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Novel Magnetic Retrievable Visible-Light-Driven Ternary Fe₃O₄@NiFe₂O₄/Phosphorus-Doped g-C₃N₄ Nanocomposite Photocatalyst with Significantly Enhanced Activity through a Double-Z-Scheme System

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ABSTRACT: Nickel ferrite (NiFe₂O₄) and magnetite (Fe₃O₄) are established earth-abundant materials and get tremendous attention because of magnetic and high photocatalytic activity. First we fabricated novel Fe₃O₄@20 wt % NiFe₂O₄/phosphorus-doped g-C₃N₄ (M@NFOPCN) using a convenient simple coprecipitation method followed by calcination at 400 °C. Then M@NFOPCN composites were prepared by the in situ growth of Fe₃O₄ nanorods and cubes on the surfaces of a porous agglomerated NFOPCN nanostructure, varying the weight percentage of Fe₃O₄. A series of characterizations like X-ray diffraction, UV–vis diffuse-reflectance spectroscopy, photoluminescence, Fourier transform infrared, thermogravimetric analysis–differential thermal analysis, vibrating-sample magnetometry, scanning electron microscopy, trans-



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mission electron microscopy, and X-ray photoelectron spectroscopy techniques confirm that changing weight percentage of M can constructively control the textural characteristics, internal strain, size of the crystals, and other aspects meant for photocatalytic activity. When M was coupled with NFOPCN, magnetic loss was lowered and also an appreciable saturation magnetization (M_s) was obtained. 40 wt % M@NFOPCN showed admirable photostability and was capable of evolving 924 µmol h⁻¹ H₂ when irradiated under visible light. The percentage of degradation for ciprofloxacin (CIP) by this ternary nanocomposite was almost 2-fold greater than those of the pure M and NFOPCN photocatalysts. A plausible photocatalytic mechanism for the degradation of CIP antibiotic was established. Hence, this study presents a reusable, low-cost, noble-metal-free, environmentally friendly, fast, and highly efficient 40 wt % M@NFOPCN photocatalyst, achieving 90% degradation of CIP antibiotic under visible light. The double-Z scheme triggers charge separation and migration, enhances visible-light harvesting, and helps in internal electric-field creation, thus headed toward dramatic augmentation of the photocatalytic activity.

1. INTRODUCTION

With a growing population and recent developments, this new era has headed toward a level of crisis in energy shortage and an increase in environmental pollution. Auspiciously, utilizing solar energy, heterogeneous photocatalysis is a potential platform for these crises.¹ It helps in the conversion of environmental contaminates to nontoxic products as well as in the harvest of renewable energy through water splitting.² Therefore, to extend the best way of utilizing renewable solar light, researchers from all over the globe have stimulated their skills and experiences through productive photocatalysis by using low-cost or waste materials.³ Furthermore, recent developments of composites acquire stronger oxidizing and reducing abilities through a Z-scheme-based system.⁴ In recent times, soft magnetic ferrites like MFe₂O₄ (M = Fe, Ni, Cu, Co, Zn), because of their crystalline, anisotropic magnetic nature,

and average grain size obtained by excitation under large flux density, are highly appreciated by researchers because of their range of applications like water treatment, magnetic devices, catalysis, lithium-ion batteries, microwave-absorbing materials, gas sensors, and medical care.^{5–10} Among them, mixed spinel oxides Ni_xFe_{3-x}O₄ (0 < x < 1) have been investigated for their photocatalysis, admirable enduring stability, ease of recovery by magnetic separation, and ability to check secondary pollution for treated water.^{11–14} Hence, because of their

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Table 1. Comparison Study of a Magnetic Photocatalyst

material ((magnetic component in bold)	model pollutant	source of light	photocatalytic degradation measure	ref
ZnO/AgBr/Fe ₃ O ₄	/Ag ₃ VO ₄	rhodamine B	50 W light-emitting diode	0.029 min^{-1}	20
NiAl-layered doub oxide	le hydroxide/ Fe_3O_4 /reduced graphene	ciprofloxacin	500 W xenon lamp (>420 nm filter)	0.0235 min^{-1}	21
Fe_3O_4/TiO_2		reactive brilliant red 3	300 W xenon lamp	$0.03 - 0.035 \text{ min}^{-1}$	22
$Bi_2MoO_6/ZnFe_2O_6$	4	rhodamine B	150 W xenon lamp	0.0034 min^{-1}	23
CoFe ₂ O ₄ /polyanili	ne	methyl orange	10 W light-emitting diode	85% degradation in 2 h	24

unmatched supremacy in separation and recycling, magnetic nanoparticles (NPs) have been extensively used as a platform for the construction of a range of efficient photocatalysts.^{15,16} In particular, NiFe₂O₄ (NFO), because of its high Curie temperature, environmental benignity and stability, high electrical resistivity, and low price and the large abundance of nickel, has became the most important magnetic material. Within this inverse spinel, the Ni²⁺ and Fe³⁺ ions at octahedral sites and balanced Fe³⁺ ions at tetrahedral sites having antiparallel spins give rise to ferrimagnetism. The Fe²⁺ ion present in the system and hopping of electrons from Fe²⁺ to Fe³⁺ are accountable for the conductivity as well as the n-type behavior, whereas Ni³⁺ is responsible for p-type activities, and the shifting of holes from Ni³⁺ to Ni²⁺ gives rise to conductivity.⁶ Also, as reported by Ding and co-workers, the use of minor or noble metals should be given the least priority for the assembly of proper sustainable systems, and recently nickel NPs have been used in place of platinum NPs for photocatalytic H₂ evolution.¹⁶ However, again the fast reunion of photoelectron-hole pairs in NFO has made it a poor photocatalyst. Hence, to enhance the activity, composite formation with NFO is advisible. As reported by our group, after NFO was combined with phosphorus-doped g-C₃N₄ (P-CN), there was a tremendous enhancement in the photocatalytic activity. This variation endowed carbon nitride materials with superior optical absorption, outstanding H_2 generation under visible light by water splitting, and improved dye adsorption and degradation. These were all possibly due to the increased surface area, better charge-transfer rate, and narrowing of the band gap by phosphorus doping.⁷ We deliberately designed a novel magnetic NFO-based composite photocatalyst paired with P-CN and coupled with Fe₃O₄. Meticulously, Fe₃O₄ is suitable for the best recycling properties, excellent chemical stability, wide frequency ranges, large saturation magnetization, electromagnetic wave absorption in the high frequency range, high complex permeability, and eddy current loss as well as low alternating-current (ac) electrical conductivity.^{17–19}

In this paper, we have synthesized Fe_3O_4 @20 wt % NiFe₂O₄/phosphorus-doped g-C₃N₄ (M@NFOPCN), a Z-scheme-based heterostructure-agglomerated porous rod like composites through an in situ calcined route that is pertinent to a range of nanomaterials. The obtained results shed new light on the interface and composition-related photocatalytic properties like H₂ evolution and antibiotic degradation.¹⁹ The prominent appreciable activity of Fe_3O_4 as well as ferrites against environmental pollution has already been established by many research. Without much effort, we combined the above two and modified the result for our purposes. It was observed that the ternary M@NFOPCN nanocomposite showed significantly enhanced activity compared to Fe_3O_4 and 20 wt % NFOPCN photocatalysts, and it could be effortlessly recovered from the polluted water using a magnet.

