Enhanced solar-light-driven photocatalytic properties of novel Z-scheme binary BiPO₄ nanorods anchored onto NiFe₂O₄ nanoplates: Efficient removal of toxic organic pollutants

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Abstract
Global environmental problems have been increasing with the growth of the world economy and have become a crucial issue. To replace fossil fuels, sustainable and eco-friendly catalysts are required for the removal of organic pollutants. In this study, nickel ferrite (NiFe₂O₄) was prepared using a simple wet-chemical synthesis, followed by calcination; bismuth phosphate (BiPO₄) was also prepared using a hydrothermal method. Further, NiFe₂O₄/BiPO₄ nanocomposites were prepared using a hydrothermal technique. Numerous characterization studies, such as structural, morphology, surface area, optical, photoluminescence, and photoelectrochemical investigations, were used to analyze NiFe₂O₄/BiPO₄ nanocomposites. The morphology analysis indicated a successful decoration of BiPO₄ nanorods on the surface of NiFe₂O₄ nanoplates. Further, the bandgap of the NiFe₂O₄/BiPO₄ nanocomposites was modified owing to the formation of a heterostructure. The as-prepared NiFe₂O₄/BiPO₄ nanocomposite exhibited promising properties to be used as a novel heterostructure for tetracycline (TC) and Rhodamine B (RhB) removal. The NiFe₂O₄/BiPO₄ nanocomposite degrades TC (98%) and RhB (99%) pollutants upon solar-light irradiation within 100 and 60 min, respectively. Moreover, the trapping experiments confirmed the Z-scheme approach of the prepared nanocomposites. The efficient separation and transfer of photogenerated electron-hole pairs rendered by the heterostructure were confirmed by utilizing electrochemical impedance spectroscopy, photocurrent experiments, and photoluminescence. Mott–Schottky measurements were used to determine the positions of the conduction and valence bands of the samples, and the detailed mechanism of photocatalytic degradation of toxic pollutants was projected and discussed.

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Introduction

In recent years, extensive efforts have been exerted to enhance the solar energy utility in various fields of applications, such as photocatalysis, photovoltaic cells, catalytic hydrogen generation, and energy storage devices (Acar and Dincer, 2019; Khan et al., 2019; Wang et al., 2017). Global environmental problems are crucial issues and have been increasing with the growth of the economy worldwide. Furthermore, water is considered a critical resource for mankind as well as for other creatures on earth. However, rapid growth in industrialization requires a significant amount of water for processing and releasing hazardous organic contaminants (Nguyen et al., 2020; You et al., 2019). Recently, the presence of pharmaceutical antibiotics in wastewater has gained significant consideration as toxic pollutants owing to its high impact on human lives. Among various pharmaceutical antibiotics, tetracycline (TC) is one of the most commonly used antibiotics and is extremely water soluble (Fanourakis et al., 2020; Lee et al., 2017; Lu et al., 2019). The TC antibiotics move into the soil by various paths and cause harmful effects directly on the soil ecosystem as well as on human health through a series of physical, chemical, and biological processes. Therefore, as a replacement of fossil fuels, sustainable eco-friendly catalysts are required to degrade organic pollutants (Song et al., 2017b). Moreover, a progressive heterogeneous photocatalysis and photoelectrochemical analysis have gained significant attention for water treatment. Thus, photoelectrochemical analysis coupled with the removal of toxic pollutants is a potentially expandable technique for solar energy consumption, which is expected to better solve energy and environmental issues (Song et al., 2018).

Over the years, owing to their excellent catalytic activity, low cost, natural abundance, and stability, metal oxide semiconductors have been extensively investigated as photocatalysts for the removal of pollutants from wastewater (Koutavarapu et al., 2020b). The effective usage of solar energy is crucial to water oxidation and photocatalytic removal of toxic pollutants (Zhang et al., 2019). Therefore, scientific and engineering groups have been working extensively to develop heterogeneous photocatalysts for environmental applications under solar irradiation (Zhang et al., 2016). In the past few decades, magnetic semiconductors have been used for the photocatalytic activity and water oxidation. However, most of the materials studied till date are limited by inadequate bandgap and mobility of charge carrier (Dietl et al., 2019). Among these materials, nickel ferrite (NiFe$_2$O$_4$) has been renowned as a potentially appropriate visible material for organic pollutant degradation and water oxidation, owing to its acceptable bandgap ($1.73$ eV), non-toxicity, and moderate magnetic separation (Gebreslassie et al., 2019). However, the catalytic performance of pure NiFe$_2$O$_4$ is fairly low owing to its rapid reunion of photo-induced charge carriers (Moradi et al., 2018).

