄/Bi₂O₃ [19] and g-C₃N₄/Ag/MoS₂ composites have been prepared with several enhanced photocatalytic performance. The synergistic performance of the SCs involved in a heterostructure that involving with two SCs is extremely valuable for outstanding photo-reduction and photo-oxidation of various organic impurities [8,19].

The Z-scheme heterojunction PCs originate their efficient charge transfer and/or separation mechanism for accelerating the photo-excited electrons and holes (e^-/h^+) [17]. In the Z-scheme transfer paths, not only recombination rate has inhibited, but also could preserve the worthy redox ability, with more negative conduction band (CB) and positive valance band (VB) edge potential is sustained for active produces of radical species [18,20]. Moreover, the introduction of a third counterpart semiconductor is encouraging, as this raises the photocatalytic performance by agreeing to a double Z-scheme charge transfer mechanism. Very recently, a novel dual Z-scheme charge transfer system, including two visible-light reactive solid-state PCs with two charge transmission networks are probably efficient

photocatalytic activity [21,22]. Along with the close interfacial interfaces, the photo-excited electrons (e^-) on the components are transported to the other two components, leading to vastly improved charge separation, which is a favourite for upgraded photocatalytic performance [23,24]. Hence, the extremely placed CB edges of two components could make the sufficient superoxide ($\bullet O_2^-$) radicals, and more hydroxyl ($OH\bullet$) radicals were created via the VB. In this photo-reaction, the photo-excited $\bullet O_2^-$, and $OH\bullet$ radical species can straightly decompose with organic contaminants to harmless molecules such as H_2O , CO_2 , Cl^- and NO_3^- etc., [25]. Compared with various SCs, the vanadium pentoxide (V_2O_5) is an important transition metal-oxide semiconductor with an effective environmental catalyst owing to its low-cost and less toxicity nature [26]. Also, the V_2O_5 has extensive properties, such as typical lesser bandgap energy (2.2 eV), great chemical stability, good visible-light capturing ability owing to its outstanding properties [27]. Also, it possesses a very efficient electron transport capacity, which leads to rapid transfer of photo-excited e^-/h^+ pair's to the catalyst surface, which may be enhanced by suppressing the charge recombination rate and also it's suitable for Z-scheme based photocatalytic hetero-systems [28]. Hence, the mechanistic way to improve the photocatalytic performance has been explained based on dual Z-scheme charge carrier in the assessment by efficient heterojunction formation with strong reducibility and oxidizability, respectively [29].

In the existing work, we have successfully fabricated with effective dual Z-scheme $g-C_3N_4/\alpha-Fe_2O_3/V_2O_5$ composite heterostructure PCs by facile calcination and hydrothermal approach. Magnetic PCs are beneficial for originating separation problems from the photocatalytic reaction mixture [30]. Magnetically recoverable GFV composites were thus anticipated as an active PCs for the photo-degradation performance of MY and MB mixed organic dye molecules in the aqueous system under visible-light exposure. Both dye molecules are high-toxic and colouring textile, ink, paper, and pharmaceutical productions, etc., Additionally, these ternary GFV heterostructure junction composite exhibits admirable charge separation, hindered the rapid recombination rate, synergistic interfacial effect and suitable band edge potential by dual Z-scheme transfer ability, which improving the photocatalytic enhancement [24]. Also, $\alpha-Fe_2O_3$ and V_2O_5 are visible-light responsive short bandgap (2 and 2.2 eV relatively) SCs, both are liable for the efficient photo-degradation of these dye molecules based on novel dual Z-scheme constructed $g-C_3N_4$ photo-degradation system. Likewise, the low CB bottom level of $\alpha-Fe_2O_3$ agrees to the photo-excited e^- by the fewer energies, which is proficient for constructing photo-reduction reactions with adsorbed O_2 , H_2O , and CO_2 . Also, the consistent photo-degradation mechanism is projected. Moreover,

the optimum GFV composite sample revealed the optimal photo-degradation action also influenced as outstanding stability after five successive recycling.

2. Experimental section

2.1 Materials

Melamine ($C_3H_6N_6$, 99 %; A.R.), ethanol (CH_3CH_2OH , 99 %; A.R.), ammonia ((NH_3) (aq.), 99 %; A.R.), and ethylene glycol ($C_2H_6O_2$, 99 %; A.R.) were supplied from Merck Chemical Reagent Co. Pvt. Ltd. Ferrous chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98.5 %, A.R.) and ammonium metavanadate (NH_4VO_3 , 98 %, A.R.) were bought from the Alfa Aesar Chemical Reagent Co. Pvt. Ltd. All the chemical reagents were directly used without further refining processing. Deionized (D.I.) water was used in the entire experiment.

2.2 Photocatalysts synthesis

The $g-C_3N_4$ was prepared by facile thermal calcination of melamine. 10 g of melamine was calcined at 550 °C for 2 h in a silica crucible. The yellowish bulk $g-C_3N_4$ nanopowder was then centrifugal washed with ethanol and D.I. water repeatedly and then dried at 80 °C [20]. In a typical mixture, 100 mg of as-synthesized $g-C_3N_4$ was dispersed into 20 mL D.I. water, with protonation by typical acid treatment process to get sheet-like $g-C_3N_4$ [28,31].

2.3 Synthesis of $g-C_3N_4/\alpha-Fe_2O_3/V_2O_5$ (GFV) nanocomposite

Synthesis of V_2O_5 : In the typical process, 0.58 g of NH_4VO_3 was added with 30 mL of ethylene glycol. The resultant mixture was then heated to 100 °C with constant stirring followed to transferred into Teflon-lined stainless autoclave at 160 °C for 4 h, hence the resultant precipitate was obtained and dried at 80 °C overnight [26,32].