Some recently published works related to this are given in Table 1. $^{20-24}$

From our previous work, we have already proven that NFOPCN not only is a promising photocatalyst but also has many more appreciable properties. However, to check further the secondary pollution for treated water, we tried to furnish a more environmentally benign photocatalyst with enhanced catalytic properties by reaping the benefits of the previous work.^{10,25} A series of Fe₃O₄-deposited NFOPCN nanocomposites were synthesized by simple in situ coprecipitation methods by varying the concentration of Fe_3O_4 (30–50%). These were all investigated mainly for photocurrent, photocatalytic antibiotic degradation, i.e., ciprofloxacin (CIP), and H₂ evolution and uses as supercapacitors under visible-light irradiation. The 40 wt % Fe₃O₄ (M)-deposited NFOPCN sample exhibits optimum photocatalytic activity for CIP degradation and H₂ production and also shows satisfactory photostability after four photocatalytic cycles. Also, the coupling of M with a NFOPCN lattice gives rise to new dopant energy levels suitable under visible-light irradiation, for the enhancement of interfacial charge transport of both holes (h⁺) and electrons (e⁻) for better photoredox reaction of $H_2O.^{26,2}$

2. EXPERIMENTAL SECTION

2.1. Chemicals Used in the Reactions. $Fe(NO_3)_3\cdot 9H_2O$ (99.9%), $FeCl_3\cdot 9H_2O$ (99.9%), $FeCl_3\cdot 9H_2O$ (99.9%), $FeCl_3\cdot 4H_2O$ (98%), $Ni(NO_3)_2\cdot 6H_2O$ (99.9%), melamine (99.9%), citric acid ($C_6H_8O_7$; 99.9%), and NaOH (97%) were all of analytical grade (Sigma-Aldrich) and were used with no further purification. Required aqueous solutions of all chemicals used throughout the experiment were prepared from deionized water (DW), which was obtained by means of a double-distillation unit.^{10,27,28}

2.2. Synthesis Procedure. 2.2.1. Fabrication of NFO and P-CN Nanocomposites (NFOPCN). As reported earlier, the synthesis of pure NFO and P-CN was furnished through sol-gel and chemical routes, respectively, followed by calcination. The composite NFOPCN (20 wt % NFO@P-CN) was also obtained by a calcination route.¹⁰

2.2.2. Preparation of M (Fe_3O_4). Taking FeCl₃ and FeCl₂ as precursors, the magnetite particles M (Fe₃O₄) were synthesized by a coprecipitation method from their aqueous solutions at strongly basic pH (pH = 12). The molar ratio maintained between the precursors was Fe²⁺:Fe³⁺ = 1:2 ([Fe³⁺] = 0.5 M and [Fe²⁺] = 0.25 M). At 30 °C, a 2 M NaOH solution was added dropwise to maintain the pH under vigorous stirring in the presence of N₂ gas. Complete chemical precipitation was achieved after stirring for 5 h at 70 °C. Finally, the product was collected after cooling, magnetically separating, and washing thoroughly with DW followed by acetone. The obtained blackish M was dried in an oven at 60–70 °C.^{27,28}

2.2.3. Preparation of x wt % Fe_3O_4 @Ni Fe_2O_4/P -g- C_3N_4 (x wt % M@NFOPCN). The x wt % (x = 30–50) M@NFOPCN nanomaterials were synthesized by an in situ coprecipitation method. In a distinctive procedure, different weight percentages (30–50 wt %) of M with a fixed weight of NFOPCN were dispersed in 250 mL of DW/ethanol (2:1) and ultrasonicated for 5 h at ambient temperature. A dark-

Scheme 1. Synthesis of M@NFOPCN by the Coprecipitation of Sol Gel via an In Situ Method



brown suspension was produced in almost all cases followed by centrifugation. Further it was washed twice with DW and ethanol and finally obtained through magnetic separation. The produced darkbrown material was dried in an oven at 60 °C for 24 h. The composites were finally ground properly and then calcined at 400 °C for further analysis.^{29,30}

2.3. Formation Mechanism. The in situ growth method has been extensively used to synthesize a range of nanocomposites. A similar approach was chosen for the synthesis of M@NFOPCN hybrid nanomaterials, as given inScheme 1. Ultrasonic dispersion helped in the deposition of nickel and iron ions on the surface of P-CN via chemical adsorption. The use of basic NaOH during precipitation helped to control the growth of iron ions by conversion to Fe₃O₄ NPs. Thus, through ethanol sonication, the uniform distribution and deposition of Fe₃O₄ NPs were effectively performed on the surfaces of the P-CN sheets. Again the double-Z-scheme-type heterojunction led by the as-prepared Fe₃O₄ NPs at the interface of NFOPCN and M (Fe₃O₄) in the synthesized nanocomposite system reduces the surface energy. The agglomeration of M (Fe₃O₄) NPs is also avoided because of in situ growth.^{10,31}

2.4. Methods of Characterization. A Rigaku Miniflex Advance powder X-ray diffractometer (set at 30 kV and 15 m A) using Cu K α radiation ($\lambda = 1.54056$ Å) at a scan rate of 2° min⁻¹ with 2 θ degree angles ranging from 10° to 70° and a step size of 0.01° was used for analysis of the crystal structure of the nanocomposites. The IR spectra were analyzed at a resolution of 4 cm^{-1} by a JASCO FT/IR-4600 Fourier transform infrared (FTIR) spectrophotometer using KBr as the reference diluent. Within a frequency range of $400-4000 \text{ cm}^{-1}$, the vibrational modes and chemical compositions of M@NFOPCN were analyzed. The composition and surface framework of the assynthesized composite, M@NFOPCN, and neat materials were measured by scanning electron microscopy (SEM; Hitachi S-3400N). Transmission electron microscopy (TEM) images at different scales were examined by a JEOL-2010 200 kV instrument. This helps to study the morphology interface, interaction between M and NFOPCN, and microstructure of the prepared catalysts. The magnetic study was carried out by using vibrating-sample magneto-metry (VSM; Microsense EZ9). The room-temperature photoluminescence (PL) spectra of M, NFOPCN, and 30-50 wt % M@ NFOPCN were investigated utilizing a fluorescence spectrophotometer (JASCO FP-8300) equipped with a xenon (Xe) lamp with an excitation wavelength of 330 nm. UV-vis diffuse-reflectance spectroscopy (DRS) spectra were found using a UV-vis spectrophotometer (JASCO 750), and transformation from reflection to absorbance for the Kubelka-Munk method was chosen by using BaSO₄ as the reference. A monochromatic X-ray source (Mg K α Xray) was used in order to accomplish X-ray photoelectron spectroscopy (XPS) by a VG Microtech Multilab ESCA 3000 surface analyzer.

2.5. Photoelectrochemical (PEC) Measurements. Cyclic voltammetry (CV), Mott–Schottky (MS) plots, linear-sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were carried out under the essential conditions to analyze the PEC response of the synthesized nanocomposites. An Autolab electrochemical analyzer (Ivium potentiostat) with a standard three-

electrode system was used for photocurrent studies and measurements. The electrolyte used for the study was an aqueous solution of Na_2SO_4 (0.1 M) at pH = 6.7. Again, for the reference, working, and counter electrodes, Ag/AgCl, the prepared electrode, and platinum wire were used, respectively. For the source of light, a 300 W xenon lamp through an UV cut-off filter (λ = 400 nm) was used. A powdered photocatalyst (0.02 g) with iodine (0.02 g) in acetone (30 mL) was dispersed and then used for the preparation of electrodes by electrophoretic deposition. The two parallel fluorine-doped tin oxides (FTOs) were dipped in the solution at a distance of 10–15 mm at 60 V bias underneath potentiostat control for 3 min. Then the FTOs having a coated area of almost 1 cm² were dried. A frequency range from 0.1 Hz to 100 kHz and an ac voltage of 10 mV amplitude were used to determine EIS. Under dark conditions at 1500 Hz, the MS plots of the nanocomposites were well illustrated. The polarization curves (LSV) were furnished by a potential sweep from -0.5 to +1.5V.

2.6. Photocatalytic Experiment. 2.6.1. Measurement of Photocatalytically Furnished H_2 . A gas distribution, an evacuation system, and a Pyrex quartz reactor enclosed in a 100 mL sealed round-bottomed flask were used for the H_2 evolution reactions. A 150 W xenon arc lamp ($\lambda > 420$ nm) of medium pressure as the light source was taken to activate the reaction using a 1 M NaNO₂ solution as a UV cut-off filter. The distance from the photoreactor was almost 20 cm. The measured density of normal light was found to be 120 mW cm⁻². A total of 20 mL of an aqueous solution containing the target powdered catalyst of 20 mg and a solution of 10% methanol was taken. N₂ gas was purged for 20 min for the total removal of CO₂ and O₂ dissolved in H₂O prior to irradiation. The H₂ gas produced was collected by downward displacement of H₂O.