Currently, under ultra-violet (UV) lighting, wide bandgap nanostructured semiconductor photocatalysts have exhibited enhanced photocatalytic performance, but these materials suffer from the reunion of photogenerated electron-hole pairs (Jung et al., 2018; Zhu and Zhou, 2019). Among various wide-bandgap semiconductor photocatalysts, bismuth phosphate (BiPO$_4$) is one of the best performing solar-light-driven photocatalysts and light-absorbing materials for organic dye degradation owing to its distinctive properties caused by its band positions (Lv et al., 2020). However, the catalytic performance of pure BiPO$_4$ is restricted to the UV region because of the rapid reunion of its photo-induced charge carriers. Numerous efforts, such as the formation of a heterostructure, doping with other materials, and Z-scheme method, have been performed to avoid this problem (Babu et al., 2020b; Low et al., 2017; Xia et al., 2019). Among these, the construction of the Z-scheme heterostructure is an effective method for improved separation of excited charge carriers and extended absorption capability toward the solar spectrum. Thus, the fabrication of NiFe$_2$O$_4$-based BiPO$_4$ heterostructure has been proposed to utilize BiPO$_4$ in a solar region and enhance the photocatalytic performance.

Liu et al. (2019) systematically constructed graphitic carbon nitride (g-C$_3$N$_4$) based TiO$_2$ photocatalysts using hydrothermal synthesis. The proposed nanocomposite exhibited an enhanced Z-scheme photocatalytic degradation of wastewater pollutants under the illumination of sunlight (Liu et al., 2019). Further, novel SnS$_2$/BiOBr photocatalysts were fabricated using a hydrothermal process. The catalytic activity of the as-prepared SnS$_2$/BiOBr nanocomposite clearly demonstrated the Z-scheme approach, which remarkably improved the removal of toxic pollutants under visible irradiation (Qiu et al., 2017). Wang et al. successfully fabricated Z-scheme AgI/WO$_3$ photocatalysts using a facile precipitation technique. The photocatalytic degradation of TC has been improved by the fabricated AgI/WO$_3$ photocatalysts over visible-light illumination (Wang et al., 2016). All these reports established that the Z-scheme heterostructures have exhibited exceptional productivity for environmental remediations.

Motivated by these results, to enhance antibiotic TC and Rhodamine B (Rhb) dye degradation under solar irradiation, a facile hydrothermal route has been used in this study for the successful synthesis of a binary NiFe$_2$O$_4$/BiPO$_4$ nanocomposite. The crystal phases and morphology of the as-prepared nanocomposites were determined. The prepared materials were described in detail, and a possible degradation mechanism was established. Thus, the functionalization of a structurally combined Z-scheme binary nanocomposite is a successful methodology that can degrade antibiotic and toxic organic pollutants under sunlight illumination.

1. Materials and methods

1.1. Materials

Given that all the chemicals used in this experiment were pure and analytical grade, no purification treatment was further performed. Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O, ≥ 99.9%), iron chloride hexahydrate (FeCl$_3$·6H$_2$O, ≥ 98.9%), basic nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, ≥ 98.0%), sodium phosphate tribasic dodecahydrate (Na$_3$PO$_4$·12H$_2$O, ≥ 98.0%), sodium hydroxide (NaOH, ≥ 98.0%), sodium sulfite (Na$_2$SO$_3$, ≥ 98.0%), and tetracycline (C$_{22}$H$_{24}$N$_2$O$_8$, ≥ 98.0%) were purchased from Sigma-Aldrich Co., Ltd., Korea. Meanwhile, ben-
zoquinone (BQ, >98.0%), isopropyl alcohol (IPA, >99.5%), triethanolamine (TEOA, >98.0%), and ethanol were obtained from Daejung Co., Ltd. Korea. Deionized (DI) water was used for the preparation of all aqueous solutions.

1.2. Synthesis of NiFe$_2$O$_4$/BiPO$_4$ nanocomposites

The detailed experimental procedure for the preparation of pure NiFe$_2$O$_4$ was provided in our previous studies (Babu et al., 2020b). Using the hydrothermal technique, the NiFe$_2$O$_4$/BiPO$_4$ nanocomposites were prepared with 100 mg of as-prepared NiFe$_2$O$_4$ and various loaded quantities of BiPO$_4$ (10, 20, and 30 mg). Briefly, the NiFe$_2$O$_4$ nanoparticles were dispersed in 50 mL of ethanol and sonicated for 30 min. After a clear dispersion of NiFe$_2$O$_4$ nanoparticles, BiPO$_4$ nanorods were added to the solution of NiFe$_2$O$_4$ nanoparticles, and sonication was continued for another 1 hr. The resulting suspension was transferred into a Teflon lined autoclave of 100 mL volume, which was maintained at 180°C for 24 hr. The obtained nanocomposite solution (hereinafter referred to as NFBP-10, NFBP-20, and NFBP-30) was washed properly with deionized water and ethanol. After the centrifuged product was dried overnight in an oven at 80°C, the final product of NiFe$_2$O$_4$/BiPO$_4$ nanocomposites was obtained. Similarly, pure BiPO$_4$ was prepared using the above-mentioned method with Bi(NO$_3$)$_3$·5H$_2$O and Na$_3$PO$_4$·12H$_2$O precursors having an equal molar ratio. Appendix A Fig. S1 presents the digital photographs of the as-prepared nanomaterials.

