A Novel α-Fe2O3/TiO2 heterostructured nanocomposite with Enhanced Visible-light Photocatalytic Performance for Degradation of Organic Pollutant

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Research Article

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Abstract

A novel heterostructured catalyst of TiO$_2$/α-Fe$_2$O$_3$ nanocomposite (NC) was successfully fabricated by the facile hydrothermal method and mutual ultrasonication. To characterize the as-fabricated photocatalysts (PCs) by PXRD, FT-IR, HRSEM, HRTEM, UV-Vis DRS absorption, and PL spectra analysis relatively. The optical absorbance of TiO$_2$/α-Fe$_2$O$_3$ NC was measured in the wavelength range from ~320–800 nm and the optical bandgap ($E_g$) was declined from 3.21 to 2.72 eV. The photocatalytic efficiency of TiO$_2$/α-Fe$_2$O$_3$ composite catalyst was assayed in the degradation of aqueous methylene blue (MB) dye in the visible-light influence. The results showed that the heterostructured α-Fe$_2$O$_3$/TiO$_2$ catalyst was much faster and higher removal efficiency of MB dye (~92.7 %) than the other photocatalytic degradation of pristine TiO$_2$ (33 %) and α-Fe$_2$O$_3$ (47.3 %) in 100 min. The enriched photocatalytic efficiency also accredited to enlarged energy harvesting ability, enhanced in the widened absorption in visible-light region, synergistic effects produced a great number of photo-produced electron-hole ($e^−$/h$^+$) separation, stronger oxidation ability by hydroxyl radicals (•OH.) via the interfaces of α-Fe$_2$O$_3$ dispersed TiO$_2$ heterojunction. All these outcomes specify that the highly stable and recyclable TiO$_2$/α-Fe$_2$O$_3$ photocatalyst has the possibility of the practical application for wastewater treatment.

Introduction

To meet the shortage in water supply worldwide and improving the environmental pollution, the elimination of several impurities from adequate water has major pervasive problem worldwide with widespread concerned. Nowadays the rapid industrialization of modern society exclusively in the developing countries, organic dyes are widely used in paper, leather, textile, pigment, cosmetic, food, and drug manufacturing [1–3]. Besides, the industrial and sanitary sewage comprises dyes cause water contamination as serious health problems and they are hazardous effects toward aquatic organisms, plants, humans, animals and aquatic ecosystem. Therefore, it is urgent to eliminate organic dyes from wastewaters. From former few decades, various techniques have been adopted to remove the dye-containing waters such as advanced oxidation processes (AOPs), physical adsorption, ozonation, photolysis and biological decomposition [3, 4]. Among them, semiconductors (SCs) heterogeneous photocatalytic AOPs decomposition has been expected to be effective strategies for used by many researchers since of its high degradation/mineralization efficiency to remove organic pollutants from wastewater due to the reactive•OH•, also low toxicity, low-cost, and ability to function under ambient settings [5].

Among various semiconductor photocatalysts (PCs), the well-known Titania (TiO$_2$) has attracted extensive courtesy owed to their preponderant potential features such as low-cost, non-toxicity, high photo-stability, fine electronic assets, great photochemical corrosive resistance, strong oxidizing power and photocatalytic movement [6–8]. This is based on the absorption of a photon of appropriate energy (~3.2 eV) and the creation of charge carriers (photo-electrons ($e^-$) and photo-holes ($h^+$)) that could oxidize organic pollutants into CO$_2$ and H$_2$O. However, the practical application of TiO$_2$ catalyst is
hindered by the serious agglomeration of TiO\textsubscript{2} nanoparticles (NPs) and the quick recombination of the photo-produced \((e^-/h^+)\) pairs \([9, 10]\). Moreover, the wide bandgap of TiO\textsubscript{2} limits its photocatalytic property in the ultraviolet (UV) region, which accounts for 3–5% of the total solar-light proportion spectrum. Since utilizing the visible-light is much more abundant (~43%) than UV light in the solar source, hence its efforts to synthesize efficient visible-light-responsive TiO\textsubscript{2}-based PCs are highly desired \([11]\). Several methods have been employed for enlightening the photocatalytic activity, the tremendous efforts are going to develop visible-light-driven (VLD) semiconductor PCs with heterojunction architecture for the TiO\textsubscript{2} PCs were coupled with various narrower bandgap SCs, such as CeO\textsubscript{2}, WO\textsubscript{3}, g-C\textsubscript{3}N\textsubscript{4}, MoS\textsubscript{2}, GO, Cu\textsubscript{2}O, Fe\textsubscript{2}O\textsubscript{3} and CdS \([11-16]\).