Synthesis of $g-C_3N_4/\alpha-Fe_2O_3/V_2O_5$ nanocomposite: To fabricate a ternary $g-C_3N_4/\alpha-Fe_2O_3/V_2O_5$ sample, the 0.5 g of $g-C_3N_4$, 0.81 g of $FeCl_3 \cdot 6H_2O$ and 0.1 g of as-prepared vanadium-based precipitate were dissolved into 60 mL of mixed D.I water and ethanol absolute solution by continuous stirring at 60 °C for 5 h. The pH of the above-mentioned suspension was tuned at 9-10 using ammonia (aq.) solution, hence to grow a FeOOH modified $g-C_3N_4/V_2O_5$ homogeneous mixture [10,33]. Thus, the resultant suspension was further moved into 100 mL of Teflon-lined autoclave and 160 °C of heat oven for 12 h. Then it was followed by ultrasonication for 1 h. Also, the as-obtained suspension was allowed to cool and followed by washing repeatedly with D.I. water/ethanol to use a centrifuge and further completely dried overnight at 80 °C [34]. The resultant mixture was then annealed at 500 °C for 2 h, and the $g-C_3N_4/\alpha-Fe_2O_3/V_2O_5$ composite catalyst was formed successfully. The scheme of the synthesis process is signified in Fig. 1. For comparison, the $g-C_3N_4/\alpha-$

Fe_2O_3 and $\text{g-C}_3\text{N}_4/\text{V}_2\text{O}_5$ composites were also synthesized by the aforementioned similar procedure without adding $\alpha\text{-Fe}_2\text{O}_3$ and V_2O_5 sources respectively. The obtained products of pristine $\text{g-C}_3\text{N}_4$, $\text{g-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$, $\text{g-C}_3\text{N}_4/\text{V}_2\text{O}_5$ and the $\text{g-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ composite catalysts were labelled as GCN, GF, GV and GFV respectively.

2.4 Characterization details

The powder X-ray diffraction (XRD) patterns were employed to find the crystalline structure and phase purity of obtained pristine, binary and ternary composite samples. Fourier transform infrared (FT-IR) spectra of all the obtained samples were obtained using the Shimadzu apparatus. The surface morphology and microstructure of the pristine and ternary heterostructures were analyzed by field-emission and high-resolution scanning electron microscopy (HR-SEM; FEI Quanta FEG 200) instrument. The deep nanostructure and shape were analyzed by high-resolution transmission electron microscopy (HR-TEM) using FEI Tecnai G² 20 HR-TEM instrument imaging. The elemental composition and oxidation states were analyzed by high-resolution X-ray photoelectron spectroscopy (XPS) measurement was done by a PHI-VERSAPROBE III tool with a monochromatic X-ray beam. UV-Vis diffuse reflectance spectra (DRS, Lambda 950 PerkinElmer) were employed to illustrate the optical absorption and bandgap (E_g) energy of the catalytic samples. Photoluminescence (PL) spectra of the obtained samples were directed using a Shimadzu Japan at an excitation wavelength (λ_{ex}) of ~320 nm. The magnetic field properties were analyzed by a vibrating sample magnetometer (VSM; Lakeshore VSM 7410S) instrument. The Electrochemical impedance spectroscopy (EIS) measurement was conducted using an electrochemical analyzer with a standard three-electrode configuration by Model-660E, Austin, TX workstation. The glassy carbon electrode was modified with as-obtained samples, a platinum wire and the saturated Ag/AgCl (sat. KCl) were utilized as working, counter and reference electrodes respectively. Besides, in which covering the frequency range of 0.1 Hz to 100 kHz at 10 mV applied AC potential. The 0.1 M KCl solution containing $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ were used as the electrolyte in this system. Thermal stability of the as-obtained samples was performed using thermogravimetric analysis (TGA) with a Perkin Elmer STA 600 analyzer during temperature ranging from 30-800 °C and the heating rate at 10 °C/min in nitrogen (N_2) gas.

Fig. 1. The schematic synthesis route for fabrication $g\text{-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ composite samples

2.5. Evaluation of photocatalytic degradation activity

The photocatalytic performance of the as-obtained catalyst samples was assessed by the photo-degradation of MY and MB mixed aqueous dye mixture as a target pollutant [35], which were carried out in a water-cooled tubular Pyrex reactor. Specifically, for 300 W of xenon lamp by a $\lambda > 420$ nm cut-off filter was being used as a simulated UV-visible light source, which tailored on the top of photo-reactor [36]. Before the light exposure, 50 mg of as-obtained PCs sample was mixed with 100 mL of MY+MB mixed organic dye (30 ppm; 0.01 g dye/L) into every trial. In a characteristic photocatalytic test, the reaction suspension was magnetically stirred in the dark environment for 30 min to achieve the absorption-desorption equilibrium between catalysts and the attained dye molecules [17]. During this visible-light exposure, the 2.5 mL of reaction suspension were tested by centrifugation to eliminate the catalyst nanoparticles (NPs) in certain time intervals (15 mins.). After centrifugal filtered the mixed dye solutions were further monitoring by UV-vis absorption spectra and the variations of absorption wavelength maximum are ~ 460 nm for MY and ~ 664 nm for MB aqueous dye solutions respectively. Besides, the percentage (%) of photo-degradation was assessed by subsequent equation; $\% = C_t/C_0 \times 100$. Whereas, C_0 and C_t are the primary and remaining dye concentrations in the reaction dye mixture at time t [37].

To determine the possible mechanism for the mixed dye photo-degradation reaction, the radical trapping tests were also carried out to the following process [38]. By the different scavengers, with isopropyl alcohol (IPA), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and benzoquinone (BQ) was served as the main scavenging reagents of hydroxyl radical ($\bullet\text{OH}$), holes (h^+), and superoxide radical ($\bullet\text{O}_2^-$) species, respectively [18].