1.3. Photocatalytic activity

The degradation of antibiotic TC and RhB in an aqueous solution was examined to determine the catalytic performance of the prepared catalysts. In these experiments, to attain adsorption–desorption equilibrium, 15 mg of the photocatalysts was mixed into a 50 mL of antibiotic TC solution with a dye concentration of 40 mg/L and stirred for 30 min in the dark. Similarly, the procedure was repeated for RhB dye with a concentration of 100 mg/L. Subsequently, the solution was exposed to solar irradiation using a 100-W solar simulator to investigate the degradation effect of antibiotic TC and RhB dye. During catalytic experiments, 3 mL samples were obtained from the reacted solution and centrifuged, and the concentration of TC and RhB was then measured using UV–Vis spectroscopic analysis at a wavelength of 357 and 552 nm, respectively.

1.4. Photoelectrochemical analysis

A (SP-200, Bio-Logic, France) potentiostat was used to examine the photoelectrochemical studies using 0.1 mmol/L Na$_2$SO$_3$ solution as an electrolyte. Moreover, NiFe$_2$O$_4$/BiPO$_4$ was used as the working electrode, Pt as the counter electrode, and Ag/AgCl as the reference electrode, and exposed on the working electrode covering an active surface area of 1 cm$^2$.

1.5. Characterization

The following were used to examine the as-prepared samples: powder X-ray diffraction (XRD; 6100 X-ray diffractometer, Shimadzu, Japan) with Cu $K\alpha$ radiation (wavelength (λ) = 0.15418 nm), X-ray photoelectron spectroscopy (XPS; K-alpha surface instrument, Thermo Fisher Scientific, South Korea), scanning electron microscopy (SEM; S-4800, Hitachi, Japan), transmittance electron microscopy (TEM; H-7600, Hitachi, Japan), high-resolution TEM (HRTEM; G2 F20 S-Twin, Tecnai, Spain), diffuse reflectance spectroscopy (DRS, Cary 5000, Craic, South Korea), photoluminescence spectra (Horiba IHR550, Persee, USA) using a xenon lamp with an excitation wavelength of 325 nm, and photoelectrochemical analysis (SP-200, Bio-Logic, France) in a standard three-electrode system. Further, Brunauer–Emmett–Teller (BET) theory and Barrett–Joyner–Halenda (BJH) desorption isotherms are used for surface area analysis.

2. Results and discussion

2.1. X-ray diffraction studies

The structural properties of the as-prepared BiPO$_4$, NiFe$_2$O$_4$, and NiFe$_2$O$_4$/BiPO$_4$ nanocomposites were examined through XRD analysis, and they are presented in Fig. 1. The XRD of NiFe$_2$O$_4$ shows diffraction peaks at 2θ values of 30.29°, 35.53°, 37.26°, 43.19°, 53.61°, 57.15°, and 62.79° assigned to the (220), (311), (222), (400), (442), and (440) planes, respectively. The XRD pattern obtained for NiFe$_2$O$_4$ was in good harmony with the structural data of NiFe$_2$O$_4$ (JCPDS No. 00-054-0964) (Bongurala and Gorge, 2019). For pristine BiPO$_4$, the various diffraction patterns observed at 19.08°, 21.43°, 25.19°, 27.24°, 29.17°, 31.32°, 35.83°, 42.06°, 42.81°, 46.36°, 48.93°, 52.91°, 60.43°, 63.98°, 68.06°, and 69.24° could be indexed to the (011), (111), (200), (120), (012), (211), (−311), (−131), (212), (320), (132), (240), (223), and (−143) crystallographic planes of the monoclinic BiPO$_4$, respectively, with JCPDS No. 01-089-0287 (Naciri et al., 2019). Furthermore, the XRD pattern of NiFe$_2$O$_4$/BiPO$_4$ nanocomposites reflects the XRD peaks of NiFe$_2$O$_4$ (λ) as well as BiPO$_4$ (#). Additionally, the XRD peak intensities of BiPO$_4$ progressively increase, and NiFe$_2$O$_4$ gradually decreases with an increase in the loading of BiPO$_4$. Meanwhile, no significant shifting in the XRD peak positions of the nanocomposite with respect to the individual counterparts was observed. Thus, the adopted synthesis process produces a favorable dispersion of BiPO$_4$ nanorods over NiFe$_2$O$_4$, and the physicochemical bonding between BiPO$_4$ and NiFe$_2$O$_4$ forms the NiFe$_2$O$_4$/BiPO$_4$ nanocomposite.