Among diverse metal-oxides (MOs) semiconductor PCs, hematite (\(\alpha\text{-Fe}_2\text{O}_3\)) is kind of typical n-type SCs also facilitate the promising photocatalytic water splitting and water treatment applications. Because of its narrow bandgap (~2.0-2.2 eV), which exhibits excellent properties such as non-toxicity, environmentally friendly, natural abundance, superior chemical steadiness, high corrosion resistance, good conductivity, better visible-light fascination ability and solid oxidation power \([17]\). To resolve this inadequacy, it is an attractive route to organize the effective PCs by incorporating magnetic \(\alpha\text{-Fe}_2\text{O}_3\), which not only prevents the agglomeration of other NPs during recovery but also deals the synergetic enrichment of catalytic activity to some extent by forming a hybrid structure \([18]\). Nevertheless, the photo-produced \((e^-/h^+)\) pairs in the valence band (VB) and conduction band (CB) of \(\alpha\text{-Fe}_2\text{O}_3\) are easier to be excited under visible-light exposure \([19]\). Besides, the coupling between \(\alpha\text{-Fe}_2\text{O}_3\) and TiO\textsubscript{2} NPs forms most promising nanostructures (NSs) could support to the spatial electron \((e^-)\) transfer, preventing the recombination of \(e^-/h^+\) pairs and supplying more reaction active sites for widely improve the photocatalytic performance and recycling uses. Therefore, band bending might occur that the CB edge of \(\alpha\text{-Fe}_2\text{O}_3\) is higher than that of TiO\textsubscript{2} when their Fermi levels are equalized \([17]\). As well, \(\alpha\text{-Fe}_2\text{O}_3\) ions particularly adsorb on the negatively charged TiO\textsubscript{2} NPs by electrostatic dealings. Also, the modification of their band structures via unique properties of \(\alpha\text{-Fe}_2\text{O}_3\) makes a suitable aspirant for coupling with TiO\textsubscript{2} would progress a new energy-level mismatch for visible-light photocatalysis. Therefore, \(\alpha\text{-Fe}_2\text{O}_3\) has been extensively used as combined for VLD TiO\textsubscript{2}-based PCs by the hydrothermal assisted technique with the ultrasonic wave’s supports. Since, hydrothermal assisted precipitation has applied most effective route among various techniques, to fabricate the effectual NPs and nanocomposites (NCs) samples due to its high purity, simple preparation, stoichiometry control and homogeneous distribution of coupling components \([20]\). Fortunately, Magnetic PCs might be proficiently separated and reprocessed by applying an external magnetic field.

In this existent document, a novel TiO\textsubscript{2}/\(\alpha\text{-Fe}_2\text{O}_3\) coupled heterogeneous photocatalyst were synthesized by facile hydrothermal assisted precipitation with then ultrasonic dispersion strategy. The as-fabricated NCs were characterized by various physicochemical analysis systems. Consequently, the effect of structural parameters, outstanding photocatalytic efficiency of MB dye decomposition under visible-light
treatment and excellent reusability of the used catalyst. Also, an interrelated major photocatalytic
mechanism was proposed systematically.

2. Experimental

2.1. Materials and reagents

Sodium Hydroxide (NaOH) was obtained from Pure Chem Chemical Co., India. Titanium (IV) isopropoxide (TTIP; Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> 98.5 %) was attained since Alfa Aesar Chemical Co., India. ((FeCl<sub>3</sub>, 6H<sub>2</sub>O), 99 %), Polyvinylpyrrolidone (PVP, (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub>) 98 %), 2-propanol (C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>, 98 %) and Ethanol Absolute (C<sub>2</sub>H<sub>6</sub>O, 96 %), were attained from Merck Chemical Co., India. Entire chemicals were used here in analytical reagent (A.R) grade without auxiliary refinement, and reaction solutions were formed with high purity deionized (D.I.) water.

2.1 Material synthesis

The pristine TiO<sub>2</sub> NPs was fabricated by facile sol-gel process. Initially, the typical 5 mL of TTIP was added into 30 mL of 2-propanol solution. Then, the 0.1 g of PVP mixed with 20 mL of D.I. water was openly added to the solution through magnetically stirred for 60 °C at 4 h, next it was chilled and washed numerous times. Finally, the harvested TiO<sub>2</sub> NPs was dried overnight, and it’s also crushed gently with mortar to acquire TiO<sub>2</sub> NPs [21]. The α-Fe<sub>2</sub>O<sub>3</sub> NPs were prepared via the precipitation route. In a typical experiment, 0.1 M FeCl<sub>3</sub>. 6H<sub>2</sub>O and 0.1 g of PVP were dissolved in 100 mL of D.I. water and 50 mL of ethanol absolute solution composed under continuous vigorous stirring for 1 h at a temperature of 70 °C. Next, the ammonia aqueous solution was slow added dropwise into beyond colloidal suspensions to adjust the pH ~11 and subsequently aged at 60 °C. After naturally cooling at room temperature, the resultant dark red precipitates were obtained which were collected by centrifugation (3000 rpm), rinsed with D.I. water and ethanol to remove excess chlorine ions from the filtered material [22]. The obtained wet precipitous was then dried for 10 h at 80 °C and then calcined in air at 750 °C for 3 h to obtain α-Fe<sub>2</sub>O<sub>3</sub> NPs.

TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> NC samples were also fabricated via the effective hydrothermal precipitation approach: As-fabricated TiO<sub>2</sub> and of α-Fe<sub>2</sub>O<sub>3</sub> NPs content were dispersed into ethanol and intensively sonicated for 30 min by probe ultrasonication. The resulting mixed suspension was after transferred into a 100 mL of Teflon-lined stainless steel autoclave and then finally treated at 150 °C for 5 h to attain TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> heterogeneous composite in powder form [23].

2.2. Structural characterizations

Powder X-ray diffraction (XRD) analysis was passed out to define the crystal structure and phase of the as-fabricated PCs by Rigaku Miniflex II X-ray diffractometer, which was a Cu Kα radiation (λ = 1.54056 Å). Fourier-transform infrared (FT -IR) spectra were noted on a Perkin Elmer RX-1 spectrometer via a KBr
pellet method in the ranges of 4000-400 cm\(^{-1}\) for exploring the functional features. To identify surface morphologies and elemental configuration (weight %), High-resolution scanning electron microscope images, including Energy dispersive X-ray spectra (EDXS) were documented through HR-SEM; FEI Quanta FEG 200. The shape and deep microstructure were advance categorized by High-resolution Transmission electron microscopy (HRTEM) analysis consuming a JEOL/JEM 2100, operated at an accelerating voltage of 200 kV. UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) analysis was attained the optical absorption spectra on a UV2550; Shimadzu device. The room temperature photoluminescence (PL) spectral analysis was conceded out using a Perkin-Elmer-LS 100 by the excitation wavelength series on \(\lambda_{ex} = \sim 330\) nm.

2.3. Photocatalytic activity

The photocatalytic acts of as-fabricated catalysts were assessed by VLD photodegradation with 50 mg of the as-fabricated PCs were dispersed into 20 ppm of MB aqueous dye solution injected into a 100 mL on the cylindrical quartz reflux system. To realize adsorption-desorption ability in the dark with actively stirred for 30 min. Then combined the decolourization performance scrutinized under the irradiation of visible-light and the 300 W -Xe lamp furnished by a reflection cutoff filter (\(\lambda > 420\) nm) was resolute typically to prompt the photocatalytic response [24]. Every 20 minutes, to acquire nearly 2.0 mL of the liquid suspension was reserved out and centrifuged the pure solution was examined by UV-Vis spectra (Perkin Elmer-Lambda 35) at the utmost absorption band wavelength for MB (~664 nm) [25]. The photodecomposition removal efficiency % of MB dye was intended by the equation; Efficiency (%) = (\(C_0 - C_t\))/\(C_0\)*100. Besides, the kinetic study of dye elimination enactment was deliberated agreeing to an equation of linear pseudo-first-order relation model, -Ln(\(C_0/C_t\)) = kt. Wherever \(C_t\) was the absorption found to MB dye in the preferred time intervals, k stands for the dye removal pseudo-first-order rate constant, \(C_0\) has the initial absorbance of the MB dye at t = 0 min, and relative time t. For photocatalytic recycling trials, the investigational ailment was fixed as similar as aqueous MB photo-degradation format, and hence the catalysts have further washed, dried to succeeding reaction cycle [26]. The remaining concentration of aqueous MB dye was projected in each cycle for assessing the reusability of the as-fabricated PCs.

3. Results And Discussion

Figure 1 illustrates the XRD pattern of as-fabricated pristine TiO\(_2\), \(\alpha\)-Fe\(_2\)O\(_3\) and TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) NC samples. Crystalline planes consistent to the peaks for TiO\(_2\) and \(\alpha\)-Fe\(_2\)O\(_3\) were well-indexed in this Fig. 1 (A). Numerous characteristic crystalline peaks are sensed for pristine TiO\(_2\) sample at \(\Theta = 25.2^\circ, 38.4^\circ, 48.2^\circ, 53.9^\circ, 55.2^\circ\) and \(62.8^\circ\) indexed to the (101), (112), (200), (105), (211) and (213) crystalline planes signifying the presence of prime TiO\(_2\) tetragonal anatase crystallization phase (JCPDS file no. 21-1272) individually [18, 27]. Conversely, minor peaks are noticed at around \(27.4^\circ\) owed to the presence of a slight portion of TiO\(_2\) rutile phase. Also, chief diffraction peaks at \(24.3^\circ, 35.4^\circ, 40.7^\circ\) and \(54.2^\circ\) could be consigned to (012), (110), (113) and (116) crystal planes in the best contract (JCPDS file no. 01-1053)
with rhombohedral hematite $\alpha$-Fe$_2$O$_3$ phase relatively. Accordingly, the XRD outcomes exposed that there effectively formation of $\alpha$-Fe$_2$O$_3$ NPs on the TiO$_2$ provision. No further impurity peaks are noticed, specifying the high phase pureness of TiO$_2$/α-Fe$_2$O$_3$ composite heterojunction has been fruitfully fabricated [28]. The average crystalline sizes of as-fabricated pristine TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/α-Fe$_2$O$_3$ catalysts were intended by Scherrer equation [1] and the detected values are 31, 19 and 23.5 nm separately. Hence, it's due to the substantial interface among the anatase and rhombohedral crystallites phases of TiO$_2$/α-Fe$_2$O$_3$ composite and would stabilize the surfaces by precluding auxiliary evolution of crystallization.