3. Results and discussion

3.1. Powder XRD analysis

Fig. 2. (A) Powder XRD patterns of (a) pristine GCN, (b) $\alpha\text{-Fe}_2\text{O}_3$, (c) V_2O_5 , (d) GF, (e) GV and (f) GFV composite PCs (B) FT-IR spectra of the (a) GCN, (b) GF, (c) GV and (d) GFV samples

Fig. 2(A) illustrates the characteristic XRD patterns of as-obtained (a) pristine GCN, (b) $\alpha\text{-Fe}_2\text{O}_3$, (c) V_2O_5 , (d) GF, (e) GV and (f) GFV composite photocatalysts samples. The XRD pattern for $\text{g-C}_3\text{N}_4$ illustrates the two typical weak and strong peaks at 12.9° and 27.6° conforming to (100) in-plane structural units and the stacking of layers along with (002) planes, respectively (JCPDS Card No. #87-1526) [39]. The XRD pattern for $\alpha\text{-Fe}_2\text{O}_3$ displays (Fig. 2b, d) in the $\text{g-C}_3\text{N}_4/\alpha\text{-Fe}_2\text{O}_3$ sample, the peaks for (102), (104), (110), (113), (202), (024), (116), (214) and (300) diffraction planes corresponding at 25.9° , 33.1° , 35.7° , 40.8° , 43° , 49.4° , 54.1° , 62.4° and 64.1° respectively, which is the existence of rhombohedral crystal structure of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS Card No.#33-0664) [40]. Furthermore, the observed additional peak of 28.9° was may denoted in the hematite phase of Fe_2O_3 NPs respectively. For V_2O_5 the distinctive peaks consist of (200), (001), (101), (301), (002), (411), (600), (020),

and (710) planes of the orthorhombic phase of V_2O_5 nanomaterial phases, which is in good contract with the typical JCPDS Card No. #89-0612 [41]. The XRD pattern of Fig. 2(f) displays that all the diffraction peaks for g- C_3N_4 , α - Fe_2O_3 and V_2O_5 nanomaterials are observed mutually within slight shifts of the position could also detect. In addition, there are no other new impurities crystal phases appeared in all the XRD patterns. This might be attributed to the slight structural adjustments owing to mutual interactions respectively, hence the XRD patterns authorizes that the effective composite formation of heterostructure nature.

3.2 FT-IR spectra analysis

Fig. 2(B) displays the chemical bonds by FT-IR spectra of as-obtained (a) pristine GCN, (b) GF, (c) GV and (d) GFV composite samples respectively. The bands at 3440 and 1386 cm^{-1} are owing to the stretching and bending vibrations of N-H and C-N, correspondingly [4]. Although, those broad bands between 3050-3300 cm^{-1} was associated with the stretching and bending vibration manners of the O-H bonds, which are related to the free adsorbed water (H_2O) molecules, respectively [37]. Moreover, the main distinctive bands recognized at 1660-1250 cm^{-1} region are ascribed to the typical stretching vibration agreeing to C-N-C and C-N heterocycles of the benzene ring and s-triazine modes [34]. Besides, the sharp peak situated at 807 cm^{-1} was allotted to the distinctive breathing mode of the heptazine ring [42]. The characteristic peaks that appeared between 560-671 cm^{-1} are allotted to the symmetric stretching vibrations of Fe-O and V-O-V or V=O bonds in α - Fe_2O_3 and V_2O_5 networks for GFV composites relatively [41,43]. Accordingly, no other impurity peaks were presented in the FT-IR outcomes and also signified the effective construction of α - Fe_2O_3/V_2O_5 over the g- C_3N_4 surface.

3.3 Surface morphologies analysis

Fig. 3 illustrates that the SEM images of as-prepared (a) pristine GCN, (b) α - Fe_2O_3 , (c) V_2O_5 NPs and (d-f) GFV composite PCs. Fig. 3(a) represents the SEM images of obtained pristine g- C_3N_4 , which has several stacking layers structure with crumpled surface morphology, also its recently described in the previous work [44]. From Fig. 3b, α - Fe_2O_3 shows that many irregular spherical shaped NPs structures with flat surfaces. Also, Fig. 3c displays that the SEM image of V_2O_5 exhibits some irregular-shaped NPs morphologies was observed. In this case, GFV composite (Fig. 3(d-f)) displays that the α - Fe_2O_3 and V_2O_5 NPs are uniformly dispersed over these g- C_3N_4 nanosheets [31]. The SEM images (Fig. 3e) specified that the catalyst confined quasi-spherical and plate-like shapes, with irregular-shaped NPs [45]. Besides, the rough surface of the obtained composite was probably owed to the effective polymerization of the wrinkled g- C_3N_4 , after merging with aggregation of α -

Fe_2O_3 and V_2O_5 NPs, which ascribed to the oxide phases caused by the calcination process [42,45]. The corresponding EDX elemental spectrum and the mapping distribution for ternary GFV nanocomposite catalyst could be realized in Fig. 3(g). The reliable atomic percentage (At. %) of the as-obtained nanocomposite is exposed in (inset) Fig. 3(g). All the relative elemental abundance (C, N, O, Fe and V) are uniformly distributed in the GFV nanocomposite, which confirms the successful formation of ternary heterojunction $\alpha\text{-Fe}_2\text{O}_3$ and V_2O_5 NPs on the $\text{g-C}_3\text{N}_4$ surfaces [46].