2.2. X-ray photoelectron spectroscopy analysis

The XPS technique is used to identify the chemical binding states and elemental compositions of the prepared nanocomposite (NFBP-20), and the results are shown in Fig. 2. Using the survey spectra (Fig. 2a), the main elements including P, Bi, O, Fe, and Ni are identified. The XPS spectrum of P 2p (Fig. 2b) shows an evident peak located at 133.09 eV and is attributed to the 2p state of phosphate group (Azzam et al., 2019). The peaks associated with Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, which are characteristic peaks of Bi$^{3+}$ species, (Fig. 2c) are observed at 159.18 and 164.47 eV with an orbital splitting of 5.29 eV. Additionally, the peaks observed at 160.14 and 165.34 eV can be ascribed to Bi metal (Gao et al., 2019). The identified C element peak at 284.35 eV
may be attributed to an adventitious hydrocarbon that occurs in the XPS instrument. The O 1 s peaks (Fig. 2d) identified at binding energies of 529.51, 530.44, and 531.89 eV are attributed to metal–oxygen bond, Ni–O–H, and O^{2−} species of lattice oxygen, respectively (Hua et al., 2018; Xu et al., 2019). The high-resolution spectrum of Fe 2p (Fig. 2e) exhibits two prominent peaks at 710.69 and 724.16 eV, which are attributed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Reddy et al., 2015). The characteristics of Fe^{3+} are the additional peaks at 713.73 and 726.63 eV, and 720.27 eV is attributed to the Fe^{2+} ions. Further, the binding energy peaks located at 717.57, 729.15, and 732.59 eV were accredited to the satellite peaks (Hao et al., 2017; Kumar et al., 2018). The peaks associated with Ni 2P_{3/2} and Ni 2P_{1/2} are observed at 854.71 and 872.48 eV, as shown in Fig. 2f, which are the characteristic peaks of Ni^{2+} species (Dutta et al., 2017). A peak identified at 856.69 eV is caused by the +3 oxidation state of Ni, whereas the peaks positioned at 847.78, 851.19, 861.13, 863.04, 866.71, 874.72, 878.89, and 881.76 eV were ascribed to the satellite peaks (Chen et al., 2017; Koutavarapu et al., 2020c; Zhang et al., 2017). The XPS results indicate strong interactions between NiFe_{2}O_{4} and BiPO_{4}.

### 2.3. **Morphology analysis**

The microscopic morphology and synergistic interfaces of the prepared samples were investigated using field-emission SEM, TEM, and HRTEM analysis. Fig. 3a shows the SEM image of NiFe_{2}O_{4}, which appears similar to two-dimensional (2D) nanoplates. The surface of these nanoplates appears extremely smooth and clean. Moreover, the morphology of these nanoplates does not have uniform shape and size, which is also confirmed from the TEM image of NiFe_{2}O_{4} (Fig. 4a). The SEM image of the NiFe_{2}O_{4}/BiPO_{4} (NFBP-20) photocatalyst is shown in Fig. 3b, which indicates that the one-dimensional (1D) BiPO_{4} nanorods are decorated on the surface of NiFe_{2}O_{4} nanoplates.

The TEM images of pure NiFe_{2}O_{4} and BiPO_{4} and the nanocomposites (NFBP-10, NFBP-20, and NFBP-30) are provided in Fig. 4. As shown in Fig. 4a, the TEM image of NiFe_{2}O_{4} resembles 2D nanoplates with a smooth surface. Meanwhile, the morphology of pure BiPO_{4} (Fig. 4b) shows a rod-like structure with a diameter of approximately 20–30 nm. The TEM images of NiFe_{2}O_{4}/BiPO_{4} nanocomposites are shown in Fig. 4c–e. It is observed that the BiPO_{4} nanorods are decorated over the NiFe_{2}O_{4} nanoplates surface. Furthermore, the dispersion of BiPO_{4} nanorods over the NiFe_{2}O_{4} nanoplates surface gradually increases with an increase in the amount of BiPO_{4}. Thus, preparing the NiFe_{2}O_{4}/BiPO_{4} nanocomposite using the hydrothermal approach provides a favorable physicochemical contact between the NiFe_{2}O_{4} and BiPO_{4}, which improves the synergistic interfaces.

Additionally, the HRTEM image of NFBP-20 nanocomposite is shown in Fig. 5a. The HRTEM image confirms that the BiPO_{4} nanorods are well distributed on the surface of NiFe_{2}O_{4} nanoplates. Moreover, a lattice fringe spacing (Fig. 5b) of 0.246 and 0.326 nm can be indexed to the (311) and (200) plane of NiFe_{2}O_{4} and BiPO_{4}, respectively (Li et al., 2014; Sivakumar et al., 2012; Su et al., 2018). Additionally, the selected area electron diffraction configuration (Fig. 5b, inset) exhibits several distinct coaxial rings, indicating the formation of NiFe_{2}O_{4}/BiPO_{4} heterostructure. The composition of NFBP-20 nanocomposite was examined using HRTEM-EDS elemental color mapping, and these are shown in Fig. 6. Elements Ni, Fe, O, Bi, and P are recorded in the NFBP-20 nanocomposite.
Fig. 2 – (a) High-resolution X-ray photoelectron survey spectra, (b) P 2p, (c) Bi 4f, (d) O 1 s, (e) Fe 2p, and (f) Ni 2p of the NFBP-20 nanocomposite.

Fig. 3 – Field-emission scanning electron microscope images of (a) NiFe₂O₄ nanoplates and (b) NiFe₂O₄/BiPO₄ (NFBP-20) nanocomposite.