The FT-IR spectra were employed to inspect the chemical bonding of the as-obtained NMs. Figure 2 displays the FT-IR spectra for as-fabricated pristine TiO$_2$, $\alpha$-Fe$_2$O$_3$ and TiO$_2$/α-Fe$_2$O$_3$ composites. The wide and high-intensity absorption peaks regions supposed under 800 cm$^{-1}$ (i.e.,) 462, 567 and 721 cm$^{-1}$ could be consigned to the grouping of Ti-O-Ti, Ti-O bond bridging stretching vibrations, and Fe-O asymmetric stretching, vibration kinds resulting from the chemical interface amid TiO$_2$ and $\alpha$-Fe$_2$O$_3$ crystalline nanostructures designating that the co-presence of TiO$_2$ and $\alpha$-Fe$_2$O$_3$ in the heterojunction [29, 30]. However, C = O and C-O are widening vibration absorption bands performed at 1753 and 1045 cm$^{-1}$ for almost atmospheric carbons in the FT-IR absorption spectra. The absorption peaks in the array of 2830–2980 cm$^{-1}$ agree to CH vibrations. The typical extensive absorptive peak regions at 1632 and 3451 cm$^{-1}$ are allotted to the OH bending and stretching vibrations appeared from free adsorbed water (H$_2$O) molecules respectively [31].

Fig. 3 (a) exhibits the HRSEM image of pristine TiO$_2$ NPs, while nanostructure observation exposes that the uniform circulation comprises irregularly shaped morphology. In Fig. 3 (b), it was found that the pristine $\alpha$-Fe$_2$O$_3$ NPs have composed of the flake-like structures morphology and copious agglomerated certain dispersed NPs [32]. Also, it is observed that TiO$_2$/α-Fe$_2$O$_3$ catalyst composite (Fig. 3 (c)) for the flake-like nanostructured $\alpha$-Fe$_2$O$_3$ materials were self-possessed on TiO$_2$ assembly and fairly agglomerated with randomly distributed, which is supposed to be beneficial for augmenting the catalytic belongings [2]. Besides, EDXS spectrum was used to conclude the elemental weight ratio for the TiO$_2$/α-Fe$_2$O$_3$ composite sample in Fig 3 (d). The outcomes exposed (insert Fig. 3 (d)) that the O, Ti and Fe elements were 42.11 %, 40.15 % and 17.74 % (weight %) relatively. The EDXS element mapping images (Fig. 4 (a-d)) of TiO$_2$/α-Fe$_2$O$_3$ composite for auxiliary established that there spatial distribution and the pinpointed/isolated spots of the O, Fe and Ti elements [5,33]. Therefore, it is decided that TiO$_2$ NPs were effectively covered on the even superficial of cubic $\alpha$-Fe$_2$O$_3$ NSs.

HRTEM images were demonstrated that $\alpha$-Fe$_2$O$_3$ NPs were uniformly distribution decorated of NPs on the aggregation of TiO$_2$ surfaced spherical morphologies, as obtainable in Fig. 5 (a-f). What's more, the characteristic HR-TEM images have further disclosed that the composite maintains of flake-like structure with homogenous crumpled nanosheets [34]. The lattice fringes of as-achieved heterostructured TiO$_2$/α-Fe$_2$O$_3$ composite typically exposed to the (101) facets of TiO$_2$ and (012) crystallographic planes of
α-Fe$_2$O$_3$ are discrete through measured the fringe spacing of 0.31 nm as presented in Fig. 5 (e, f). Hence the characteristic lattice lines for the selected area electron diffraction (SAED) pattern reveals the highly polycrystalline nature [6] of the NC in Fig. 5 (d). Also confirms the fruitful incorporation of both identical TiO$_2$ into α-Fe$_2$O$_3$ composite could be probable for the electrostatic interface among negatively charged TiO$_2$ and positively charged α-Fe$_2$O$_3$ NPs which is augmenting the charge carriers separation also notable for enlightened photocatalytic enrichment of TiO$_2$/α-Fe$_2$O$_3$ catalyst [35]. These consequences were which suggest in good promise with that of the XRD outcomes.

To investigate the UV-Vis DRS absorbance spectra of as-fabricated samples were shown in Fig. 6 (A). As revealed in Fig. 6, the UV-Vis absorption edges of pristine TiO$_2$ NPs are about ~ 325 nm in the spectra, whereas endorsed to the electronic transition of O$_{2p}$ to Ti$_{3d}$ [36]. For pristine α-Fe$_2$O$_3$ NPs exhibit, apparent visible-light absorption is detected in the curve (λ$_{ab}$ upto ~ 590 nm). In contrast, the TiO$_2$/α-Fe$_2$O$_3$ composite catalyst presented not only stronger light absorption threshold in the UV region of less than ~ 390 nm, then the suitable and robust absorption edges found in the visible-light province of ~ 400–700 nm could be witnessed in Fig. 6 (A). These fallouts which proposed that they TiO$_2$ were red-shifted into the visible-light after adding the α-Fe$_2$O$_3$, hence it has been stated the charge transfer by the direct transition from O$_{2p}$ to Fe$^{3+}$ (3d) could change the visible absorbance to the elongated wavelength from the indirect transition among Fe$^{3+}$ (3d) electrons (e$^-$) [27]. Hence, it has not only encourage the separation and migration of photo-produced charges but also contribute to the CB in the upper situation. Thus, the UV-Vis spectra effects proved the incorporation of Fe$^{3+}$ in TiO$_2$. Remarkably, this would be extended the visible-light photocatalytic movement of the heterostructured TiO$_2$/α-Fe$_2$O$_3$ composite photocatalyst, also utilized by realizing the solar light [37].