2.6.2. Experiment for CIP Reduction. The photocatalytic degradation efficiency of the synthesized nanocomposites was established by decomposing CIP under solar-light irradiation. Aqueous solutions of CIP and photocatalyst were taken in 100 mL stoppered conical flasks and agitated in the dark using a magnetic stirrer for 30 min. Then they were irradiated under solar light for 1 h from 11:00 am to 12:00 noon. The average luminosity throughout the course of the experiments was found to be 102000 k. Then, the suspension was centrifuged, followed by filtration to reobtain the catalyst aliquots. The concentration of the remaining CIP was analyzed using a UV–vis spectrophotometer. Further, in addition to that, the initial concentration of the CIP solution, time duration of exposure to visible light, and effects due to the weight percent variation in the composition of photocatalysts on the probable photocatalysis of M@NFOPCN were investigated.

3. STUDY OF THE MORPHOLOGY, CRYSTAL STRUCTURE, AND COMPOSITION OF AN AS-SYNTHESIZED PHOTOCATALYST

3.1. Crystal Phase and Phase Purity by PXRD Studies. As obtained from PXRD analysis, the phase, crystalline nature, and interlayer stacking of synthesized samples are displayed in Figure 1, which reveals the XRD patterns of neat M (Fe₃O₄), a NFOPCN composite, and the hybrid nanocomposites x wt %



Figure 1. XRD patterns of M, NFOPCN, and 30–50% M@ NFOPCN composites.

M@NFOPCN (x = 30, 40, 45, and 50 wt %), which are used to clarify the structural parameters. The well crystallization is confirmed from the strong and sharp diffraction peaks. In NFOPCN, the peaks at 18.4°, 30.3°, 35.7°, 37.3°, 43.4°, 53.8°, 57.4°, and 62.9° are ascribed to the (111), (220), (311), (222), (400), (422), (511), and (440) planes of NFO, as shown in Figure 1 (JCPDS 10-0325). Also, the other two distinct diffraction peaks of lower intensity than g-C₃N₄, at 27.41 and 13.11 indexed as the (002) and (100) planes, were obtained for neat P-CN, as reported in our previous paper.¹⁰ The obtained diffraction peaks of neat M are in good harmony with JCPDS 65-3107 for pure cubic M.²⁷ The peaks at 30.1°, 35.5°, 43.4°, 57.4°, and 62.9° are attributed to the (220), (311), (400), (511), and (440) planes of M. After hybridization with NFOPCN, it is observed that the crystal phase of M does not change, but there is a slight dislocation toward higher angles in comparison to pure M, signifying a strong interaction within NFOPCN and M.^{27,28} Although there are two ferrites, there are no double reflections in the PXRD pattern due to broadening of the diffraction lines.²⁹ It is also well observed that, with a gradual increase in the wt % of M from 30% to 50%, an increase in the intensities of the ferrite peaks and a decrease in the intensity of the P-CN peaks along with the appearance of a peak at 33.5°, which is attributed to a tendency of varying phases of M to support $Fe^{2+} \rightarrow Fe^{3+}$ oxidation-state shuttling.^{30,31} Further, as was already reported, the increasing magnetic interaction within the magnetic materials also supports that above.²⁸ The above XRD pattern of the as-synthesized M@NFOPCN photocatalyst given in Figure 1 matches well with the magnetite (Fe₃O₄; JCPDS 65-3107) and maghemite (γ -Fe₂O₃; JCPDS 39-1346) structures. Because of the similarity in the XRD patterns of maghemite and magnetite, XPS measurements are taken into account to avoid unambiguity.15,32

3.2. FTIR. To illustrate the surface chemistry and different bonds of the as-synthesized 30-50 wt % M@NFOPCN composite, FTIR spectroscopy was used, as given in Figure 2. The broad peaks at around 3100-3500 cm⁻¹ are indicative of surface-adsorbed H₂O molecules and uncondensed N–H stretching vibrations of the P-CN spectrum. The two enlarged broadening bands almost centered around 3367 and 1638 cm⁻¹ belong to the stretching and bending vibrations of the



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Figure 2. FTIR spectra of M, NFOPCN, and 30–50 wt % M@ NFOPCN composites.

O-H groups, respectively.^{10,33} This finding specifies the existence of crystal H2O in the compound.9 The distinctive bands in the area ranging from 1240 to 1640 cm⁻¹ are assigned to either the bridging C-NH-C or trigonal C-N(-C)-Cunits (full condensation).³⁴ The P-N stretching vibration in NFOPCN is well identified by a feeble peak present at 950 cm⁻¹.¹⁰ Again, the sharp peak located at 810 cm⁻¹ can be related to the breathing vibration of the typical s-triazine ring.³⁵ The weak typical low-frequency peak at 560 cm⁻¹ is ascribed to Fe-O stretching in the tetrahedron and the band at 608 cm⁻¹ to metal-oxygen deformation in the octahedron. The possibility of formation of other phases for M could also be eliminated because the existence of a Fe-O vibrational mode at 560 cm⁻¹ is only ascribed to the M magnetite phase, whereas the band at 470 cm⁻¹ typical for γ -Fe₂O₃ is absent.^{36,} Further, in the case of pure M, the peak at 586 cm^{-1} is ascribed to the symmetric stretching vibration of the Fe-O band in the tetrahedral FeO₆ groups of spinel-type compounds.³⁴ It is also observed that all of the main distinctive peaks of NFOPCN and M are well maintained in the M@NFOPCN composite spectra, further confirming the evidence of NFO and M on the surface of P-CN.

3.3. SEM. The influence of $[Ni^{2+}]$, $[Fe^{2+}]$, and $[Fe^{3+}]$ on the morphology, size, elemental distribution/composition, and structure of the sintered composites is revealed by electron microscopy techniques [SEM, TEM, high-resolution TEM (HRTEM), and selected-area electron diffraction (SAED)].⁹ The SEM images of the nanocomposite in Figure 3a-c clearly reveal the presence of pores and voids in the sample. This may be due to the discharge of a huge amount of gases during the combustion process adopted for the synthesis. In a spongy structure, fine multigrain crystallites are found to undergo agglomerations.³⁸ Pure NFO having granular unstructured morphology and flakelike, globular agglomerates of P-CN were already reported in our previous paper.¹⁰ Figure 3b shows cubical agglomerated M with some rodlike morphology. Further, as shown in Figure 3a-c, there are numerous smooth rodlike nanocrystals of M, allowing a large amount of mesoporous agglomerated nanocrystals on the surface of those M rods. These nanomaterials linked to each other and shaped the successive conductive network at [Ni²⁺]. These thin nanorods and cubes of M are quite capable of increasing the photoredox reactions during photocatalysis.³⁹ This type of



Figure 3. (a) SEM image of NFOPCN and rod and cubic agglomerated porous structures of (b) M (Fe₃O₄) and (c) 40 wt % M@NFOPCN hybrid nanomaterial.



Figure 4. (a and d) TEM images of M (Fe_3O_4) and NFO agglomerated over the P-CN sheets in 40 wt % M@NFOPCN. (b and e) HRTEM images presenting the lattice fringes of the planes of a 40 wt % M@NFOPCN nanocomposite and neat M. (c and f) SAED images of 40 wt % MNFOPCN and M.

increased surface area by rod and cubic morphology as well as agglomerated porous NFOPCN facilitates the enhancement of electron channelizing, enhancing the photocatalytic activity.⁴⁰ The specific surface area of the M@NFOPCN NPs estimated by the Brunauer–Emmett–Teller equation is 147.143 m² g⁻¹, which is much higher than that of NFOPCN, i.e., 37.316 m² g⁻¹.³⁷

3.4. TEM. The crystalline orientation and texture of the two neat samples NFOPCN and M and composite M@NFOPCN are confirmed by TEM, as shown in Figure 4a,b,d,e. Agglomerated porous structures composed of numerous pseudocubic crystals or small cubes signify magnetite, and its rodlike structure having lengths from 50 to 200 nm is observed. The arrangement of M NPs on a NFOPCN seed most likely leads to diverse structural parameters.²⁹ This



Figure 5. (a) EDS layered spectrum and (b) elemental EDS spectrum of M@NFOPCN.



