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ARTICLE

Magnetically Separable $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ Composites with Enhanced Photocatalytic Activity

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Magnetically separable $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ (APO/NFO) composites were prepared by *in-situ* precipitation method. The photocatalytic activity of photocatalysts consisting of different APO/NFO mass ratios was evaluated by degradation of methylene blue (MB) under visible light irradiation. The excellent photocatalytic activity was observed using APO/NFO5 (5% NFO) composite with good cycling stability which is higher than that of pure Ag_3PO_4 and NiFe_2O_4 . All the APO/NFO composites showed good magnetic behavior, which makes them magnetically separable after reaction and reuse for several experiments. Photoconductivities of pure and composite samples were examined to study the photo response characteristics. The current intensity greatly enhanced by loading NFO to APO. Furthermore, the photocatalytic performance of the samples is correlated with the conductivity of the samples. The enhancement in photocatalytic activity of APO/NFO composite for MB degradation is attributed to the excellent conductivity of APO/NFO composite through the co-catalytic effect of NFO by providing accelerated charge separation through n-n interface.

Introduction

Visible light active photocatalyst which can directly harvest solar energy to remove various toxic organic pollutants from water through the photocatalysis process is of great importance.¹⁻² Photocatalysis serves as an ideal process which mainly involves generation, migration and separation of electron-hole pairs. TiO_2 , ZnO , SnO_2 are among the mostly studied efficient photocatalysts, but they only absorb photo energy in the UV range, which is less than 4 % of the whole solar light spectrum. Similarly, visible light responsive photocatalysts have been also extensively studied in the recent years, such as $\text{TiO}_{(2-x)}\text{N}_x$,³ BiVO_4 ,⁴ Ag/AgCl ,⁵ InMO_4 ($\text{M}=\text{Nb}$, Ta) and $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$,⁶ which exhibit good photocatalytic performance for the degradation of organic pollutants under visible light irradiation. However, the efficiency of these photocatalysts is still too low to be used practically.⁷ The reasons behind low photocatalytic activity are fast recombination of photo-induced charge carriers, incapability of photocatalyst to utilize a significant fraction of the solar

spectrum and instability of photocatalyst.^{8,9}

In this regards, Ag_3PO_4 was found to be the most popular photocatalyst, because of its high photo oxidative capabilities with quantum efficiency nearly 90% for the oxidation of water and the photodecomposition of organic dyes under visible-light.⁹⁻¹¹ The origin of its high-efficiency comes from a constructive effect of both the large dispersion of conduction band and the inductive effect of PO_4^{3-} owing to contribute electron-hole pairs separation.¹²⁻¹³ So far, APO with different morphologies have been prepared such as cubic APO microcrystals,¹⁴ hierarchical APO porous microcubes,¹⁵ dendritic APO,¹⁶ concave trisoctahedral APO microcrystals,¹⁷ and APO polypods.¹⁸ More specifically, Bi *et al.*¹¹ have studied facet exposed photocatalytic activity of APO rhombic dodecahedrons and cubes; the rhombic dodecahedrons with exposed active {110} facets have shown higher activity than the cubes with the exposed {100} facets for the degradation of rhodamine B (RhB). However, APO itself has relatively weak photocatalytic stability. It is prone to photo-reduction and decomposition if no sacrificial reagent is supplied.¹⁹⁻²⁰ For an ideal photocatalyst, stability and recyclability are very important parameters in order to achieve high photocatalytic efficiency. Therefore, the photocatalytic stability of APO need to be further improved. To overcome this problem, many studies have focused on hetero-coupling the semiconductor materials with matched band-edges, which could facilitate the immigration and separation of photogenerated electrons and holes, and indeed benefit the photocatalytic activity and stability. Some APO coupled semiconductor materials were exemplified like $\text{Fe}_3\text{O}_4/\text{Ag}_3\text{PO}_4$,⁵ $\text{CQDs}/\text{Ag}_3\text{PO}_4$,¹⁵