Figure 6 (B) illustrates the Tauc plots of (αhv)$^2$ versus photon energy (hv) for the optical bandgap energies of as-attained catalysts, which were intended founded on the optical absorption edge attained from UV-Vis DRS spectra using Kubelka-Munk Eqn; αhv = A (hv Eg)$^{n/2}$. Wherever, A, Eg, α, h, ν, are the relatively constant, bandgap energy, absorption coefficient, Planck’s constant, incident light frequency, and where, n = ½, and 2 for direct and indirect bandgap consistently [32]. The outcomes show that the intercepts of band-gap energies of pristine TiO$_2$, α-Fe$_2$O$_3$ and TiO$_2$/α-Fe$_2$O$_3$ PCs are estimated roughly 3.21, 2.11, and 2.72 eV, individually. In the existing form, Fe$^{3+}$ was mixed with the TiO$_2$ lattice, ensued in the decreasing the bandgap of TiO$_2$ NPs, greatly upgraded to enabled the visible-light fascination assets of the heterostructured TiO$_2$/α-Fe$_2$O$_3$ PCs [38]. As advised for owed to an exclusive electronic arrangement, implying that the Fe$^{3+}$ has the ability to the form novel narrowing energy levels occurs in the bandgap of TiO$_2$ NPs and declines the bandgap with active photo-excitation between VB and CB. This might be correlated to particle size, surface morphology and the novel accumulation of α-Fe$_2$O$_3$, as well the Fermi level of TiO$_2$/α-Fe$_2$O$_3$ heterostructured NC hints to energy bandgap declined [39]. Conferring to the UV-Vis DRS outcomes, the as-fabricated TiO$_2$/α-Fe$_2$O$_3$ PCs with a narrow bandgap are projected to
expose the outstanding photocatalytic action for decomposing organic impurities in the visible-light expanse, which agreed to the VLD photo-degrading manner [40].

PL emission spectra could be carried out to explore the efficiency of photo-produced (e\(^-\)/h\(^+\)) pairs, transfer, separation, trapping, immigration and to understand the rate of charge-carrier recombination in the specified semiconductor PCs, as one of the essential factors disturbing the photocatalytic exploit. Figure 7 (A) confirms the PL spectra of as-obtained heterostructured PCs and the emission intensity peaks of the as-fabricated pristine TiO\(_2\), α-Fe\(_2\)O\(_3\) and TiO\(_2\)/α-Fe\(_2\)O\(_3\) catalyst were at 461, 447 and 459 nm, congruently. The PL emission peak of TiO\(_2\) was upper than that of TiO\(_2\)/α-Fe\(_2\)O\(_3\) NC which designated that occurrence of α-Fe\(_2\)O\(_3\) reduced the (e\(^-\)/h\(^+\)) recombination rate [41]. In contrast, novel configurations of the heterostructure amongst α-Fe\(_2\)O\(_3\) and TiO\(_2\) NMs which declines the PL emission intensity of the near band edge emission (NBE) and might owed to the intrinsic/extrinsic luminescence defects related NBE. The Fe\(^{3+}\)/Fe\(_2\)O\(_3\) ions could be integrated into the TiO\(_2\) lattice either by substituting Fe\(^{3+}\) ions fashioning especially ionized oxygen vacancies (V\(_o\)) or as interstitial of Fe\(^{3+}\). So the lesser PL emission intensity of the TiO\(_2\)/α-Fe\(_2\)O\(_3\) PCs has a significant for the extent of charge separation are species the effectively restrained recombination rate primary to admirable light-harvesting capability hence, the photocatalytic efficacy was heightened [28].

**Photocatalytic activity analysis**

The photocatalytic efficiency of as-fabricated TiO\(_2\)/α-Fe\(_2\)O\(_3\) PCs was widely evaluated by the decomposition of MB dye and the absorption peak declined steadily under visible-light exposure (Fig. 7 (B)) at diverse time intermission from 0 min to 100 min [37]. Also, the MB aqueous solution alone without photocatalyst (blank) was directed to check the self-photodegradation of MB dye have exceptionally low and with under dark situation in the existence of PCs hence it has negligible [25]. The photo-degradation efficacy of C/C\(_0\) curves for MB over as-fabricated TiO\(_2\) and α-Fe\(_2\)O\(_3\) catalysts were only 33 % and 47.7 %, individually. Moreover, the TiO\(_2\)/α-Fe\(_2\)O\(_3\) heterostructured composite catalyst resulting in the superior photocatalytic activity (92.7 %) could be achieved amongst all the as-fabricated PCs after 100 mins of visible-light exposure. Figure 8 (A) demonstrates the consistent concentration changes of the MB aqueous dye solution and the response rate (k) as a function of visible-light exposure time [35]. The photo-degradation proficiencies of MB aqueous dye by as-obtained PCs are originated to the succeeding order: TiO\(_2\)/α-Fe\(_2\)O\(_3\) > α-Fe\(_2\)O\(_3\) > TiO\(_2\).