Figure 6. (a) TGA for thermal stability. (b) VSM study for magnetic behavior of neat M and NFOPCN and M@NFOPCN.

noteworthy rodlike and pseudocubic crystal or small cube formation of a typical magnetite also goes well with the XRD patterns of as-prepared magnetite, which were obtained by annealing the precursor for M at 400 °C for 2 h. However, as soon as the composites of M and NFOPCN are obtained, agglomerated porous structures of numerous petite nanocrystals on the surface of nanorods appeared.⁴¹ This signifies the addition of Ni²⁺ ions to the system. The measured lattice spacing in Figure 4b are 0.251 and 0.148 nm, which assigned well with the (311) and (440) planes having corresponding d values (*d* = 0.2514 and 0.148 nm) of NFO (JCPDS 10-0325), respectively. Similarly, in Figure 4d, the lattice fringe spacings of 0.252 and 0.292 nm ensure the (311) and (220) planes of M.^{12,13} The SAED patterns of the photocatalyst shown in Figure 4c,f depict distinct rings and spots. It sheds light on the polycrystalline nature and structure of the composite in the synthesized materials. Agglomerated spherical NPs with a wide range of size distributions (5-15 nm) are observed. During the photocatalytic activity, the nanorod morphology of M is quite promising and facilitates the photoredox reactions by delaying the recombination and helping in the electron channelizing.

The lattice plane present in the agglomerates is well identified by SAED, confirming the presence of the spinel phase. The existence of elements like P, C, N, O, Fe, and Ni in the M@NFOPCN nanocomposite is confirmed by elemental color mapping obtained by EDS analysis, as given in Figure 5a,b. The obtained EDS spectra of M and NFOPCN, as shown in Figure 5b, distinctly show the well-defined spatial arrangement of all elements C, N, O, Ni, Fe, and P, confirming formation of the M, NFOPCN, and M@NFOPCN composite. The weight percentages of the elements are displayed in the inset of Figure 5b. However, the analogous ferrites cannot be differentiated by this. Hence, XPS spectra are needed for further confirmation.¹⁷

3.5. Thermogravimetric Analysis (TGA) and VSM. TGA and differential thermal analysis have been carried out to investigate the thermal stability and actual content of M on M@NFOPCN nanocomposites from 25 to 1000 °C in a N_2 atmosphere, and the results are shown in Figure 6a. As was already reported, an overall weight loss of the ferrite sample is almost 7.6%.⁴² Becaise of the burning of P-CN, the decomposition of P-CN occurs almost up to 800 °C. From earlier reports due to thermal decomposition, CN has two

weight loss regions from 100 to 400 °C and from 550 to 800 °C. Some weight loss within 100-400 °C may also be attributed to the adsorption of surface-bound H₂O.¹⁵ The criteria of exothermic measures were taken into account for the related heat-flow effects. The endothermic affair from 25 to 400 °C could be ascribed for the physical adsorption and removal of crystallized H₂O, from both the interlayer space and outer surface.³⁴ Again, as was already reported by Deng et al., the decomposition of hydroxides and carbonates that occurs between 400 and 800 °C as a second event is also endothermic, as shown in Figure 6a.⁴² From TGA, the weight loss obtained in the M@NFOPCN composites is around 21.034%, which is quite low in comparison to other reported ferrite g-CN composite samples.43 This confirms that the coupling of M with NFOPCN increases the thermal stability. The presence of NFO and P-CN may be responsible for the relatively low decomposition temperature in comparison to pure CN.³⁴ Hence, it is concluded that the stability of M is retained.

VSM was used to measure the magnetic measurements of asprepared M@NFOPCN with a peak field of 15 kOe. The characteristic behavior of prepared soft magnetic material (samples $V_1 = M@NFOPCN$ and $V_2 = NFOPCN$) are shown by the hysteresis loops in Figure 6b. An increase in the saturation magnetization (M_s) value is observed for $V_1 = M@NFOPCN$ rather than $V_2 = NFOPCN$ in Figure 6b. The M_s value of M@NFOPCN is higher than that of NFOPCN. As shown in Figure 6b, without any remanence and coercivity, M@NFOPCN possesses superparamagnetic character. The magnetic effect of M is well observed from Scheme 2. NFO is

Scheme 2. Schematic Representation of the Interactions within Two Magnetic Materials in Their Magnetic Field



an inverse spinel-type soft magnetic material having a crystal structure of $(Fe^{3+})_A[Ni^{2+},Fe^{3+}]_BO_4^{2-}$. Among the three main types A–O–A, A–O–B, and B–O–B, the superexchange interaction in A–O–B among the A and B sites is the major one. Because of less decomposition of the M and NFO phases, there is an increase in $[Ni^{2+}]$, resulting in the improved superexchange interactions in A–O–B, thus favoring the increase of $M_s^{37,38}$.

3.6. XPS. An XPS study has been carried out to give further confirmation about the surface chemical composition as well as oxidation states. The high-resolution spectra of Ni 2p, Fe 2p, C 1s, N 1s, O 1s, and P 2p for the M@NFOPCN photocatalyst and Fe 2p and O 1s for the M photocatalyst are represented in Figure 7a-f. As given in Figure 7a, the P 2p binding energy peak at ca. 133.7 eV confirms the presence of P incorporated in the CN structure through P–N coordination. In Figure 7b, the peak at 285.5 eV is attributed to C–O interaction.³³ The peaks at 284.5 and 287.7 eV are for neat graphitic carbon (C-C) and the distinctive peak for N-C=N bonding in P-CN, respectively. As shown in Figure 7c, the deconvoluted XPS spectra for N 1s have three peaks. The two at 398.1 and 399.4 eV confirm the sp²-hybridized nitrogen in pyridine like C=N-C and tertiary pyrrolic $N-(C)^3$ groups.⁴⁴ Another at 401.06 eV reveals the typical graphitic C-N-C peak.¹⁰ A blue shift in the binding energy of about 0.4 eV is observed for the O 1s peak for the M@NFOPCN nanohybrid, confirming a strong coupling within M and NFOPCN. The peaks at 529.8 and 531.2 eV are ascribed to the chemisorbed oxygen of surface-adsorbed hydroxyl (OH⁻) or H₂O-type oxygen vacancies and oxygen species, respectively, as depicted in Figure 7d, whereas the peak at 532.7 eV may be assigned for interstitial oxygen.45 In M@NFOPCN, without much conflict with the previously reported literature, two main peaks of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ are noticed at 856.3 and 875.3 eV as binding energies of Ni²⁺, as shown in Figure 7e. This core level is absent in the iron oxide XPS spectra, thus confirming it as nickel XPS spectra. After hybridization of the NFOPCN nanocomposites with M via in situ coprecipitation, followed by calcination growth, there is an upshift of ca. 2.7 eV for Ni $2p_{3/2}$ and 3.5 eV for Ni $2p_{1/2}$ at the binding energy of the peaks in M@NFOPCN compared with those for Ni in NFOPCN.¹⁰ Two shakeup peaks of Ni at around 860.5 and 891.2 eV as satellite peaks are observed at the high binding-energy regions of the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ edges. This blue shift of the binding energies for the Ni 2p peaks accounts for the firm coupling between NFOPCN and M in the nanohybrid, maybe via the Ni-O-Fe bands during the in situ calcination treatment.¹⁸ NFO and M show almost similar XRD patterns but different valences of the iron ion. This is cleared by their XPS spectra. The detailed chemical state of the iron ions was confirmed through deconvolution. M as a mixture of the Fe³⁺ and Fe²⁺ chemical states can be expressed as FeO/Fe₂O₃.²⁶ In Figure 7f of the high-resolution XPS spectrum of Fe 2p, two major peaks of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ situated at 711.2 and 725.4 eV are found.^{10,36,43} The Fe 2p peak well-fitted with the Fe³⁺ and Fe²⁺ peaks confirms the presence of M in the oxidation layer. Again the upshifts of ca. 2.0 eV for Fe $2p_{3/2}$ and 4.3 eV for Fe $2p_{1/2}$ for the binding energy of the peaks in M@NFOPCN further confirm the strong coupling within M and NFOPCN.