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$\text{Ag}_3\text{PO}_4/\text{TiO}_2/\text{Fe}_3\text{O}_4$,¹⁶ $\text{Ag}_3\text{PO}_4/\text{TiO}_2$,²¹ $\text{Ag}_3\text{PO}_4/\text{graphene oxide}$,²² $\text{BiOCl}/\text{Ag}_3\text{PO}_4$,²³ $\text{Ag}_3\text{PO}_4/\text{CNTs}$,²⁴ and $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$,²⁵ which shown to have superior photocatalytic activity by improving stability and separation of photogenerated charge carriers.²⁶ However, in all the above studies the stability of the photocatalysts was checked with their recyclable ability by reusing them for consecutive photocatalytic experiments. Similarly, the enhanced photocatalytic activity of the composite photocatalysts was evaluated by proposing a charge separation mechanism using heterojunction models. There was no any experimental evidence provided to confirm the stability as well as enhanced photocatalytic activity of the composite. So an attempt has been made to provide the direct evidence for stability and enhanced photocatalytic activity by correlating the photocatalytic activity with conductivity of the photocatalysts. Recently, P. Zhang *et al.* has reported that incorporation of other elements into the ZnO photocatalyst could decrease its resistivity and extend its photoresponse, which in turn enhance its photocatalytic performance.²⁷ The enhanced photocatalytic activity for doped ZnO photocatalyst was attributed to high conductivity.

Apart from stability of the photocatalysts, it is important to remove and recover the photocatalyst from aqueous suspensions after a photocatalytic reaction in order to avoid loss of material. Magnetic photocatalysts are an alternative for addressing this problem, that can be easily recovered by a magnet and can be reused for photocatalysis reaction several times without any appreciable reduction in photocatalytic efficiency.^{28,29} Although, magnetic photocatalysts are easily recovered, their photocatalytic activities are very weak. They usually take long time to degrade the organic pollutant. Therefore, it is desirable to couple the magnetic photocatalyst with photocatalyst having high photocatalytic efficiency. Such composite photocatalysts can exhibit good magnet-controlled recyclability as well as superior photocatalytic activity with improved stability. In this regards, cubic NiFe_2O_4 (NFO) is known to have high electromagnetic performance as well as excellent chemical stability, and NFO nanoparticles themselves have a strong magnetic property, and therefore, NFO based catalysts can be magnetically separable in a suspension by virtue of their own magnetic properties without introduction of additional magnetic particles.

Herein, we report the synthesis of magnetically separable $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ (APO/NFO) composite photocatalysts by *in-situ* precipitation method and their photocatalytic activity for the Methylene blue (MB) degradation. MB is quite well known as a pollutant from textile industry and also for its toxicity.³⁰⁻³² In comparison to conventional methods³⁰⁻³³, photocatalysis is environmentally sustainable and effective method, hence photocatalytic activity for MB degradation has been evaluated. As synthesized APO/NFO photocatalyst showed comparatively higher photocatalytic performance than bare Ag_3PO_4 with good stability. We have further studied the effect of photoconductivity of the material on the photocatalytic activities. The photoconductivity of the composites is found to be very stable and overall conductivity of the composites is

increased by 5 orders resulting in enhanced photocatalytic activities.

Experimental

Synthesis of $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ (APO/NFO) composites

Nickel (III) nitrate [$\text{Ni}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], Ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (Qualigen Chemicals Limited), Silver nitrate AgNO_3 (SD Fine Chemicals Limited), Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) (Qualigen Chemicals Limited) were used as starting materials. All the chemicals were of AR grade and were used without any further purification.