Fig. 3. SEM images of (a) GCN, (b) $\alpha\text{-Fe}_2\text{O}_3$ NPs, (c) V_2O_5 NPs, (d-f) GFV catalyst composite sample (g) corresponding EDX spectra and the related elemental mapping images of ternary GFV composite

The corresponding deep morphology and nanostructures of the heterostructured composite were further determined via HRTEM analysis. Fig. 4 (a-d) illustrates the $\alpha\text{-Fe}_2\text{O}_3$ and V_2O_5 NPs were uniformly distributed over the $\text{g-C}_3\text{N}_4$ matrix confirming the heterojunction nanostructure, which also intimate interfacial contact with each other [46]. Both higher (Fig. 4 (d, e)) and lower (Fig. 4 (b, c)) magnification of HR-TEM images

exposed that the existence of α - Fe_2O_3 and V_2O_5 NPs (indicated by ring) are highly aggregated [47]. As revealed in Fig. 4a, the interplanar lattice fringe belonging at 0.35 nm, 0.392 nm and 0.301 nm were associated to the (012), (101) and (002) crystal planes of α - Fe_2O_3 , V_2O_5 and g- C_3N_4 crystallites, which is in good agreement with the XRD results. Additionally, the SAED pattern (Fig. 4f) of the GFV composite displays the high crystallinity of the obtained photocatalyst. Meanwhile, the (310), (110) and (002) planes of the SAED pattern were well-recognized to V_2O_5 , α - Fe_2O_3 and g- C_3N_4 nanocrystals for the GFV composite. The above outcomes confirmed that the effective heterostructure formation among oxide phases with g- C_3N_4 on the ternary GFV nanocomposite [45]. The as-obtained ternary GFV catalyst nanocomposite could deliver an improved photocatalytic activity than pristine and binary composite due to mutual unique properties of g- C_3N_4 with heterostructured α - $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ NPs.

Fig. 4. (a-f) HR-TEM images and corresponding (inset) SAED pattern of ternary GFV nanocomposite catalyst

3.4 High-resolution XPS analysis

Fig. 5. High-resolution XPS spectra of (a) survey spectra, (b) C 1s and (c) N 1s of pristine GCN and GFV composite, (d) O 1s (e) Fe 2p, and (f) V 2p elements for the as-obtained GFV composite photocatalyst

The XPS study was further used to investigate the surface chemical composition, electronic environment and oxidation state of the pristine GCN and GFV ternary nanocomposites. The high-resolution survey scan (Fig. 5(a)) of the XPS spectra displays the peaks for all the essential elements, (i.e.,) C and N were presented in the GCN sample. Additionally, O, Fe and vanadium elemental regions were authorized to their existence in the as-obtained GFV composite nanomaterial. As displayed in Fig. 5b, the high-resolution C 1s XPS spectra of the GFV sample. The strong peak at 283.4 eV is can be ascribed to the sp^3 -bonded carbon of the adventitious carbon species. For another strong C 1s peak appears at 286.6 eV which may be consistent with the sp^2 hybridized carbon bonded to N in the aromatic rings (N-C=N) of GCN units [48]. Generally, the C 1s peak originated from the adventitious carbon is may be defined to be 284.8 eV or 284.6 eV, which could change the binding energy caused by the surface charge effect [14,49].

The deconvoluted high-resolution N 1s spectrum of GFV sample is exposed in Fig. 5(c). Although the two typical peaks at 397.3 eV and 398.5 eV correspond to the pyridine N

(sp^2 -hybridized N) involved in the triazine rings, tertiary hybridized nitrogen and amino functional groups, (i.e.,) C=N-C, N-(C)₃ and N from (C-N-H) respectively [50]. Hence, this outcome reveals the presence of GCN complex in all the two samples. Compared with GCN, the spectra of C 1s and N 1s region (Fig. 5b, c) in the GFV composite have been slightly shifted towards the higher binding energies which is mostly owing to the effective integration of α -Fe₂O₃ and V₂O₅ influence in the graphitic C₃N₄ surfaces. Additionally, the GFV composite exhibits a much stronger N 1s peak than pristine GCN. The high-resolution O 1s strong spectrum (Fig. 5(d)) shows the two deconvoluted peaks at 531.2 eV, and 528.6 eV are consistent to surface oxygen-containing oxides, and adsorbed hydroxyl groups, individually [51]. Also, a shoulder peak at 529.7 eV for the O 1s spectrum corresponds to the binding energies of lattice oxygen in V-O and/or Fe-O species. GCN displays a weak O 1s peak at 532.4 eV, conforming to the surface adsorbed H₂O species. Also, the changes in the O 1s spectrum generously verify the influence of α -Fe₂O₃ and V₂O₅ phases loaded. Besides, the adsorbed -OH groups on the catalyst surfaces are beneficial for the construction of $\bullet$ OH and $\bullet$ O₂⁻ radical species in the progression [48]. In addition, the Fe 2p and V 2p signals are also sensed in the GFV composite sample.

Fig. 5(e) shows the deconvoluted high-resolution XPS spectrum of Fe 2p comprises that two key peaks located at 710.6 eV and 723.8 eV accredited to the Fe 2p_{3/2} and Fe 2p_{1/2} spin-orbit peaks are in good contract with the standard α -Fe₂O₃, respectively [36]. Fig. 5(f) demonstrates that the V 2p spectrum for V₂O₅ reveals that two typical peaks with binding energies of 523.2 eV and 515.8 eV were might be denoted to the 2p_{1/2} and 2p_{3/2} peaks. Since, the deconvoluted peak at 515.3 eV can be associated with V⁴⁺ species, although the peak of 516.2 eV also initiates from V⁵⁺ species which could be attributed to the typical spin-orbital splitting respectively [41,52]. The width of V 2p_{1/2} is a few wider than that of V 2p_{3/2} cores, due to the Coster-Kronig Auger broadening transitions. Additionally, the atomic % of C 1s, N 1s, O 1s, Fe 2p and V 2p in the GFV ternary heterostructure nanocomposite, calculated from the respective peak parts, whereas ~ 44 %, 33.9 %, 17.4 %, 1.9 % and 2.8 %, individually. Hence, these results might also confirm that the successful loading and intimate contact of heterostructures interaction among the effective α -Fe₂O₃ and V₂O₅ with the g-C₃N₄ surface, which could beneficial for efficient photo-degradation performance of organic impurities [48].