4. OPTICAL BEHAVIOR AND ELECTRONIC BAND STRUCTURE

4.1. UV–Vis DRS. Parts a–d of Figure 8 depict the UV–vis DRS spectra of 30-50 wt % M@NFOPCN, NFO, pure P-CN, neat M, and hybrid nanocomposite samples in the range of 200-800 nm. The photon receptive behavior of the M@ NFOPCN nanocomposite is expressed through the optical band gap and absorbance range. As reported in our previous paper, a sharp absorption edge at 450 nm for P-CN corresponding to a band gap of 2.7 eV and a wide range

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Figure 7. XPS spectra of 40 wt % M@NFOPCN: (a) P 2p; (b) C 1s; (c) N 1s; (d) O 1s; (e) Ni 2p; (f) Fe 2p.



Figure 8. (a) UV-vis spectra of all neat compounds and composites. (b-d) UV-vis DRS spectra of pure NFO, M, and pure P-CN.

within 200–720 nm for NFO analogous to a band gap of 1.7 eV were already established.¹⁰ In Figure 8a, a bathochromic shift toward the near-IR range was apparently observed with an increase of the M weight percentage in M@NFOPCN, which may be ascribed to the interface interaction between NFOPCN and M in comparison to NFOPCN. With increased M weight percentage, the absorption intensity of the asprepared different weight percentage samples also notably strengthened with more light-harvesting capacity.¹⁷

Further, the Kubelka–Munk equation was used to estimate the band gap value.

$$\alpha h \nu = k (h \nu - E_{\rm g})^{n/2} \tag{1}$$

where α = absorption coefficient, n = type electronic transition, $E_{\rm g}$ = optical band-gap energy, ν = frequency of light, and A = proportionality constant, i.e., $n = \frac{1}{2}$ for a direct type transition and n = 2 for an indirect type transition, and in our case, the materials suffer direct transitions, respectively.

In the case of M, the strong absorption with an energy of 1.6 eV covering at ~690 nm is due to the transition of an electron from the valence band (VB) O 2p to the crystal field (e_{σ}) on the tetrahedral site. Another absorption around ~565 nm assigned to the recombination of electrons from $e_g \rightarrow t_{2g}$ on the octahedral site and the transition of $t_{2g} \rightarrow e_g$ and O $2p \rightarrow$ t2g in the tetrahedral site. The oxygen vacancies as well as electron traps on the tetrahedral site are responsible for near-IR absorption at around ~840 nm. Similarly, in NFO, the transition of Ni²⁺-O-Fe³⁺ to Ni⁺-O-Fe⁴⁺ is accountable for a strong absorption up to around 720 nm. The $n-p^*$ transition in the heptazine/triazine ring system of P-CN, due to the lone pair of electrons on the nitrogen atoms, is liable for a absorption band edge at 450 nm.¹⁰ Hence, under the same visible-light irradiation, the superior light absorption by the prepared nanocomposites helps in the production of more electron-hole pairs, which consequently results in better photocatalytic activity. However, when the amount of M is increased in M@NFOPCN, M may act as a reunion center for photogenerated exciton pairs, thus reducing the photocatalytic activity of the nanocomposites.⁴⁶

4.2. PL Spectral Analysis for the Confirmation of Photogenerated Electron–Hole Separation. Figure 9 represents the characterized PL spectra for pure M, NFOPCN,



Figure 9. PL spectra of neat M (Fe₃O₄), NFOPCN, and 30–50 wt % M@NFOPCN at excitation wavelength λ_{ex} = 330 nm.

and 30-50 wt % M@NFOPCN with an excitation wavelength of 330 nm and a Gaussian-like peak at ca. 435 nm.⁴⁷ The PL emission spectra give details about the recombination, migration, and shifting of photogenerated charge carriers. From Figure 9, it can be observed that the peak intensity of the 40 wt % M@NFOPCN photocatalyst is guite low in comparison to those of M, NFOPCN, and other prepared photocatalysts. This indicates an improved charge-separation efficiency in M@NFOPCN. As given in our previous work, the foremost emission peak for the pure P-CN sample is centered at about 440 nm and is responsible for the band-band PL trend, with the light energy almost equal to the band-gap energy of P-CN.¹⁰ As was already established, phosphorus doping enhances photogenerated electron-hole pair separation, which was initiated by an $n \rightarrow \pi^*$ electronic transition in P-CN obtained from the lone pair of electrons available on the nitrogen atom.¹⁰ Also, a weak peak for NFO was obtained because of defects of NFO from excitation PL as well as from the surface oxygen vacancies. Combining NFO with P-CN brings a noticeable drop off in the intensity of the PL spectra.^{10,45} However, the UV-vis absorption statistics of M and the 30-50 wt % M@NFOPCN nanocomposite do not show any peak as given above in the Gaussian wavelength range. Hence, structure-related defects are more accountable than band-edge transitions. Because of its narrow-band-gap value (1.6 eV), M might show high PL intensities, leading to fast recombination. The d-orbital electrons responsible for the narrow band gap of M are accountable for the high electrical conductivity. Further, in a restricted volume, quantum confinement of the charge carriers of M due to size-related quantization may be responsible for the strong emission peaks. This effect may be ascribed to the electron-channelizing capacity of P-CN; it traps the photoexcited electrons of M on its π skeleton and checks the e^{-}/h^{+} recombination rate. As a result, the electron-hole pair recombination rate is suppressed, and the charge separation increases in the M@NFOPCN nanocomposite.¹⁰ Therefore, M@NFOPCN nanocomposites are likely to achieve first-rate photocatalytic activity toward the degradation of antibiotics. Further, EIS measurement justifies these PL data.

4.3. Photogenerated Electron-Hole Transport from EIS Analysis. Among the prepared photocatalysts, 40 wt % M@NFOPCN has the best efficiency. This was further confirmed by EIS measurement. Distinctive Nyquist diagrams representing the reaction rate at the surface of the electrode, charge separations obtained by incident photons, charge transfer, and resistance given by the photocatalysts are given in Figure 10. According to its principle, the arc radius of the Nyquist plot varies inversely with the charge-separation efficiency of the working electrode; i.e., the smaller the semicircle radius of the photocatalyst, the less the interface charge-transfer resistance and thus the more active the separation of photogenerated e⁻/h⁺ pairs and vice versa.⁴⁸ Figure 10 shows the Nyquist plots for neat M, NFOPCN, and M@NFOPCN composites at zero biasing potential. Generally, the conductivity of the catalyst is expressed by the semicircular part in the high-frequency region and the Warburg resistance by the straight line in the low-frequency region.⁴⁹ The arc radius for M, NFOPCN, and synthesized M@NFOPCN are found to be 63, 120, and 49 Ω , respectively. Delocalization of the lone electron pairs in P-CN, electron hopping in M from Fe²⁺ to Fe³⁺, and hole shifting from Ni³⁺ to Ni²⁺ in NFO are the main sources of conductivity.¹⁰ Hence, M@NFOPCN,



Figure 10. Nyquist plots for the NFOPCN, M, and M@NFOPCN nanocomposites.

with the smallest arc indicating the utmost electron—hole pair separation and with the enhanced straight line part for superior conductivity, proved to be a better photocatalyst. P-CN π conjugation is the most important reason behind this result because it channelizes the photoexcited electrons through the framework and thus decreases the reunion process.

4.4. Electrochemical Study for MS, LSV, and PC Measurements. The flat band potentials $(E_{\rm fb})$ of NFO, P-CN, and M were investigated by the MS plots (Figure 11a-c). The positive slope of the MS plot is representative of n-type character, while negative slope is p-type character. The flatband potentials are +1.54, -1.47, and -0.6 V for NFO, P-CN, and M versus Ag/AgCl electrode, respectively, or +2.11, -0.87, and -0.0012 V versus normal hydrogen electrode (NHE). The $E_{\rm fb}$ value of p-type semiconducting materials is close to the VB potential and that of n-type materials is close to the conduction band (CB) potential. Again, to be in harmony, considering the carrier concentration and effective mass of the electron (m_e), the conduction band minimum (CBM) is 0.1 V lower than $E_{\rm fb}$.⁵⁰ The Nernst equation as given below is used for the conversion.

$$E_{\rm fb}(\rm NHE) = E_{\rm fb}(\rm pH)$$

= 0, vs Ag/AgCl) + E(Ag/AgCl) + 0.059pH (2)

As explained and reported earlier, because of the shifting of holes from Ni³⁺ to Ni²⁺, NFO accounts for p-type behavior. The actual oxidation and reduction potentials in the nano-composites are determined from the band-edge potentials (VB and CB) of the samples calculated from the extent of the band gap ($E_g = VB - CB$). The VB positions as obtained from the Tauc/Davis–Mott model derived from the UV–vis DRS spectra are found to be 2.11, 1.8, and 1.68 eV for NFO, P-CN, and M, respectively, and the CB positions are +0.4, -0.8, -0.0012 eV for NFO, P-CN, and M, respectively. Because of the CB and VB positions, we put on extra impending into the mechanism during this MS plot.¹⁰



Figure 11. MS plots of (a) NFO, (b) P-CN, and (c) M.