Synthesis of NiFe_2O_4

NiFe_2O_4 powder was synthesized by auto combustion method. 0.5 M $\text{Ni}(\text{NO}_3)_3$ and 1 M $\text{Fe}(\text{NO}_3)_3$ were dissolved in distilled water. Subsequently, 1 M Glycine was added in it. This solution was then heated on a hot plate under continuous stirring condition to its boiling temperature until all the liquid got evaporated. Towards the end of reaction, an immense evolution of brown fumes was observed, a fluffy brown mass was obtained at the base of the beaker, which was then ground into powder and then calcined at 500 °C for 2 hrs and subjected for further characterization.

Synthesis of $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ nanocomposite

As obtained NFO powder was used for composite preparation. Synthesis of APO/NFO composites were carried out by an *in-situ* precipitation method. The required amount of NFO powder were dispersed in 20 ml of Deionised (DI) water and ultrasonicated for 10 min. After that (4.8 mmol) of $\text{NH}_4\text{H}_2\text{PO}_4$ solution in 10 mL water was added. Subsequently 10 mL aqueous AgNO_3 (8.9 mmol) aqueous solution was added drop wise under vigorous stirring condition for 4h. As obtained composite powder were washed with DI water thoroughly, dried and used for further characterization. The APO/(x wt% NFO) composites (x wt% is the nominal mass ratio of NFO to APO) with the mass ratios (x=5, 10, and 15 %) were synthesized using the same process. All the prepared samples have been labeled as APO, NFO, APO/NFO5 (APO/5% NFO), APO/NFO10 (APO/10% NFO) and APO/NFO15 (APO/15% NFO), respectively.

Structural Characterization

The phase formation was investigated via powder X-ray diffraction (XRD) technique using (XRD-D8, Advance, Bruker-AXS). The morphological features of composites were investigated by field emission scanning electron microscopy (FESEM; Hitachi, S-4800 II, Japan). The absorbance spectra of the samples were recorded by a UV-Vis spectrometer (Perkin-Elmer, Lambda 950 spectrometer) in the range of 300–900 nm. Photoluminescence analysis was performed by using Shimadzu (RF-5301 PC) spectrophotometer. Magnetic properties of material were measured using a Vibrating Sample Magnetometer (Lakeshore model 7307).

Photocatalytic degradation of dye

In this study, methylene blue (MB), with a major absorption band at 664 nm, was chosen as a model pollutant for testing photocatalytic activities of APO, NFO and APO/NFO composites. The photocatalytic degradation of MB (10 ppm) dye was performed in an aqueous solution using 300 W Xe lamp ($\lambda \geq 420$ nm) as the light source. The photocatalytic reaction was carried out in specially designed borosilicate glass reactor with water-cooling system to maintain the solution at room temperature. A photocatalyst sample of ~ 10 mg was dispersed in an aqueous solution of MB for every run. Prior to the irradiation, the suspension was magnetically stirred in dark for 90 min to establish an adsorption-desorption equilibrium between the photocatalyst and the MB. The solution was then exposed to light irradiation under magnetic stirring. Aliquots of 3 mL were drawn and filtered after regular time. The measurement of the MB concentration in the filtrate was carried out using UV-Vis spectroscopy (Perkin Elmer, Lambda 950 spectrometer). The initial absorbance intensity of the solution at 663.89 nm (the characteristic absorption peak of methylene blue) was monitored.

Photoconductivity measurement

The sample was prepared by depositing APO, NFO and APO/NFO5 materials on pre-patterned silver electrode with electrode spacing (gap) of 100 micron and photon catchment length of 10 mm on square ($6\text{ mm} \times 6\text{ mm}$) alumina substrate. The samples were thermally annealed in air atmosphere at 300 °C to improve electrical contact. The resultant devices were electrically characterised using two probe method to measure IV characteristic. Visible light from a source composed of Halogen lamp (150W) was focussed and guided onto the sample perpendicularly. A computer interfaced I-V (Keithley 4200 SCS) system was used to monitor photo-induced effect. All measurements were performed in air and at room temperature.