2.4. Surface area analysis

The adsorption–desorption isotherms were recorded at liquid N₂ temperature to determine the specific surface area and pore-size distributions of the as-prepared samples. From the obtained isotherms, the specific surface area and pore size and volume values were calculated using the BET and BJH methods, respectively. Fig. 7 demonstrates that the isotherms for all prepared samples exhibited a typical type IV isotherm, indicating that the samples were mesoporous materials.

Table 1 presents the values of the specific surface area (S_BET), pore size, and pore volume, wherein NiFe₂O₄, BiPO₄, and the NFBP-10, NFBP-20, and NFBP-30 nanocomposites exhibited surface area values of 7.1651, 9.3236, 10.0543, 24.1085, 11.4966, 24.1085, and 11.4966 m²/g, respectively.
and 11.4966 m²/g, respectively. After the deposition of BiPO₄ nanorods onto the surface of NiFe₂O₄ nanoplates, the BET surface area value increases with the BiPO₄ content, and the NFBP-20 nanocomposite shows the highest surface area of 24.1085 m²/g. Similarly, a higher pore size and pore volume of the NFBP-20 nanocomposite are beneficial in providing a higher number of active sites, thereby improving the photocatalytic activity.

2.5. Optical and photoluminescence properties of the NiFe₂O₄/BiPO₄ nanocomposites

The DRS was used to investigate the optical absorption properties of the as-prepared NiFe₂O₄, BiPO₄, and NiFe₂O₄/BiPO₄ nanocomposites, which are presented in Fig. 8. The absorption peak of BiPO₄ was observed at approximately 306 nm, in the UV region, and the corresponding bandgap was estimated as 4.079 eV (Lu et al., 2015). Further, the absorption band edge of NiFe₂O₄ was observed at approximately 724 nm in the visible range, and the bandgap was estimated as 1.712 eV (Babu et al., 2020b). After preparing the nanocomposite using NiFe₂O₄ and BiPO₄, the absorption band edge and corresponding bandgaps were remarkably modified toward the visible region of wavelengths ranging from 671 to 687 nm. Using Tauc plot (Fig. 8b), the bandgap of NFBP-10, NFBP-20, and NFBP-30 nanocomposites was estimated to be approximately 1.848, 1.804, and 1.826 eV, respectively. The modification in the bandgap is caused by the band bending of two semiconduc-

Fig. 4 – Transmission electron microscope (TEM) images of (a) pure NiFe₂O₄, (b) pure BiPO₄, (c) NFBP-10, (d) NFBP-20, and (e) NFBP-30 nanocomposites.

Fig. 5 – (a) High-resolution TEM (HRTEM) image and (b) lattice fringe pattern of the NFBP-20 nanocomposite. Inset shows the selected area diffraction (SAED) pattern.
tors. Owing to the formation of the heterostructure between NiFe$_2$O$_4$ and BiPO$_4$, the alignment of band bending occurs, which results in bandgap tuning. This heterostructure formation helps in preventing the reunion of the photo-induced charge carriers and eventually helps in enhancing the performance of light-related applications.

Photoluminescence (PL) technique was used at an excitation wavelength of 325 nm to investigate the efficient detachment of the photo-excited charge carriers and charge carrier transmission. Fig. 9 presents the results. From the PL spectra of BiPO$_4$, two emission bands are observed at 449 and 605 nm. The identified emission peaks are associated with the recombination of photo-excited charge carriers (Zhang and Park, 2017). Further, NiFe$_2$O$_4$ shows two emissions at approximately 463 and 583 nm, which are caused by the occurrence of oxygen vacancies and structural imperfections (Zhang et al., 2014). Moreover, the PL intensity of the NiFe$_2$O$_4$/BiPO$_4$ nanocomposite (NFBP-20) dropped, indicating the mutual effect of NiFe$_2$O$_4$ and BiPO$_4$. This effect remarkably progresses the separation of excited charge carriers, thereby improving the photocatalytic ability of the nanocomposite.

2.6. Photocatalytic activities and evaluation of stability

The antibiotic TC and RhB dye were used as modal pollutants to study the photocatalytic performance of the prepared catalysts upon solar light illumination. Fig. 10 presents the results associated with the antibiotic TC. First, the solution was agitated for 30 min in the dark to achieve an adsorption–desorption equilibrium between the catalyst and pollutant. Fig. 10a presents the optical absorption spectra of the NFBP-20 nanocomposite for the degradation of TC antibiotic. It can be clearly observed that the absorption peak intensity at approximately 357 nm gradually reduces with an increase in the light irradiation duration and the pollutant was degraded within 100 min of solar-light illumination. Fig. 10b shows the rate of degradation of TC for BiPO$_4$, NiFe$_2$O$_4$, and NiFe$_2$O$_4$/BiPO$_4$ nanocomposites. It can be observed that
the NFBP-20 nanocomposite exhibited greater photocatalytic activity (98%) of TC degradation within 100 min, whereas the other catalysts BiPO₄, NiFe₂O₄, NFBP-10, and NFBP-30 exhibited a removal efficiency of 35%, 43%, 74%, and 86% after 100 min, respectively. Accordingly, an increase in the amount of BiPO₄ (>20 mg) can diminish the generation of active radical species, which weakens the catalytic performance (Bathula et al., 2020).