4.4.1. LSV. The charge-separation efficiencies of M, NFOPCN, and M@NFOPCN were predicted by their photocurrent densities. Under light irradiation, it was clearly found out that M produces an anodic photocurrent of nearly 1.37 mA cm⁻², thus an n-type semiconductor. Furthermore, it was also shown that NFOPCN produced both anodic $(+531.38 \ \mu A \ cm^{-2})$ and cathodic $(-127.43 \ \mu A \ cm^{-2})$ photocurrents at +1.5 and -0.5 V, respectively.¹⁰ However, a noteworthy increase was observed toward the anodic direction with respect to the applied bias, confirming an n-type semiconductor, whereas NFO is proven to be a p-type semiconductor under light conditions showing a cathodic current density of $-96.64 \ \mu A \ cm^{-2}$ and finally ending in a saturated value.¹⁰ In contrast, under the forward and reverse applied bias potentials, a 40 wt % M@NFOPCN n-n-p-type nanocomposite generates different photocurrents. Further, with positive bias potential, there is a sharp increase in the photocurrent and nearly 1.87 mA cm⁻² is achieved at +1.5 V, whereas a negligible reverse photocurrent is experienced at -0.5 V, as shown in Figure 12. Both the oxidation and



Figure 12. Photocurrent densities of M, NFOPCN, and M@ NFOPCN nanocomposite.

reduction responses of M@NFOPCN are due to the anodic and cathodic photocurrents. Hence, the combined synergetic effect of M, NFOPCN, and M@NFOPCN resulted in a higher photocurrent response.

4.4.2. Supercapacitive (SC) and Charge–Discharge (CD) Study by CV Analysis. SC nature of M@NFOPCN has been evaluated by means of CV. Standard Ag/AgCl, M@NFOPCN composite, and platinum electrodes were used as reference, working, and counter electrodes, respectively. The scan rate was calibrated at a scan rate of 10 mV s^{-1} by taking 3 M KOH as the standard electrolyte. Transition-metal ions Ni^{2+/3+} and Fe^{3+/2+} present in M@NFOPCN undergo redox reactions and are thus responsible for oxidation reduction peaks of CV, as shown in Figure 13a. The scan rate was varied as 10, 20, 40, and 100 mV s^{-1} while keeping the potential window constant. During the electrochemical process at high scan rates, only surface species of the electrode can participate, whereas at low scan rates, time allows for the diffusion of ions into the electrode material, thus utilizing active sites of the electrode.⁵¹ With increasing scan rate, there is no significant change in the shape of the CV curves, indicating a fast surface kinetic response from the electrode material with respect to the rapidly varying potential step and firm synergetic interaction within the electrode surface and electrolyte. Thus, the pseudocapacitive behavior of the M@NFOPCN electrode is the output of those redox peaks. Again, this confirms its large active surface area for energy storing. The typical CD plots of the electrodes at 0-0.5 V Ag/AgCl are shown in Figure 13b. The shape of the discharging curves implies Faradaic interaction, thus leading to SC properties.

5. INVESTIGATION OF THE PHOTOCATALYTIC PERFORMANCE OF M@NFOPCN

The photocatalytic efficiencies of M@NFOPCN were evaluated by CIP degradation as well as H_2 evolution under visible-light irradiation.

5.1. Photocatalytic Reduction of CIP. In order to identify the photocatalytic efficiency of M@NFOPCN, CIP, a major antibiotic of ecosystem, was considered as a specimen to be degraded under solar-light irradiation. The photocatalytic performance was investigated by taking into account the degradation of a 20 mg L^{-1} aqueous CIP solution exposed to sunlight. The same experimental conditions were followed for a comparison study of the prepared ternary and parent catalysts. The type of reaction was a photocatalysis process rather than photolysis, which was also confirmed by performing degradation without the photocatalyst. It was observed that not more than 1% of the initial concentration of CIP was



Figure 13. (a) CV analysis and (b) CD curves of M@NFOPCN.

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a b In (C/C₀) ပီပို -1.4 40%M@(NFOPCN) 40%M@(NFOPCN) -1.3 45%M@(NFOPCN) 50%M@(NFOPCN) 5%M@(NFOPCN) 50%M@(NFOPCN) 30%M@(NFOPCN) 30%M@(NFOPCN) 0.2 -2.6 M(Fe₃O₄) M(FerOa) NFOPCN NFOPCN .2 15 30 Time (min) 45 10 20 50 30 Time (min) 40 c d Percentage of degradation (%) 0.6 C/C_a(%) 44 6M@(NFOPCN) M@OFOPC M@(NFOPC) %M@(NFOPC 0.2 Recycli Photocatalyst nin

Figure 14. (a) Kinetic study of CIP degradation by M@NFOPCN in every successive time interval. (b) Kinetics of CIP decolorization in the first cycle. (c) Assessment of the degradation percentage of CIP by NFO, P-CN, and 30-50 wt % M@NFOPCN nanocomposites. (d) Reusability plot of CIP degradation over M@NFOPCN for four consecutive degradation experiments.



Figure 15. (a) XRD of the used and unused M@NFOPCN. (b) SEM image of the used M@NFOPCN.

decreased. Initially the adsorption-desorption of CIP on the catalysts was carried out in the dark by stirring for 30 min at pH = 6. The accomplishment of adsorption-desorption equilibrium was confirmed from the invariance in the C/C_0 value, as shown in Figure 14a, and the results of the kinetic study performed, as shown in Figure 14b, are given under 5.2. The residual concentration of CIP was measured after 1 h of exposure to sunlight at an outdoor temperature $(35 \pm 5 \text{ °C})$.⁵² Degradations of around 43% and 48% for neat NFOPCN and M are observed, whereas, surprisingly, an excellent 90%

degradation was achieved by the 40 wt % M@NFOPCN nanocomposite, as shown in Figure 14c. CIP degradations by 30, 45, and 50 wt % M@NFOPCN nanocomposites were 52%, 73%, and 62%, respectively. With increasing weight percentage of M, the number of M@NFOPCN nanocomposites and adsorption sites available on the M@NFOPCN surface also improved, resulting in an augmentation in the degradation efficiency. However, a further increase in the concentration of M in M@NFOPCN (from 40 to 50 wt %) decreases the degradation. This may be due to light scattering, agglomeration

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Figure 16. (a) Percentage degradation of CIP over M@NFOPCN in the presence of scavenging agents. (b) Confirmation of $^{\circ}$ OH generation through a TA test. (c) $^{\circ}$ O₂- generation by a NBT test in M@NFOPCN.

of nanoparticles, and a screening effect, which hinders solar light from reaching active sites and thus decreases the photocatalytic degradation efficiency from 90% to 62%.^{10,52}

5.2. Kinetics of CIP Reduction. A kinetic study of the solar photodegradation of CIP solutions by M@NFOPCN was carried out in detail. Initially, to accomplish adsorption–desorption stability, 20 mg of M@NFOPCN was dissolved in 20 mL of the antibiotic CIP solution and set aside in the dark under constant stirring for 30 min. Then, at the outset, a CIP solution with the best obtained photocatalyst, as given above, was taken and subjected to solar irradiation for 1 h, giving a time interval of 15 min. The remaining solution was collected at 15 min time intervals and studied to determine the reaction kinetics. A 20 mg L⁻¹ CIP solution was degraded by 20 mg L⁻¹ M@NFOPCN in 60 min under solar-light irradiation. Centrifugation, followed by filtration, was used to extract degraded CIP and then analyzed using a UV spectrophotometer (Figure 14c).