Results and Discussion

Structural, morphological, optical and magnetic properties

The XRD patterns of APO/NFO composites are shown in Figure 1. All the APO/NFO composites exhibit a coexistence of both APO and NFO phases without any impurity phase indicating successful synthesis of composites. All diffraction peaks from the composites were consistent with the diffraction patterns of NiFe_2O_4 (JCPDS no. 44-1485) and Ag_3PO_4 (JCPDS no. 06-0505). In comparison to APO, peaks of NFO are less sharper, which may be resulting from the smaller crystal size and also lesser concentration of NFO. Furthermore, the intensity of the NFO peak increases as per the increase in the NFO concentration. The XRD pattern of pure APO, pure NFO and APO/NFO composite is also given (see supporting Information, Figure S1).

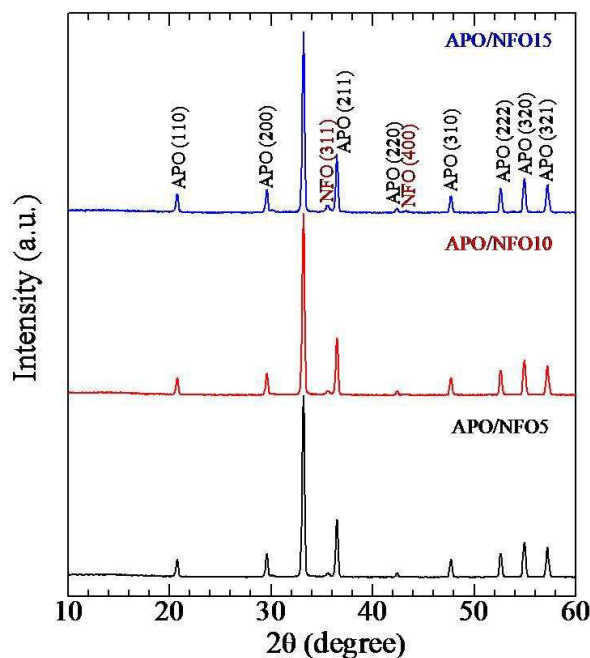


Figure 1: XRD patterns of $\text{Ag}_3\text{PO}_4/\text{NiFe}_2\text{O}_4$ (APO/NFO) composites (a) APO/NFO5 (b) APO/NFO10 and (c) APO/NFO15.

Morphology and particle size of the as prepared samples were investigated by using Field Emission Scanning Electron Microscopy (FESEM). Figure 2 (a-d) depicts the FESEM micrographs of APO, APO/NFO5, APO/NFO10 and APO/NFO15 samples, respectively. As shown in Figure 2, particles of pure NFO have diameters in the range of 20–90 nm, while APO possessed submicron sized irregular polyhedral morphology. Growth process of APO/NFO hierarchical composite nanostructures is shown in Scheme 1. This growth process was occurred via *in-situ* precipitation method wherein as-prepared NFO powder and APO precursor solutions mixed together. Initially, the nuclei of APO were formed as a result of precipitation reaction between AgNO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in solution. APO crystal nuclei gain the irregular shapes and starts to aggregate in particular crystal growth direction leading to form larger crystals which again reorient and finally produce rhombic dodecahedrons.

From structural point of view, a careful look at FESEM images reveals that irregular structures such as triangles, spheres and squares were formed for APO and APO/NFO samples (see Supporting Information, Figures S2 and S3). Interestingly, some micron sized rhombic dodecahedrons of Ag_3PO_4 were found, indicating mixed morphology formation (see Supporting Information, Figures S2, S3). Previously it was shown that the formation of different morphologies of APO such as triangles, cubes, rhombic dodecahedrons, tetrapods and spheres were strongly influenced by the controlled growth of different facets.^{11, 35} It is noteworthy that, facet surface energy plays a very important role in the determining photocatalytic activity since photocatalysis is a surface phenomenon and facet effect strongly relates with formation of surface active sites. For example, Y. Bi *et al.*¹¹ have demonstrated shape and facet