3.5 Optical absorption properties by UV-DRS spectra

The UV-visible spectra studies reveal that the optical absorbance contribution and bandgap properties of the obtained composite samples are provided in Fig. 6a. The g-C₃N₄

displays a visible absorption with a typical absorption edge near ~390-430 nm [48]. With the introduction of α -Fe₂O₃ and V₂O₅ in the g-C₃N₄ surface, the GF and GV binary composite exhibits substantial increases in the visible-light absorption and the intensity also [36]. Coupling the α -Fe₂O₃ and V₂O₅ SCs in the g-C₃N₄ surface, the resulting composites display an absorption edge shifted towards a higher wavelength with visible-light region compared to pristine g-C₃N₄ due to redshift [37]. Since the greater absorption in the visible-light region leads to upgraded photocatalytic performance in the related region.

Fig. 6. (a) The UV-Vis DRS absorption spectra; (b) Bandgap values via Tauc plot $((\alpha h\nu)^2$ vs. $h\nu$) calculation of the as-obtained samples; (c) PL spectra measured by room temperature; (d) EIS Nyquist plots of as-obtained samples; (e) TGA curves of as-obtained GCN and GFV samples; (f) UV-Vis absorption spectra of MY+MB mixed aqueous dye over GFV sample under visible-light

Moreover, the optical bandgap (E_g) energies of the obtained catalysts samples are inferred from a typical Tauc plot from transformed Kubelka-Munk function [53] via UV-vis absorbance spectra is publicized in Fig. 6b. According to the above calculation, the optical bandgap of corresponding as-obtained GCN, GF, GV and GFV catalyst samples are 2.7, 2.61, 2.44 and 2.37 eV respectively. From the results observed from the Tauc plot that the bandgap

of the GFV composite was originated to decrease owing to effective coupling with g-C₃N₄ and α -Fe₂O₃/V₂O₅. Also, these outcomes show that the coordination of α -Fe₂O₃/V₂O₅ coupled on g-C₃N₄ composite reformed the electronic structure of the graphitic C₃N₄, which can absorb the visible-light range, and favorable for the charge transport with a recombination rate of photo-excited e^-/h^+ pairs [54]. Moreover, the enhanced visible-light absorption response and reduced bandgap might be dual Z-scheme heterojunction structure formation and the up-conversion effect due to the incorporation of α -Fe₂O₃ and V₂O₅ NPs.

3.6 PL spectra analysis

Fig. 6c reveals the PL spectra of as-obtained GCN, GF, GV and GFV composite photocatalyst samples. The PL outcome displays that the GCN sample shows a strong emission signal at ~446 nm owed to the electron transition of $n-\pi^*$ in graphitic C₃N₄, and the photo-excited electrons (e^-) is highly recombined with the holes (h^+) [55]. However, the PL spectra intensity of the obtained samples are weakened in the sequence of GCN > GF > GV > GFV nanocomposite. Generally, having a lesser PL intensity is signifying that the more outstanding photo-excited charge separation ability with lower recombination and electron binding rate, also the prolonged lifetimes [56]. This is because the cocatalyst of V₂O₅ on the GF composite surface which significantly promotes the photo-excited charge transfers could efficiently hinder the recombination rate. Thus, the ternary GFV heterostructure sample has a lesser PL emission intensity, which is responsible for the formation of heterojunction structure in the nanocomposite [50]. The dual Z-scheme transfer heterojunction structure formation among g-C₃N₄, α -Fe₂O₃ and V₂O₅ diminishes the recombination. Besides, the transfer of photo-excited e^- from CB of g-C₃N₄ to VB of α -Fe₂O₃ and V₂O₅ reduces the recombination in the specified SCs and increases the effective separation leading to a low PL emission range. Also, V₂O₅ ensure the dual Z-scheme charge transfer and further decreases the recombination of the GF sample [57]. This narrow bandgap of V₂O₅ arises from the d orbitals, which specifies the almost metallic nature of the V₂O₅ NPs and results in the favorable photo-excited charge recombination rate [27].

To further evaluate the charge transfer efficiency at the interface of semiconductor photoelectrodes can be specified by EIS analysis [58]. The EIS Nyquist plots of as-obtained GCN, GF, GV, and GFV composite photocatalysts were measured (Fig. 6d). Generally, the semicircles arc size is smaller, it is contributed to a lower resistance followed by the accelerated interfacial charge transfer [59]. Fig. 6d shows the EIS spectra signifying that a dramatic decline in the arc radius of the GFV heterostructure compared to GCN, implying the lowest electron-transfer resistance, which possesses the highest efficiency in the interfacial

charge separation/transfer [58,60]. Likewise, the arrangement order of the EIS arc radius is in the following order: GFV < GV < GF < GCN. The outcomes of the PL and EIS analyses suggested that the synergistic effect of g-C₃N₄ and Fe₂O₃/V₂O₅ assemblies could improve the photo-excited charge transfer/migration efficiency and lower recombination rates followed by a better oxidation capacity due to generating more active sites, which is highly beneficial for enhancing the photocatalytic activity [58].