From the results obtained, it was concluded that M@ NFOPCN efficiently irradiated 90% CIP under the above given experimental conditions. The rate constant of CIP degradation was found to be 0.0990 min⁻¹, and the data appeared to be fitted to a pseudo-first-order reaction, $C_t/C_0 = e^{-kt}$, where C_t , C_0 , and t stand for the concentration of the

solution at reaction time *t*, initial concentration of the solution, and reaction time, respectively, as shown in Figure 14a,b.^{53,10} The rate of degradation was found by the following equation: photodegradation rate = $(C_0 - C/C_0) \times 100$. In summary, from all of the above results, the rate constant in the first-order kinetics of 40 wt % M@NFOPCN is too high compared to those of neat NFOPCN (0.0490 min⁻¹) and M (0.0210 min⁻¹), proving that a better composite has been formed.

5.3. Reusability and Stability Study. The reusability and stability of 40 wt % M@NFOPCN after degradation of CIP were also tested for industrial-scale applications. The obtained nanocomposite was washed carefully using ethanol and H_2O , followed by air oven drying prior to the subsequent degradation experiment. As shown in Figure 14d, although there is a little reduction in the photocatalytic performance, the catalyst has proven to be stable for up to four cycles. As shown in Figure 15a, there is a decrease in the intensity in XRD, and in Figure 15b, a SEM image of the used sample again confirms the stability.

5.4. Effect of Scavengers for the Proposed Mechanism of CIP Degradation. During the photocatalytic activity, various photogenerated active species covering hydroxyl radicals ($^{\circ}OH$), superoxide radicals ($^{\circ}O_2^{-}$), holes (h⁺), and electrons (e⁻) were used in the photocatalytic reactions

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Scheme 3. Schematic Presentation of Degradation of CIP and Evolution of H₂ over M@NFOPCN

Scheme 4. Structure of CIP and Its Oxidation and Reduction



headed for the degradation of pollutants. Trapping experiments were performed to identify their effects. During this study, isopropyl alcohol (IPA), 1,4-benzoquinone (p-BQ),

Table 2. Amount of H₂ Evolution by the Prepared Magnetic Photocatalyst

neat and composites	light source used	H_2 evolution $(\mu mol h^{-1})$	ref
M@NFO	xenon arc lamp (l > 420 nm)	80	prepared photocatalyst
NFOPCN	xenon arc lamp (l > 420 nm)	904	prepared photocatalyst
30 wt % M@ NFOPCN	xenon arc lamp (l > 420 nm)	450	prepared photocatalyst
45 wt % M@ NFOPCN	xenon arc lamp (l > 420 nm)	520	prepared photocatalyst
50 wt % M@ NFOPCN	xenon arc lamp (l > 420 nm)	774	prepared photocatalyst
40 wt % M@ NFOPCN	xenon arc lamp (<i>l</i> > 420 nm)	924	prepared photocatalvst

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Figure 17. (a) Rate of H₂ evolution shown by various prepared catalysts. (b) Run graph showing the photostability toward H₂ evolution.

ethylenediaminetetraacetic acid (EDTA), and dimethyl sulfoxide (DMSO) were used as scavengers to arrest $^{\circ}OH$, $^{\circ}O_{2}^{-}$, h⁺, and e⁻, respectively.¹⁰ Without any scavenger, the degradation efficiency of M@NFOPCN for 10 ppm of CIP was 90% in 60 min and increased to almost 98% for DMSO as the scavenger. Conspicuously, 5 mM IPA and p-BQ decreased the degradation efficiency to almost 35% and 55%, respectively. By using EDTA as the scavenger, the degradation was found to be almost the same as that of the neat photocatalyst.⁵² Hence, it was observed that, after the addition of IPA and PBQ, around 55% and 35% of the CIP removed was quenched, indicating the significant contributions of the •OH and $\bullet O_2^-$ radicals for CIP degradation. The consequence of the percentage of degradation after using scavenging species is displayed in Figure 16a. The types of reactive oxygen species produced in the M@NFOPCN system are identified by the scavengers.⁵³ As p-BQ and IPA were added, there were significant inhibitory effects on CIP degradation. From Figure 16a, it is clearly observed that [•]OH is one of the major oxidative species for oxidizing CIP, obtained by the reaction between ${}^{\bullet}O_2^{-}$ and H₂O. Hence, it is concluded that the major active species should be $^{\bullet}OH$ rather than $^{\bullet}O_2^{-}$ and h⁺, which is in good agreement with the obtained results.

5.5. Test for 'OH Radical Confirmation [Terephthalic Acid (TA) Test]. TA was used as a probe reagent to confirm the 'OH radicals as the major active species. Because TA is insoluble in a neutral or acidic medium, 5 mM TA was dispersed in an equimolar amount of NaOH, followed by the required quantity of catalyst, kept under solar light for 30 min, and then subjected to PL measurement in order to confirm the formation of 2-hydroxyterephthalic acid (TAOH). There was no reaction between TA with other radicals and molecules ($^{\circ}O_{2}^{-}$, $^{\circ}OH$, and $H_{2}O_{2}$) in the solution, and it voluntarily interacts with 'OH. The emission peak at $\lambda = 424$ nm proves the formation of TAOH, as shown in Figure 16b. The higher the intensity of the PL peak, the more the 'OH radicals are formed. The obtained 'OH radicals in $H_{2}O$ could be related to the fluorescence intensity of TAOH:⁵³ 'OH + TA = TAOH.

5.6. Confirmatory Test for ${}^{\bullet}O_2^{-}$ Radicals by a Nitroblue Tetrazolium (NBT) Test. The formation of ${}^{\bullet}O_2^{-}$ radicals is confirmed by a NBT test as follows. A total of 0.01 g of the prepared catalyst M@NFOPCN was dispersed in 10 mL of a prepared 5×10^{-5} M solution of NBT, and the resulting solution was irradiated for 30 min under solar light. Then the solution was analyzed after separation of the

photocatalyst using a UV spectrophotometer. As shown in Figure 16c, the concentration of NBT appeared to be decreased, confirming the presence of ${}^{\bullet}O_2^{-}$ during the degradation process.

5.7. Proposed Z-Scheme Mechanism in M@NFOPCN. O the basis of the obtained band energies and band-edge positions from MS and Tauc plots as well as foregoing analyses, three types of mechanisms for charge transfer can be predicted [lane-1(a,b) and lane-2], as given in Scheme 3. M, NFO, and P-CN of M@NFOPCN are excited under solar light, and this thus allows their photoinduced electrons and holes to accumulate on their CB and VB and permit them to be channelized in the proper path, respectively. As was already established in our previously published literature, there exists a Z scheme at the interface of NFO and P-CN in 20 wt %NFOPCN, proving it as one of the best photocatalysts. Further taking into account the interfaces obtained by HRTEM of the neat materials and composites, three types of charge transfer can be considered within M, NFO, and P-CN, as shown in Scheme 3. Through the lane-1a mechanism (i.e., type II), if M would have attached to NFO, then charge transfer at the M-NFO interface would have taken place by channelizing the electrons from the CBM of M to that of NFO and holes in the opposite direction. Therefore, there would be a drastic reduction in the formation of *OH radicals due to the VB of M(1.68) being less positive than 1.99. However, this is against the scavenger test, and the generation of 'OH was already confirmed by the TA test. Hence, it can be confirmed here that this type of lane-1 (a) charge transfer at the M-NFO interface does not exist in M@NFOPCN.

Further, within M and P-CN, because the CBM of M (-0.0012) is lower than that of P-CN (-0.84), electrons migrate to M. Also, the VBM of M is less positive than that of P-CN; hence, holes gathered at M, which makes it a recombination center, as presented in lane-1b. This goes against the experimental observations of the PL study. Moreover, with this type of charge transfer, the feasibility of $^{\circ}O_2^{-}$ and $^{\circ}OH$ formation at the M–P-CN interface is obsolete because the CBM of M is more positive than the $O_2/^{\circ}O_2^{-}$ potential (-0.33 eV vs NHE) and the VBMs of M and P-CN are less positive than $OH/^{\circ}OH$ (+1.99 eV vs NHE). However, through NBT and TA tests, adequate triggering of $^{\circ}OH$ and $^{\circ}O_2^{-}$ radicals in the 40 wt % M@NFOPCN nanocomposite confirms them as the major active species. Thus, the VBM of NFO is confirmed as taking the lead on $^{\circ}OH$ generation.