The pseudo-first-order reaction kinetics could be described as the degradation rate constants (k) of the as-prepared photocatalysts, and the results are shown in Fig. 10c. The calculated k values for BiPO₄, NiFe₂O₄, NFBP-10, NFBP-20, and NFBP-30 nanocomposites were 0.0039, 0.0063, 0.0128, 0.0359, and 0.0189 min⁻¹, respectively (Fig. 10d). Thus, the k value for NFBP-20 nanocomposite was approximately 5.69 and 9.21 times greater than pristine NiFe₂O₄ and BiPO₄, respectively. Thus, the photocatalytic performance of NiFe₂O₄/BiPO₄ nanocomposite was enhanced owing to the photo-excited electron-hole pair partition, enlarged light absorption ability, and establishment of heterostructure with strong synergistic interfaces. However, the reduced catalytic activity of BiPO₄ and NiFe₂O₄ was owing to the increase in the reunion rate of the photo-induced carriers.

The removal of TC antibiotic pollutant can predominantly owing to the existence of reactive radicals, such as superoxide (·O₂⁻), hydroxyl (·OH), and hole (h⁺) radicals. In the present study, isopropyl alcohol (IPA), benzoquinone (BQ), and triethanolamine (TEOA) were used as a scavenger for ·OH, ·O₂⁻, and h⁺ radicals, respectively. Fig. 11a presents the scavengers responsible for the removal of TC antibiotic over NFBP-20 nanocomposite. Over NFBP-20 photocatalyst, the degradation of TC without any trapping agent is approximately 98%. Conversely, in the presence of IPA and BQ, a minimum degradation efficiency of 45% and 51% was observed, respectively. Meanwhile, after the addition of TEOA, a maximum degradation of 90% was observed (Fig. 11b). These results suggest that...
•OH and •O₂⁻ species are active scavengers as compared to h⁺ radicals for improved catalytic activity.

To regulate the impact of the amount of the catalyst on the removal efficacy of TC, different quantities (10, 15, and 20 mg) of NFBP-20 nanocomposite were poured into the TC solution. As presented in Fig. 11c, a superior removal of TC was observed for 15 mg of NFBP-20 nanocomposite. Further, when the amount of NFBP-20 nanocomposite increased from 10 to 15 mg, a systematic enhancement in photodegradation is observed owing to the development of •OH and •O₂⁻ radicals. However, the degradation of TC declined at a higher loading of the NFBP-20 catalyst owing to diminishing solar-light diffusion into the solution (Babu et al., 2020a). To verify the stability and reusability of NFBP-20 nanocomposite, photocatalytic experiments were performed for four cycles, and the outcomes are presented in Fig. 11d. The decline in the rate of removal of TC after the fourth cycle is extremely small and has occurred because of the loss of the catalyst during the recycling process. It is observed that the NFBP-20 nanocomposite is more stable and reusable during the photocatalytic removal of TC.

Moreover, the reusability is confirmed by the unchanged XRD and HRTEM results of the NFBP-20 nanocomposite before and after catalytic investigations, which is shown in Appendix A Figs. S3 and S4.

The catalytic performance of the NiFe₂O₄/BiPO₄ photocatalyst was further tested by evaluating the degradation of RhB dye. Fig. 12a displays the optical absorption spectra of NFBP-20 nanocomposite for the degradation of RhB dye. It is demonstrated that the absorption peak intensity at approximately 552 nm was gradually reduced with an increase in the light irradiation duration, and the pollutant was degraded within 60 min of solar-light illumination. Fig. 12b shows the degradation rate of RhB for BiPO₄, NiFe₂O₄, and NiFe₂O₄/BiPO₄ nanocomposites. Notably, the NFBP-20 nanocomposite shows superior catalytic performance (99%) toward the removal of RhB within 60 min, while the other catalysts (i.e., BiPO₄, NiFe₂O₄, NFBP-10, and NFBP-30) exhibits a removal efficiency of 38%, 45%, 79%, and 88% after 60 min, respectively. Accordingly, an increase in the amount of BiPO₄ (> 20 mg) can diminish the generation of active radical species, thus undermining
the catalytic performance. Fig. 12c presents the pseudo-first-order reaction kinetics of the as-prepared photocatalysts. The calculated k values for BiPO₄, NiFe₂O₄, NFBP-10, NFBP-20, and NFBP-30 nanocomposites were 0.0081, 0.0105, 0.0232, 0.0701, and 0.0339 min⁻¹, respectively (Fig. 12d). Thus, the NFBP-20 nanocomposite possesses the highest k value and is approximately 6.68 and 8.65 times greater than pristine NiFe₂O₄ and BiPO₄, respectively. These outcomes are in agreement with the results obtained for the removal of antibiotic TC.