In this section, TGA analysis was used to determine the thermal stability and GCN content of the as-obtained PCs [36]. For the pristine GCN sample, 99 % of weight loss is noticed. As detected, the GCN displays (Fig. 6e) that its decomposition starts nearly from 475 °C and extends upto 640 °C for closely complete decomposition. Because this weight loss is due to the burning of g-C₃N₄ to yield the carbon dioxide and diverse oxides of N₂ [36]. Besides, decomposition temperatures for the GFV composite heterostructure decreased when compared to the GCN. In the ternary GFV composite PCs, the loaded Fe₂O₃ and V₂O₅ NPs could act as an active site for adsorption of oxygen molecules from the adjacent, leading to quick oxidizing GCN portion of the PCs at lesser temperatures related to the GCN [61]. Also, it has manifested that the Fe₂O₃ and V₂O₅ NPs have significant stability in the heating process. In this case, the GFV PCs, the total weight loss is about 39 % in the thermal process, signifying that this composite sample may contain ~39 % of g-C₃N₄. Furthermore, it is vibrant that all of the as-obtained samples are thermally stable up to 435 °C [38].

3.7 Photocatalytic performance of GFV composite photocatalyst

The photocatalytic performance of all the obtained composite samples was assessed through the photo-degradation of aqueous MY and MB mixed dye under visible-light exposure [9], and the outcomes are exhibited in Fig. 6e. As shown in Fig. 6e, the decomposition of mixed dye was not detected when no catalyst was added, representing that the self-decomposition of mixed dye could be neglected in our degradation tests [62,63]. The ternary GFV heterostructure catalyst shows improved photo-degradation performance of both MY+MB dyes than that of the GCN sample. In contrast, the photo-degradation rates (Fig. 7a, b) of MY in the mixed dye for GCN, GF, GV and GFV photocatalysts samples at 90 min are 35.1 %, 64.8 %, 70.2 %, and 93.3 %, respectively. Meanwhile, the photo-degradation rates of MB in the mixed dye are 32.2 %, 58.8 %, 70.5 %, and 87.5 % are achieved (Fig. 7d, e) for as-obtained GCN, GF, GV and GFV samples within 90 min of visible-light exposure. From these results, GFV heterostructured PCs samples display the superior photo-degradation performance for both MY (93.3 %) and MB dye (87.5 %) in the mixed organic dyes compared with other as-obtained PCs.

Fig. 7. The photo-degradation rate curves of (a) MY and (d) MB dye; degradation efficiency plots of (b) MY and (e) MB dye; corresponding kinetic curves for pseudo-first-order-kinetic for the removal rate constants of (c) MY and (f) MB dye on the as-obtained PCs samples

To additionally compare the photo-degradation capability of the PCs samples, the degradation results of (MY and MB) mixed dye was fitted using the pseudo-first-order reaction kinetic model equation: $\ln(C_0/C) = k_{app} t$, where t and k_{app} are stands for degradation time and apparent reaction rate constant [37]. The photo-degradation rate constants (k) (Fig. 7c) of MY dye for obtained GF, GV and GFV PCs to be 0.0151 min^{-1} , 0.0161 min^{-1} , and 0.0291 min^{-1} , which are 2.55, 2.72 and 4.93 folds superior to that of as-obtained GCN (0.0059 min^{-1}) catalyst respectively. Also, apparent rate constants of MB dye correspond to GF, GV and GFV photocatalytic samples (Fig. 7f), which are 0.0051 min^{-1} , 0.0112 min^{-1} , and 0.0251 min^{-1} , which are 1.21, 2.66 and 4.92 folds superior to GCN (0.0042 min^{-1}) catalyst sample. Furthermore, the photo-reaction rate constant of the ternary GFV heterostructure sample is 4.93 and 5.97 times superior to that of GCN samples for the MY and MB mixed dye photo-degradation process under visible-light exposure [38]. This result validates that the GFV ternary PCs have also possessed excellent photo-degradation ability for organic dyes [64]. This is because, as a result of the longer lifetime of photo-excited carriers, enhanced visible-light utilization and also due to the synergistic effect of $g\text{-C}_3\text{N}_4$, $\alpha\text{-Fe}_2\text{O}_3$ and V_2O_5

catalysts respectively. The degradation efficiency and corresponding apparent rate constants are exposed in Table. 1.

3.7.1 Reusability studies

The sustainability of the photocatalyst plays a major role in the photo-degradation tests [8,58]. Additionally, to additional investigate the reusability of the ideal ternary GFV heterostructure composite PCs was carried out to study its sustainability, since of excessive significance in the practical applications [18,65]. As seen in Fig. 8a and b, the PCs still maintain a superb photo-degradation rate for the aqueous MY and MB mixed dye solutions after five successive recycles, and the consistent degradation rates are 84.1 % and 79.5 %, respectively under visible-light exposure. After each recycling test, the magnetic recoverable PCs sample was collected by an external magnet and washed with D.I water and ethanol several times, then the as-obtained PCs were dried at 70 °C overnight for the next cycling reused [48]. In Fig. 8c, d, there are no significant changes in the crystalline phase structure and major functional groups via XRD and FT-IR results of the recycled PCs is also observed after the five repeated testing's compared with a fresh sample [66]. Besides, the PCs also establish that superior magnetically recovery for each successive recycles (Fig. S1) in the external magnetic fields [67]. These outcomes support that the supreme ternary GFV composite PCs possess excellent photochemical stability for their practical applications of various organic pollutants degradation [68]. In addition, the photo-degradation performance of as-obtained optimum GFV ternary composite PCs was improved when compared (Table. S1) to the previous reported photocatalytic NMs and commercial P25 TiO₂ NPs.