In order to quantitatively discover the kinetics of MB dye photodegradation under visible-light exposure for the as-fabricated PCs were investigated as shown in Fig. 8 (B), and this suggests that pseudo-first-order kinetics reaction rates. The specious reaction rate constants (k) for as-fabricated TiO\(_2\), α-Fe\(_2\)O\(_3\) and TiO\(_2\)/α-Fe\(_2\)O\(_3\) PCs were determined as 0.0071 min\(^{-1}\), 0.0109 min\(^{-1}\), and 0.0252 min\(^{-1}\) relatively. It was found that the maximum photocatalytic performance for the decomposition of MB aqueous dye, which was about 3.54 and 2.31 times greater that of as-fabricated TiO\(_2\) and α-Fe\(_2\)O\(_3\) catalyst under the identical
conditions respectively [42]. Besides to photocatalytic efficacy, the stability of the specified photocatalyst is also essential for practical use for the handling of organic impurities in wastewater [30]. To inspect the reusability and stability of TiO$_2$/α-Fe$_2$O$_3$, the PCs after photocatalysis progression were composed and reused for five successive times under the identical settings. As publicized in Fig. 9 (A), the TiO$_2$/α-Fe$_2$O$_3$ PCs revealed noble reusability throughout five photo-decomposition reuses [37]. After five recycles of photo-reduction of MB dye, the TiO$_2$/α-Fe$_2$O$_3$ PCs did not display any significant loss of activity Fig. 8 (A), hence it’s understood the stability of catalyst after four consecutive catalytic reprocess. Since there was a substantial drop in the fifth recycle (80.6 %), which was ascribed to the loss of α-Fe$_2$O$_3$ catalyst during the recycling reaction. The crystalline structure and their functional groups were characterized by XRD and FT-IR individually. Hence the TiO$_2$/α-Fe$_2$O$_3$ PCs have almost no obvious structural changes were found in before and after the photocatalytic recycles investigates (Fig. 10 (A) and (B)) which outcomes signifying a good stable adequate for recycling [43]. Therefore, TiO$_2$/α-Fe$_2$O$_3$ heterostructured PCs are projected to be promising in environmental remediation since not only tremendous photocatalytic stability, also enabled energy conversion in the visible-light region [44, 45]. In contrast, with the earlier reported literature of various NCs for photodegradation of organic impurities, TiO$_2$/α-Fe$_2$O$_3$ composite PCs have displayed superb removal efficacy for MB dye, as tabularized in Table 1.

To validate the radicals of NCs in the photocatalytic decomposition process, the trapping investigates of reactive species are executed. Figure 9 (B) displays the three diverse quenching manners, for instance, 0.5 mM of isopropanol (IPA), disodium ethylene diamine-tetra acetate (EDTA-2Na), and benzoquinone (BQ) were used to sense the scavengers of hydroxyl radicals (% •OH$^-$), holes (% h$^+$) and superoxide anion radicals (% •O$_2^-$) absolutely [41]. As could be realized in Fig. 8 (B) the decomposition rate of PCs slightly decreases corresponding to the adding of BQ and EDTA-2Na, signifying that which % h$^+$ and % •O$_2^-$ are the slight responsive species on this concerned structures. Nevertheless, the accumulation of IPA caused apparent deactivation of the photocatalyst, decreasing the photocatalytic movement for the decomposition rated from 92.7 % to 16 % as exposed in the quenching investigation outcomes. This noticeably validates that active •OH$^-$ radicals are the foremost reactive species liable for VLD photocatalytic decolourization scheme over these TiO$_2$/α-Fe$_2$O$_3$ heterostructured PCs [46].
Table 1
Comparison of VLD photocatalytic degradation of MB dye (%) over of previous literature reported catalytic NMs

| S. No. | Photocatalysts       | Dye | Irradiation time (min.) | Degradation efficiency (%) | Ref.  |
|--------|----------------------|-----|-------------------------|-----------------------------|-------|
| 1.     | Ga-Ag/ZnO            | MB  | 300                     | ~ 39                        | [44]  |
| 2.     | P25 TiO$_2$          | MB  | 300                     | ~ 48                        | [47]  |
| 3.     | CNTs/TiO$_2$/Ag      | MB  | 240                     | ~ 48                        | [48]  |
| 4.     | ZnO/SnO$_2$          | MB  | 240                     | ~ 90                        | [49]  |
| 5.     | TiO$_2$/CeO$_5$      | MB  | 150                     | ~ 95                        | [30]  |
| 6.     | CdS/TiO$_2$          | MB  | 180                     | ~ 63                        | [25]  |
| 7.     | Fe$_2$O$_3$/Cu$_2$O  | MB  | 80                      | ~ 40                        | [50]  |
| 8.     | TiO$_2$/α-Fe$_2$O$_3$| MB  | 100                     | ~ 92.7                      | This work |