Further, the effect of reactive radicals for the degradation of RhB is tested using NFBP-20 catalyst upon solar-light, as shown in Fig. 13a. In the presence of NFBP-20 catalyst, the degradation of RhB dye without any scavenger is approximately 99%. However, after the addition of IPA and BQ, the lowest degradation efficiency is observed. Meanwhile, the maximum degradation of RhB is recorded after the addition of TEOA (Fig. 13b). These results indicate that the •OH and •O₂⁻ species are more active agents than the H⁺ radicals for the catalytic reaction. Further, the impact of the amount of catalyst on the degradation efficiency of RhB dye was examined using different quantities (10, 15, and 20 mg) of NFBP-20 nanocomposite, as shown in Fig. 13c. A superior degradation of RhB dye was observed for 15 mg of NFBP-20 catalyst. Photocatalytic experiments for four cycles were performed to verify the stability and reusability of NFBP-20 nanocomposite, as shown in Fig. 13d. The decrease in the degradation of RhB dye after the fourth cycle is extremely small, which occurs due to the loss of catalyst during the recycling process. Thus, the NFBP-20 nanocomposite is more stable and reusable during the photocatalytic removal of RhB dye. Moreover, the unchanged XRD and HRTEM results before and after catalytic investigations confirm the reusability of the NFBP-20 nanocomposite, as presented in Appendix A Figs. S3 and S4.

2.7. Photoelectrochemical analysis

Electrochemical impedance spectroscopy (EIS) measurement was also used to examine the separation efficiency of photo-induced charge carrier and study the charge transmission resistance to redox species in the electrolyte from the photo-electrodes. Fig. 14 displays the EIS spectra of all photoanodes at 0.1 mmol/L Na₂SO₃ electrolyte under dark and light conditions. Generally, a lower circular radius signifies a lower electron transference resistance and higher separation efficiency of photo excited charge carrier (Koutavarapu et al., 2020a). Table 2 lists the electron transfer resistance values for
Fig. 12 – (a) Absorption spectra of NFBP-20 nanocomposite for the photocatalytic degradation of Rhodamine B (RhB), (b) photodegradation analysis, (c) kinetics of RhB photocatalytic degradation: ln(C_0/C) vs. irradiation time for each catalyst; (d) k values plotted for all the samples.

Table 2 – Charge-transfer resistance obtained from electrochemical impedance spectra for all the synthesized photoelectrodes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Charge-transfer resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
</tr>
<tr>
<td>BiPO_4</td>
<td>113.12</td>
</tr>
<tr>
<td>NiFe_2O_4</td>
<td>80.55</td>
</tr>
<tr>
<td>NFBP-10</td>
<td>67.21</td>
</tr>
<tr>
<td>NFBP-20</td>
<td>39.14</td>
</tr>
<tr>
<td>NFBP-30</td>
<td>54.42</td>
</tr>
</tbody>
</table>

all prepared samples, which are observed to be 111.96, 80.16, 62.35, 35.07, and 51.32 Ω under light for pure BiPO_4, NiFe_2O_4, NFBP-10, NFBP-20, and NFBP-30 photoanodes, respectively. Among all the photoanodes, the NFBP-20 photoanode displays a smaller semicircle in the Nyquist plot, indicating that the NFBP-20 photoanode has a lower charge-transfer resistance in the heterostructure. Thus, the NFBP-20 nanocomposite exhibits a rapid charge-transfer rate; hence, more photo-excited electrons and holes take part in the redox reactions.

Further, chronomperometric (current-time (I-t)) measurements were carried out to evaluate the response of photocurrent, separation and transfer processes, and its stability under light on/off conditions. Fig. 15 shows the I-t curves for all photoanodes under the light on/off cycles. The figure clearly shows that bare BiPO_4 and NiFe_2O_4 samples exhibited a small photocurrent response, whereas the binary composite NFBP-10, NFBP-20, and NFBP-30 photocatalysts exhibit higher photocurrent density values. Among these, the NFBP-20 nanocomposite shows the highest photocurrent density, suggesting excellent photogenerated charge carrier transfer in the NFBP-20 photocatalyst. The photo-response of repeated cycles suggests good stability of the prepared electrodes. From these data, the binary nanocomposite has been confirmed to exhibit rapid generation and separation of photo-excited charge carriers, which consequently induces the highest photocatalytic activity (Song et al., 2017a; Zhang et al., 2015).