Figure. 8 (a) Recycling test for the photo-degradation of MY and MB dye over the optimum GFV composite PCs; (c) XRD patterns and (d) FT-IR spectra of before and recycling used GFV PCs

Table. 1 Photo-degradation efficiency, K_{app} and R^2 values of the as-obtained samples

S. No.	Samples	Efficiency (%)		K_{app} (min^{-1})		Correlation coefficient (R^2)	
		MY	MB	MY	MB	MY	MB
1.	GCN	35.1	32.2	0.0059	0.0042	0.9397	0.9774
2.	GF	64.8	58.8	0.0151	0.0051	0.9906	0.9303
3.	GV	70.2	70.5	0.0161	0.0112	0.9871	0.9264
4.	GFV	93.3	87.5	0.0291	0.0251	0.9266	0.9837

3.8. Possible photo-degradation mechanism

Fig. 9. Effect of radical scavengers on the photo-degradation of mixed MY+MB aqueous dye over the optimum GFV composite PCs

To study the influence of different active radicals for the degradation of MY+MB mixed dye over the optimum ternary GFV heterostructure PCs, the radical trapping test is performed. Various free radical scavengers are added to the mixed dye photo-degradation tests of ternary GFV composite PCs, and the outcomes are shown in Fig. 9. After the adding

of BQ ($\bullet\text{O}_2^-$ scavenger), the photo-degradation efficiency of the mixed dye is expressively inhibited, suggesting that $\bullet\text{O}_2^-$ is the most significant active species for both dye decomposition properties [68]. The photo-degradation efficiency of mixed dye also exhibits the substantial attenuation after the accumulation of EDTA (h^+ scavenger), which specifies that the influence of h^+ is also not negligible [69]. While the addition of IPA ($\bullet\text{OH}$ radical scavenger), the photo-degradation efficiency of mixed dye declines slightly, representing that $\bullet\text{OH}$ radical are not the key active species in the decomposition process [70]. Hence, the $\bullet\text{O}_2^-$ and few photo- h^+ are also affected by the photo-degradation of mixed dye.

Table. 2 Optical bandgap, electronegativity, VB and CB edge positions of the as-obtained samples

S. No.	Samples	Band gap (eV)	Electronegativity (eV)	CB (V)	VB (V)
1.	g-C ₃ N ₄	2.7	4.73	-1.12	1.58
2.	α -Fe ₂ O ₃	2.0	5.89	0.39	2.39
3.	V ₂ O ₅	2.2	6.10	0.49	2.71

To sense the charges transport pathway of the ternary GFV composite PCs were designed to obtain the valence band (VB) and conduction band (CB) edge positions (vs. normalized hydrogen energy (NHE)) of the relevant g-C₃N₄, α -Fe₂O₃ and V₂O₅ components. Then according to the typical Mulliken electronegativity formula (1 & 2); $E_{\text{CB}} = X - E_e - E_g$ (1) and $E_{\text{VB}} = E_{\text{CB}} + E_g$ (2) [36]. Also, the absolute electronegativity χ values for g-C₃N₄, α -Fe₂O₃ and V₂O₅ are found to be 4.73, 5.89 and 6.1 eV respectively. Whereas, E_e is the energies of the free electrons on the hydrogen scale ($E_e = 4.5$ eV); E_g is the bandgap energy of the specified SCs (for g-C₃N₄, α -Fe₂O₃ and V₂O₅ are 2.7, 2 and 2.22 eV, respectively) [71]. The CB edge potential values are corresponding to g-C₃N₄, α -Fe₂O₃ and V₂O₅ could be estimated as -1.12, 0.39 and 0.49 V (vs. NHE), respectively. Moreover, the consistent VB edge potential values were to be 1.58, 2.39 and 2.71 V (vs. NHE) for g-C₃N₄, α -Fe₂O₃ and V₂O₅ components. For it could be observed that the CB and VB edge position are such positioned that there is easy diffusion of Z-scheme charge carrier's separation along with the interfaces

[72]. Consequently, based on the above experimental results, the band structures and possible transfer pathway of photo-excited carriers could be further acquiring the effective Z-scheme components in ternary GFV composite PCs system as exposed in Fig. 10.

Under visible-light exposure, the outer g-C₃N₄ catalyst is stimulated to generate photo-excited electrons (e⁻) and holes (h⁺) respectively. Since the VB and CB edge position of V₂O₅ is higher than that of α-Fe₂O₃, and that also α-Fe₂O₃ is higher than g-C₃N₄ [21]. Hence, the charge transfer pathway of the ternary GFV photocatalytic system follows the traditional heterojunction mechanism (Fig. 10a), the photo-e⁻ on the CB of g-C₃N₄ will be transferred to the CB of α-Fe₂O₃ first, and then to the V₂O₅ with lower CB edge position [73]. Simultaneously, the photo-h⁺ on the VB of V₂O₅ will first be excitedly transferred to the VB of α-Fe₂O₃, then to the g-C₃N₄ with a higher VB edge position. Since the CB potential of V₂O₅ (0.49 V *vs.* NHE) is relatively high, also with the photo-reduction ability of photo-e⁻ on CB of V₂O₅ is weak, which cannot reduce the O₂ in the photo-reaction system to [•]O₂⁻ (E₀ (O₂/[•]O₂⁻) = - 0.33 V *vs.* NHE). Although, photo-h⁺ on VB of g-C₃N₄ (1.58 V *vs.* NHE) is very low, which cannot able to photo-oxidize H₂O to [•]OH radicals (E₀ (H₂O/[•]OH) = 2.39 V *vs.* NHE) [74]. Consequently, in this photo-excited charge transfer mechanism, the photo-h⁺ will be only the active species into visible-light photocatalytic degradation of mixed dye over the GFV heterostructure composite catalyst, which is noticeably not equal with the experimental outcomes of free radical capture, so that the traditional heterojunction photo-degradation mechanism is not reliable with the photo-reaction structure [51]. This suggests that the photo-e⁻ cannot actively transfer from the CB of GCN to the CB of α-Fe₂O₃ and/or V₂O₅, and the photo-h⁺ cannot transfer from the VB of α-Fe₂O₃ and/or V₂O₅ as in traditional heterostructure junctions SCs (Fig. 10a). Thus, it could be deduced that the charge transfer among the g-C₃N₄, α-Fe₂O₃ and V₂O₅ PCs should pathway to the effective Z-scheme, as shown in Fig. 10b.