On the base of the upstairs debate, it is noticeable that the generation and (e$^-$$-h^+$) separation process mechanism could be proficiently indorsed by the interface between TiO$_2$ and α-Fe$_2$O$_3$ catalyst under visible-light exposure [28]. The VB and CB edge potential position could be gathered via according to the Mulliken electronegativity theory for following Eqn; $E_{VB} = \chi - E_e + 0.5 E_g$ and $E_{CB} = E_{VB} - E_g$. Wherein, $\chi$ signifies the absolute Mulliken electronegativity of given SCs ($\chi_{TiO_2} = 5.81$ eV, and $\chi_{\alpha-Fe_2O_3} = 5.88$ eV), separately [51]. Moreover, the $E_g$, $E_e$, $E_{VB}$ and $E_{CB}$ were energy bandgap of specified SCs by UV-DRS spectra ($E_g$ of TiO$_2$ = 3.21 eV; $E_g$ of α-Fe$_2$O$_3$ = 2.11 eV), the energy of free electrons on the hydrogen scale (ca. 4.5 eV), VB edge potential and CB edge potential individually [52]. Agreeing to the above equations, the energy level diagram is based upon the $E_{VB}$ and $E_{CB}$ values were estimated to be of TiO$_2$ ($E_{VB} = 2.915$, $E_{CB} = -0.295$) and its favorable than α-Fe$_2$O$_3$ ($E_{VB} = 2.48$, $E_{CB} = 0.28$) discretely.

Based on the upstairs analysis and conversation, the photo-produced charge separation and transfer of the TiO$_2$/α-Fe$_2$O$_3$ heterostructured catalyst for the improved plausible photocatalytic action in visible-light preservation could be anticipated as exposed above trial outcomes in Fig. 11. Under the visible-light illumination ($\lambda > 420$ nm), both the SCs catalysts of TiO$_2$ and α-Fe$_2$O$_3$ catalyst are photo-excited primarily by photons while to produce more electron-hole (e$^-$$-h^+$) pairs, which are then separated and stimulated to diverse ways under the reaction energy [32]. In detail, the photo-electrons (e$^-$) of TiO$_2$ will transfer to the CB of α-Fe$_2$O$_3$, meanwhile, the photo-holes (h$^+$) of α-Fe$_2$O$_3$ will transport to the VB of TiO$_2$ (Ti 3d) under the exploit of a built-in electric field. Though, under the energetic reaction in the photo-electrons (e$^-$) of α-Fe$_2$O$_3$ and the photo-holes (h$^+$) of TiO$_2$ would exchange to both other and then concluding the
consequence of \((e^- - h^+)\) recombination. In photocatalytic system, the photo-electrons \((e^-)\) prompt to the reduction of Fe\(^{3+}\) ions to Fe\(^{2+}\) ions \([50]\). When \(\alpha\)-Fe\(_2\)O\(_3\) NPs were united with TiO\(_2\) NPs, the Fermi level of TiO\(_2\) and \(\alpha\)-Fe\(_2\)O\(_3\) necessity align in symmetry owed to the occurrence of the TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) heterojunction \([27]\). The authority of TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) NSs also profits from the pairing by narrow bandgap semiconductor \(\alpha\)-Fe\(_2\)O\(_3\). Thus the \((e^-/h^+)\) recombination progression is greatly suppressed and efficient \((e^-/h^+)\) separation is realized on the NC surface \([47]\). In this case, the presence of TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) fitted heterostructures, the conversion of the photo-electrons \((e^-)\) and the photo-holes \((h^+)\) would primary go through the hybrid layer simply owed the firm migration rate position which also stimulates the outstanding charge separation movement. Concurrently, the samples of TiO\(_2\) and \(\alpha\)-Fe\(_2\)O\(_3\) PCs will efforts to the photo-oxidation and reduction situates also the virtual interesting water oxidation for the photodegradation reaction could be attained, exclusively \([1]\). Also, the photo-electrons \((e^-)\) in the VB of TiO\(_2\) was auxiliary respond with molecular oxygen O\(_2\) dissolved in the solution to form the superoxide anion \((O_2^-)\) and hydrogen peroxide \((H_2O_2)\). Consecutively, the photodegradation of MB dye is reached by capture the photo-electrons \((e^-)\) and the photo-holes \((h^+)\) could also oxidize either the organic molecule directly and/or the OH ions H\(_2\)O fragments are adsorbed on the catalytic surface to the sturdy oxidizing to reactive \('OH\)' radicals by the end products on the photocatalyst surface \([42]\). Our consequences exposed that the construction of TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) PCs hinder the recombination of photo-excited electron-hole \((e^- - h^+)\) pairs and encourage the generation of more \('OH\)' radicals resulted in the development of photodegradation competence of TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) PCs \([25]\). While the amassed photo-holes \((h^+)\) in the VB of Fe\(_2\)O\(_3\) respond with OH\(^-\) species or H\(_2\)O\(^-\) prevailing on the surface of the PCs, fabricating responsive hydroxyl radicals \('OH^-\) which are auxiliary intricate in the photodegradation of MB dye, as presented in Fig. 11. To conclude, the organic-acids were photo-oxidized to form into the harmless ingredients of CO\(_2\) and H\(_2\)O \([53, 54]\). This reaction could be responsible for specified by equations (1)-(5);