effect of Ag_3PO_4 on photocatalytic performance wherein rhombic dodecahedrons with higher surface energy (1.31 J/m^2) of $\{110\}$ facets exhibited much higher activities for the degradation of organic contaminants than cubes with smaller surface energy (1.12 J/m^2) of $\{100\}$ facet. These investigations revealed that the presence of rhombic dodecahedrons in present case could help to enhance the photocatalytic activities. On the basis of experimental results formation mechanism of APO/NFO composites has been deduced (Scheme 1). From the crystallographic study of APO, the facet sequences for the variation of surface energies of APO can be written as $g\{111\} < g\{100\} < g\{110\}$.³⁶ Amongst these crystallographic facets, $\{110\}$ exhibit lower atomic density and high surface energy which has led to more open sites for attaching to foreign molecules, whereas $\{111\}$ facets are thermodynamically stable and offer less open sites. Herein, during the course of reaction, some of the irregular-shaped APO structures aggregated along the $[110]$ crystallographic direction which results in formation of APO rhombic dodecahedrons morphology.³⁷ Surprisingly, in present case, some hierarchical APO/NFO microstructures was appeared which are formed by different combination and arrangement of dissimilar units leading to multiple functionalities and it may assists to enhance photocatalytic performance (see supporting information, Figure S3).^{38, 39} Such, hierarchical APO/NFO composites represent a good design that can tailor optical, mechanical and surface properties. Thus, APO/NFO composites, consisting of irregular structures with sharp corners, edges, and smooth surfaces can be fabricated without capping agents by simple precipitation method. For APO/NFO composites, it could be easily seen that the NFO particles were uniformly and tightly decorated on the facet of APO, indicating an intimate contact between NFO and APO (see supporting information, Figure S4). As seen from the Figure 2b, a low molar ratio of APO/NFO (i.e. APO/NFO5) led to good dispersion of NFO onto the facet of APO, and the agglomeration of NFO occurred as the molar ratio increased (Figures 2c and 2d), which reduced the effective area of contact between two materials.

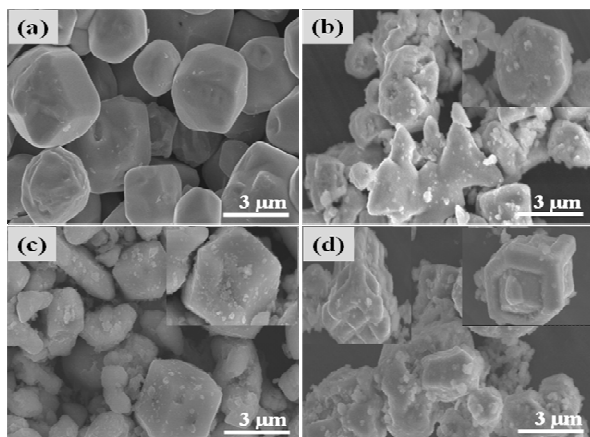


Figure 2: FESEM micrographs of (a) APO (b) APO/NFO5, (c) APO/NFO10, (d) APO/NFO15 samples.

To further confirm the crystallographic structure of APO/NFO composite as well as to determine the particle sizes, TEM images were recorded (Figure 3). TEM analysis reveals that the particles of NFO with size around 20-90 nm are in intimate contact with APO. High resolution TEM (HRTEM) image of APO/NFO sample (Figure 3a, b) clearly showed two distinct sets of lattice fringes. The uniform lattice fringes with an interplanar spacing of 0.262 nm and 0.251 nm correspond to (210) and (311) crystallographic plane of APO and NFO respectively indicating formation of APO/NFO heterojunction photocatalyst. Additionally, the corresponding fast-Fourier-transform (FFT) images (Figure 3c, d) show occasional bright spot indexed as (210) and (311) crystal plane of APO and NFO respectively.