Moreover, to estimate the dual Z-Scheme photo-e⁻ transfer mechanism of the GFV heterostructure composite PCs, as revealed in Fig. 10b, under visible-light exposure. Since the photo-e⁻ on CB of α-Fe₂O₃ rapidly transferred to the VB of g-C₃N₄ by the interfaces formed among α-Fe₂O₃ and g-C₃N₄, besides its composited with photo-h⁺ on the VB of g-C₃N₄ [8]. Equally, the photo-e⁻ on CB of V₂O₅ speedily transferred to the VB of g-C₃N₄ and composited with photo-h⁺ on the VB of g-C₃N₄. In the GFV composite system, α-Fe₂O₃ plays a role as photo-e⁻ transfer medium to sponsor photo-e⁻ and photo-h⁺ concentrate on g-C₃N₄ with higher CB position and V₂O₅ with lower VB position respectively [21], which effectually reserved the strong photo-reduction of photo-e⁻ and the strong photo-oxidation of

photo- h^+ respectively [70]. Conversely, the VB edge of V_2O_5 is lower than the typical redox potential values of $\bullet OH/H_2O$ (2.7 V vs. NHE), which proposes that the photo- h^+ in the VB of V_2O_5 also cannot oxidize the adsorbed H_2O molecules to produce the $\bullet OH$. Moreover, the external $\alpha\text{-Fe}_2O_3$ and V_2O_5 components will act as the main double Z-Scheme photo-oxidation centre to degrade the organic impurities [24].

Fig. 10. The possible steps charge transfer mechanism in the photo-degradation process of GFV heterostructure composite (a) typical pathway and (b) efficient dual Z-Scheme pathway structure

Then, the CB edge of g- C_3N_4 semiconducting nanomaterial is more negative when related with $O_2/\bullet O_2^-$. Then photo- e^- on CB of g- C_3N_4 could be reduced the surface adsorption O_2 on the catalyst surface to the reactive species $\bullet O_2^-$, therefore degrading the MY+MB mixed pollutant together with robust photo-oxidizing photo- h^+ on VB of V_2O_5 . However, they may be simply broken down into other constituents rather than final oxidized products (CO_2 and H_2O) [23,29]. Therefore, the more photo- e^- remain in the CB of g- C_3N_4 and further photo- h^+ persist the VB of $\alpha\text{-Fe}_2O_3$ and V_2O_5 to respond with the O_2 molecules and OH ions to yield the $\bullet O_2^-$ and $\bullet OH$ radicals, individually [22]. Simultaneously, the transfer of the photo-excited e^-/h^+ pairs in the above two Z-scheme paths could be significantly indorsing the charge separation, thus efficiently extending the lifetime of these charges and also prolonged to the visible-light absorption range [75]. The photo- e^- and photo- h^+ of V_2O_5 were not only separated efficiently but also the photo-recombination was inhibited effectually over the dual Z-Scheme electron transfer mechanism, which improved the photocatalytic activity

and strong redox ability of the ternary GFV catalyst. Thus, the ternary g-C₃N₄/α-Fe₂O₃/V₂O₅ (GFV) composite photocatalyst exhibits superior photo-degradation performance for organic pollutants among the obtained catalysts.

4. Conclusions

In summary, the dual Z-scheme ternary g-C₃N₄/α-Fe₂O₃/V₂O₅ (GFV) heterojunction photocatalyst was organized by simple calcination and hydrothermal method. The as-obtained synthesized GFV photocatalyst exhibited superior photo-degradation performance of mixed MY+MB dye under visible-light exposure. The pseudo-first-order constant for the ternary GFV heterostructure PCs is 4.93 and 5.97 folds superior to that of pristine GCN samples for MY (0.0291 min⁻¹) and MB (0.0251 min⁻¹) mixed dye photo-degradation process. The enhanced photo-degradation was mainly recognized to the enlarged visible-light absorption ability, quicker charge separation, restrained recombination rate, and well-supported redox capability, with extending the lifetime of the photo-excited charges which are beneficial for photo-oxidation reaction. Additionally, magnetically recovered GFV PCs continued superb photo-degradation efficiency for the aqueous MY (84.1 %) and MB (79.5 %) mixed dye solutions after the five successive recycles, signifying good photo-reaction reusability and stability. Since the V₂O₅ and α-Fe₂O₃ have synergistic interfacial contact with a g-C₃N₄ surface which enables the formation of the dual Z-Scheme heterostructure junction. The improved photo-degradation performance was elucidated in terms of promises of traditional charge transfer mechanism and proposed dual Z-scheme transfer. The outcomes of this work may deliver a novel concept for the feasible fabrication, magnetic separable and recyclable composite photocatalysts for potential wastewater treatment in the practical environmental remediation.

Declaration of competing interest

The authors declare that they have no known competing interests

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Graphical Abstract

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- GFV composite PCs revealed that superior photodegradation activity of the mixed dye
- The GFV PCs is 4.93 and 5.97 folds superior to that of GCN for MY and MB mixed dye
- Each successive recycles, the superior magnetic PCs was recovered by under magnets
- A possible dual Z-scheme charge transfer mechanism was also been proposed