Additionally, the CBM of NFO is more positive than the O_2/O_2^- potential; hence, it is not capable of producing O_2^- . From the above results, the proposed lane-1a and -1b pathways are not feasible for M@NFOPCN to be a good photocatalyst. However, 40 wt % M@NFOPCN could degrade 90% of 20 ppm of CIP in 60 min. So, ultimately, it can be inferred that a closed interface-coupled Z-scheme (CICZ) type of chargetransfer mechanism should exist here. Thus, it further confirms the existence of one Z scheme within NFO (VB, +2.1 eV; CB, +0.4 eV), P-CN (VB, +1.8 eV; CB, -0.8 eV) and another Z scheme within M and P-CN, resulting in an inverted CICZ system.⁵⁰ Thus, this type of system is beneficial with oxidant (PCN), reductant (NFO), and magnetically recyclable component M. At this point, both ferrites, NFO and M, are good donors and P-CN is a good acceptor, working all together under a wide range (UV to near-IR).54 Hence, the introduction of M enables the dual Z-scheme charge-transfer path to be accomplished through better separation efficiency and stronger redox capability of photogenerated holes and electrons. The oxidation and reduction of CIP are shown in Scheme 4.

CIP through Its Oxidation and Reduction. The oxidation and reduction of CIP are shown in Scheme 4.

Step 1: Photoexcitation of an e^{-}/h^{+} pair.

 Fe_3O_4 @NFOPCN + $h\nu$

$$\rightarrow \text{Fe}_{3}\text{O}_{4}(\text{@NFOPCN}(e^{-}cb + h^{+}\nu b)$$
(3)

$$Fe_3O_4 + h\nu \rightarrow Fe_3O_4(e^- + h^+)$$
(4)

$$P-CN + h\nu \to P-CN(e^- + h^+)$$
(5)

$$NFO + h\nu \rightarrow NFO(e^- + h^+)$$
 (6)

$$NFO@P-CN(e^{-} + h^{+}) \rightarrow NFO(h^{+}) + P-CN(e^{-})$$
(7)

Step 2: Formation of a OH[•] radical

$$Fe_3O_4@NFOPCN(h^+\nu b) + H_2O \rightarrow H + ^{\bullet}OH$$
 (8)

$$NFO(h^{+}) + H_2O \rightarrow H^{+} + {}^{\bullet}OH$$
(9)

Step 3: Conversion of the adsorbed oxygen into the superoxide radical

$$Fe_{3}O_{4}@NFOPCN(e^{-}cb) + O_{2} \rightarrow O_{2}^{-}$$
(10)

$$P-CN(e^{-}) + O_2 \rightarrow P-CN + {}^{\bullet}O_2^{-}$$
(11)

Step 4: Neutralization of ${}^{\bullet}O_2^{-}$ to HO_2^{\bullet} by protonation

$${}^{\bullet}\mathrm{O_2}^- + \mathrm{H}^+ \to \mathrm{HO_2}^{\bullet} \tag{12}$$

Step 5: Degradation of CIP by radicals

 $^{\bullet}OH$, HO_2^{\bullet} , $^{\bullet}O_2^{-}$ + CIP $\rightarrow CO_2$ + H_2O + other simpler molecules

5.8. Proposed Photocatalytic H_2 Evolution Mechanism. An inferential schematic mechanism proposed for the water splitting and photocatalytic H_2 evolution of the assynthesized 30–50 wt % M@NFOPCN, M, and pristine NFOPCN is shown in Scheme 3. All of the synthesized composites are tested for H_2 evolution under the effect of visible-light irradiation ($\lambda \ge 400$ nm). Under the same ambient setting, a reference testing was performed only with pure methanol before the proposed experiment was performed. However, no evolution of H_2 gas was found. After loading 40

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wt % M on NFOPCN, the rate of H₂ evolution increases to 924 μ mol h⁻¹ under visible light compared to NFOPCN (904 μ mol h⁻¹) and M (240 μ mol h⁻¹). The efficiency of the catalyst is monitored based on the fact that the potential of the CB should be more negative than the reduction potential of H_2O/H_2 (0 V vs NHE, pH = 0) for H_2 evolution.^{1,26,55} Out of the working catalysts, P-CN and M are suitable for producing H_2 because of their CBM positions (-0.84 and -0.0012 eV). Hence, it is clear from the results that all three components in this ternary system are well participants for H_2 evolution. Again, the two binary Z-scheme entities during formation of the CICZ system properly channelize and enhance the separation of e^- and h^+ . On the basis of our previous literature, although NFO is inactive and P-CN is less active toward H₂ evolution (234 mmol h^{-1}) under visible-light irradiation, NFOPCN is quite competent for producing H_2 (904 μ mol h^{-1}). H₂ evolution by the as-prepared 30-50 wt % M@ NFOPCN nanocomposites, neat and M@NFO, is summarized in Table 2. From the study, if the M interface would have attached to NFO, then it would have resulted in negligible H₂ production. However, because the result was different, M must have interracially composited at P-CN side, confirming the CICZ. Again from the rate of H₂ evolution, the accumulation of enough e⁻ at the CB of P-CN is confirmed, thus further giving a green signal to the CICZ. Hence, finally the electrons from the VBMs of M and NFO through Z schemes accumulated at the CBM of P-CN, enhancing H₂ evolution.

$$M@NFOPCN + 2h^{+} + 2e^{-}CBM(P-CN) + h^{+}VBM(M)$$
$$+ h^{+}VBM(NFO)$$
$$\rightarrow 2e^{-}CBM(P-CN) + 2H^{+} + H_{2}(\uparrow) \qquad (13)$$

The plausible conversion efficiency of photocatalytic H_2 evolution (924 μ mol h⁻¹) was calculated by means of the following equation:

apparent conversion efficiency

 $= (stored chemical energy/incident light energy) \times 100$ (14)

stored chemical energy = combustion heat of H_2

 $(\Delta H_{\rm c} \text{ in kJ mol}^{-1}) \times \text{number of moles of H}_2$

where

$$\Delta H_{\rm c} = 285.8 \text{ kJ/mol for } H_2 O \rightarrow H_2 + \frac{1}{2}O_2$$
 (16)

The stored chemical energy was 0.073×10^{-6} mol s⁻¹ × 285.8 kJ mol⁻¹ = 0.000073 kJ = 0.073 W. Again, the incident light energy was measured to be 70 mW cm⁻² × 3.14 × (1.5)² = 0.4947 W.

Hence, the apparent conversion efficiency of photocatalytic H_2 was 14%.

The extent of H_2 furnished by the photocatalyst with stability and time was evaluated through a reusability test. The stability was found to be maintained for up to four runs, as shown in Figure 17a,b.

In summary, the investigation reports on the in situ fabrication of a double-Z-scheme-based novel magnetically retrievable Fe₃O₄@NiFe₂O₄/P-g-C₃N₄ nanocomposite, followed by combustion and calcination. The formation of a double-Z-schemebased nanocomposite at the interface of Fe₃O₄, P-g-C₃N₄, and NiFe₂O₄ was recognized by XPS, HRTEM, and scavenger test analysis. Among the fabricated composites, the 40 wt % M@ NFOPCN nanocomposite showed superior activity under optimized conditions. The remarkable photocatalytic activity (90% CIP degradation) of M@NFOPCN compared to M and NFOPCN can be assigned to functionalized e⁻ and h⁺ charge separation, which was justified by EIS and PL analysis. The anodic photocurrent at +1.5 V around 1.87 mA cm⁻² and SC nature shown by M@NFOPCN further support it as a better photocatalyst. A good amount of H₂(energy) is confirmed with 14% conversion efficiency. Above all, the incorporation of M significantly enhances the recyclability and stability of the photocatalyst. The M_s value of 28 emu g⁻¹ of M@NFOPCN establishes it with superparamagnetic nature. Of course, with higher weight percentage of M coupling, the photocatalytic effectiveness is reduced due to agglomeration of M and thus decreasing active sites. However, an effective construction like M@NFOPCN can accomplish an excellent photocatalytic performance with a recyclable, wide-bandwidth photocatalyst under sunlight.

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Notes

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