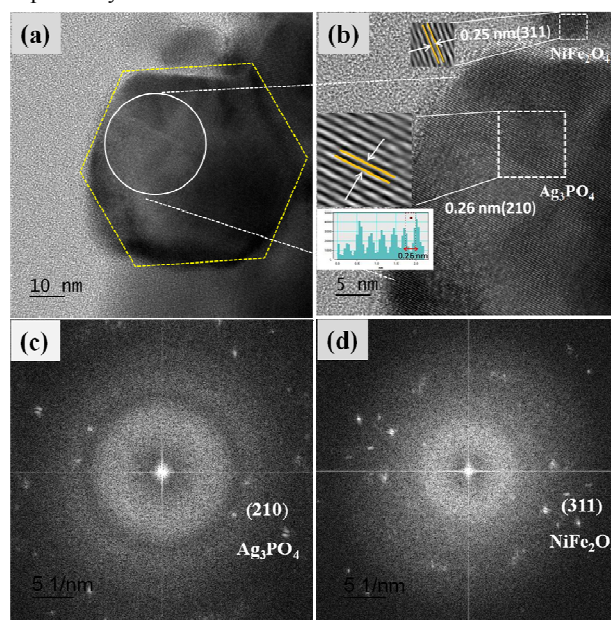


Figure 3: TEM images of APO/NFO15 sample. (a, b) HRTEM images and (c, d) corresponding fast-Fourier-transform (FFT) patterns.

The optical properties of as synthesized APO, NFO and APO/NFO composites were investigated by UV-Vis absorption spectroscopy (Figure 4). Bare APO shows absorption edge at $\sim 520 \text{ nm}$ whereas pure NFO shows absorption at around 700 nm . As evident from the optical spectra, two absorption edges were observed for all the APO/NFO composites indicating formation of hybrid structures. The band gap energies (E_g) of APO and NFO were found to be 2.42 and 1.67 eV , respectively. In case of APO/NFO composites, red shift in the absorption spectrum was observed which may be attributed to deposition of the NFO on the surface of APO. Additionally, with increasing NFO content in the APO/NFO composites the enhancement in absorption intensity in the visible region was seen compared to that of the pure APO, which indicates that APO/NFO composites absorb visible light more effectively than that of bare samples. This property should make a positive contribution to the photocatalytic activity under visible light

irradiation as more efficient utilization of solar energy could be achieved.

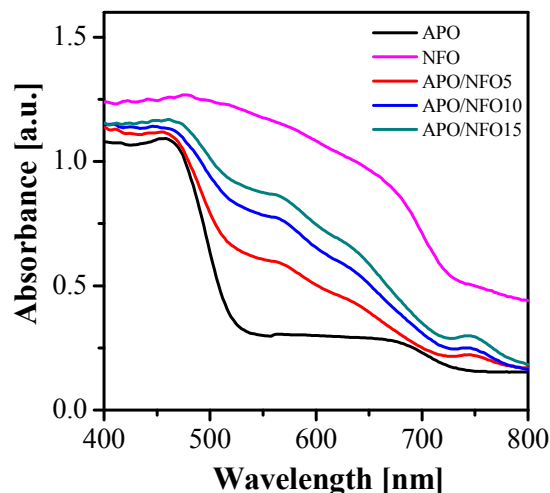


Figure 4: UV-Visible absorbance spectra of APO, APO/NFO5, APO/NFO10, APO/NFO15 and NFO samples.

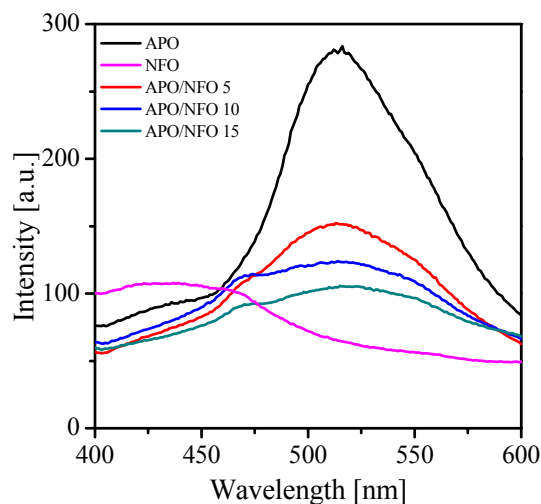


Figure 5: Photoluminescence spectra of APO, APO/NFO5, APO/NFO10, APO/NFO15 and NFO samples.