When the BiPO_4 nanorods are combined with NiFe_2O_4 nanoplates, it causes a change in the energy level potential,
thereby establishing a new interface electric field. The Mott–Schottky plots is used to investigate the type of semiconductor and flat band potential ($E_{FB}$) of the materials, as shown in Fig. 15a and b. It is observed that the slope of the Mott–Schottky plots for NiFe$_2$O$_4$ and BiPO$_4$ are negative and positive, respectively, implying that the as-synthesized NiFe$_2$O$_4$ is a p-type semiconductor and BiPO$_4$ is a n-type semiconductor (Guo et al., 2019). Furthermore, the intercept of the $x$-axis indicates the $E_{FB}$ potential of the semiconductor. As shown in Fig. 16, $E_{FB}$ of NiFe$_2$O$_4$ and BiPO$_4$ are estimated to be +0.755 and −0.219 V vs. Ag/AgCl, which are converted to +0.955 and −0.019 V vs. normal hydrogen electrode (NHE), respectively (Cai et al., 2019). Therefore, the valence band potential ($E_{VB}$) of NiFe$_2$O$_4$ nanoplates and conduction band potential ($E_{CB}$) of BiPO$_4$ nanorods are extremely close to the $E_{FB}$; hence, the $E_{VB}$ and $E_{CB}$ values are regarded as +0.955 and −0.019 V for NiFe$_2$O$_4$ and BiPO$_4$, respectively. Based on the abovementioned $E_{VB}$ and $E_{CB}$ values of the samples, the $E_{CB}$ and $E_{VB}$ potentials of NiFe$_2$O$_4$ and BiPO$_4$ were further calculated using $E_{CB} = E_{VB} − E_g$ (where $E_g$ is the energy bandgap). Consequently, the corresponding $E_{CB}$ and $E_{VB}$ potentials were estimated to be −0.757 and +4.06 V for the NiFe$_2$O$_4$ and BiPO$_4$ samples, respec-

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**Fig. 13** – (a, b) Radical trapping experiments for the degradation of RhB, (c) effect of catalyst loading, and (d) recycling test of NFBP-20 nanocomposite.

**Fig. 14** – Electrochemical impedance spectra of all the prepared samples. $Z'$: real part of impedance; $Z''$: imaginary part of impedance.
2.8. Possible Z-scheme photocatalytic mechanism

Based on the aforesaid results, a probable Z-scheme mechanism was proposed for the removal of toxic pollutants upon solar-light irradiation (Fig. 17), which is based on appropriate band potentials of the BiPO₄ and NiFe₂O₄ catalysts. Under solar-light irradiation, electron-hole pairs are generated in BiPO₄ and NiFe₂O₄. Accordingly, the electrons in the conduction band (CB) of NiFe₂O₄ can be transferred toward the CB of BiPO₄. Similarly, holes in the valence band (VB) of BiPO₄ are migrated to the VB of NiFe₂O₄ (Appendix A Fig. S5). Subsequently, the -OH radical species are generated at the CB of BiPO₄, and h⁺ radicals are generated at the VB of NiFe₂O₄. However, these results are in contrast with the trapping experiments, which supports the Z-scheme photocatalytic process (Fig. 17). In detail, the produced electrons in the CB of BiPO₄ can be transported toward the VB of NiFe₂O₄ and suffers a reunion of charge carriers. Consequently, the holes and electrons assemble at the VB and CB of BiPO₄, and NiFe₂O₄, respectively. Thus, based on the Z-scheme mechanism, the photogenerated electron-hole pairs of BiPO₄ and NiFe₂O₄ are separated successfully. Based on the oxidation mechanism, the -O₂⁻ radical species are generated at the CB of NiFe₂O₄, whereas photogenerated holes at the VB of BiPO₄ react with H₂O molecules to form the -OH radicals. Based on these results, the produced -O₂⁻ and -OH species are beneficial for the removal efficiency of antibiotic TC and RhB dye. Therefore, the formation of NiFe₂O₄/BiPO₄ heterostructure considerably stimulates the charge separation efficiency, improves
tremendous redox ability, and extends the life expectancy of photo-excited charge carriers.

3. Conclusions

In summary, the NiFe2O4/BiPO4 nanocomposites were successfully fabricated using hydrothermal synthesis. Further, the 1D BiPO4 nanorods were well decorated over the NiFe2O4 nanoplates. The analysis of modifications in the intensities of XRD and microscopy analysis using SEM and TEM confirmed the formation of a superior heterostructured nanocomposite. The formation of the heterostructure has been confirmed by the tuned bandgap and decrease in PL intensity, which remarkably increased the separation rate of photogenerated charge carriers to enhance efficiency. Compared to the individual degradation efficiency of NiFe2O4 and BiPO4, degradation efficiency of antibacterial TC and RhB dye was significantly improved for the NiFe2O4/BiPO4 nanocomposite. In particular, the NFBP-20 catalyst exhibited improved degradation of TC (98%) and RhB dye (99%) within 100 and 60 min, respectively, under solar light. NiFe2O4/BiPO4 heterostructure exhibited high carrier separation efficiency according to PL, EIS, and transient photocurrent experiments. Furthermore, the trapping experiments suggest that the -OH and -O2− species are active under the photocatalytic process, which supports the Z-scheme charge-transfer approach. From the PL and trapping experiments and the Mott–Schottky measurements, we assume that a Z-scheme heterostructure was formed between the NiFe2O4 and BiPO4. Therefore, the photo-induced electrons in BiPO4 combined with the holes in NiFe2O4; this results in enhanced charge carrier extraction and utilization upon photo-excitation. This work provides an effective approach to construct 1D and/or 2D heterstructured nanomaterials for light harvesting with high efficiency.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.09.021.

REFERENCES