\[
\begin{align*}
\text{TiO}_2/\alpha\ \text{Fe}_2\text{O}_3 + \text{Dye} + \text{hv Light} & \rightarrow \text{TiO}_2/\alpha\ \text{Fe}_2\text{O}_3 + \text{Dye} + (e^- (CB) + h^+ (VB)) \rightarrow (1) \\
\text{Dye} + e^- (CB) & \rightarrow \text{Reduction products} \rightarrow (2) \\
\text{Dye} + O_2 & \rightarrow O_2^- + \text{Degradation products} \rightarrow (3) \\
\text{Dye} + h^+ (VB) & \rightarrow \text{Oxidative products} \rightarrow (4) \\
\text{Dye} + OH & \rightarrow OH^- + H_2O + \text{Degradation products} \rightarrow (5)
\end{align*}
\]

4. Conclusion

In summary, TiO\(_2\)/\(\alpha\)-Fe\(_2\)O\(_3\) composite catalysts were efficiently fabricated by hydrothermal assisted precipitation manner and enhanced VLD photocatalytic actions were also surveyed. The powder XRD diffraction pattern peaks of TiO\(_2\) and \(\alpha\)-Fe\(_2\)O\(_3\) NPs were well accorded with the tetragonal (anatase) and rhombohedral phases are obtained. The narrow bandgap of \(\alpha\)-Fe\(_2\)O\(_3\) was engaged to outspread the
optical response of TiO$_2$ to the visible-light region. Though TiO$_2$/α-Fe$_2$O$_3$ sample has revealed the premier photocatalytic action of the organic MB aqueous dye among other as-fabricated TiO$_2$ and α-Fe$_2$O$_3$ PCs in the visible-light region. The photocatalytic materials also exhibit adequate superior cyclic stability and the dye decomposition efficiency could be 80.6 % after five successive cycle runs. It is accredited to the well-suited interface fashioned heterojunction structures between TiO$_2$ and α-Fe$_2$O$_3$, which promotes the efficient photo-produced (e$^-$$-h^+$) charge transfer/separation, restraining the recombination rate, with prolonged optical absorption into the visible region and favourable $'OH^-$ radicals invention ability. To conclude, a promising photocatalytic mechanism is projected for this novel PCs. Here consider that the expansion of the great photocatalytic actions of TiO$_2$/α-Fe$_2$O$_3$ heterostructures will deliver an auspicious platform for the highly stable and reusable performance of photocatalytic practical applications.

**Declarations**

The authors have declares no conflict of interest.

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**Figures**
Figure 1

Powder XRD pattern of as-obtained samples
Figure 2

FT-IR spectra of as-obtained samples
Figure 3

HRSEM images of as-fabricated (a) pristine TiO2 (b) α-Fe2O3 (c) TiO2/α-Fe2O3 composite and (d) consistent EDXS spectrum of TiO2/α-Fe2O3 composite
Figure 4

EDXS elemental mapping of TiO2/α-Fe2O3 NC; Pictures of (b) Ti, (c) Fe and (d) O elements
Figure 5

Typical HRTEM images of as-fabricated TiO2/α-Fe2O3 heterostructured composite
Figure 6

(A) UV-Vis DRS optical absorption spectra (B) relative Tauc plot of as-fabricated (a) pristine TiO2 (b) α-Fe2O3 (c) TiO2/α-Fe2O3 NMs

Figure 7

(A) PL intensity (a.u.) (B) Absorption (a.u.)
(A) Room-temperature PL spectra, $\lambda_{ex} \sim 330$ nm; and Photocatalytic degradation of MB over the TiO$_2$/\(\alpha\)-Fe$_2$O$_3$ composite catalyst under visible-light exposure

Figure 8

(A) Photodegradation efficiency of MB dye (B) First-order kinetic fitting plots $-\ln (C_0/C_t)$ versus reaction time $t$ for the as-obtained different PCs
Figure 9

(A) Photocatalytic recycling stability of energetic TiO2/α-Fe2O3 PCs and (B) Photodegradation of MB aqueous dye over as-obtained TiO2/α-Fe2O3 composite catalyst in the existence of dissimilar scavengers.
(A) XRD pattern and (B) FT-IR spectra of TiO2/α-Fe2O3 composite catalyst by before (a) and after (b) recycling process

![Diagram of Photocatalytic Mechanisms]

Figure 11

Photocatalytic mechanisms for schematic diagram of TiO2/α-Fe2O3 heterostructure composite catalyst under visible-light exposure