A room-temperature photoluminescence (PL) emission spectrum was recorded in order to investigate the migration and separation efficiency of photogenerated charge carriers in the as-prepared samples. Figure 5 shows the PL spectra of APO, NFO and APO/NFO composites. For APO, strong emission peak at around 530 nm was observed. The emission at about 530 nm, which has photon energy approximately equal to the band gap of APO, is caused by recombination of photo-excited electrons at the conduction band edge with holes at the valence band edge.³⁴ A similar PL spectrum was obtained for all

APO/NFO composites; however, the overall emission intensity was reduced compared to that of pure APO. Since PL emission is mainly due to the recombination of photogenerated electrons and holes, the weakened emission intensity in APO/NFO composites thus indicates inhibition of electron-hole recombination due to co-catalytic effect of NFO, which lengthens the lifetime of charge carriers and is beneficial for the improvement of photocatalytic activity.

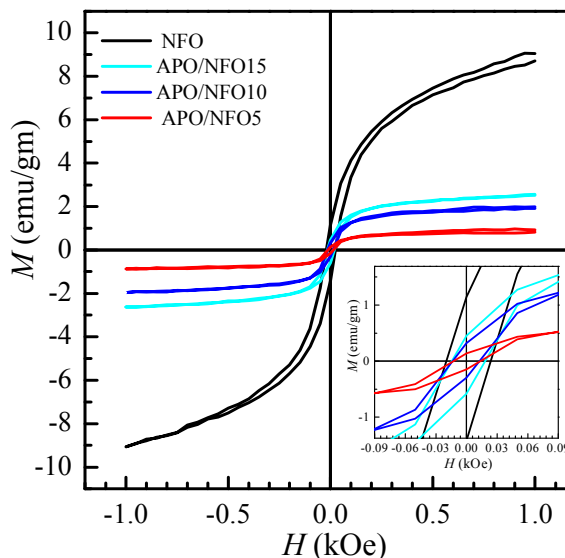


Figure 6: Magnetization of NFO, APO/NFO5, APO/NFO10, APO/NFO15 samples.

Figure 6 represents hysteresis loops of the APO/NFO composites and pure NFO, measured at room temperature. The M - H behavior of the composites undoubtedly indicates the presence of expected ferrimagnetism in the composite due to the presence of NFO with different compositions. It can also be seen that with the increase in percentage of NFO in the composites, the values of saturation magnetization (M_s) and remnant magnetization (M_r) increase linearly, which is mainly due to the increase in magnetic particles in the composites. The values of M_s and M_r are summarized in Table 1. The M_s and M_r values are found to be lesser than that of pure NFO as a result of the presence of a non-magnetic APO. The increase of M_s value with the increase in loading percentage of NFO nanoparticles can be explained by using the rule of mixing^{40,41} as given below,

$$M_{s(\text{composite})} = x M_{s(\text{NFO})} + (1-x) M_{s(\text{APO})} \quad (1)$$

Where, x is the mole fraction of NFO phase. Since,

$$M_{s(\text{APO})} = 0 \quad (2)$$

$$M_{s(\text{composite})} = x M_{s(\text{NFO})} \quad (3)$$

M_s of composite is strongly dependent on the mole fraction of NFO nanoparticles (x) and the saturation magnetization, M_s of NFO.

Photocatalytic activity study

The photocatalytic activities of APO/NFO composites were evaluated by decomposing MB under visible light irradiation. Figure 7 shows the degradation rates of MB dye over P25 TiO₂,

APO and APO/NFO composites, respectively. APO/NFO composites exhibit higher photocatalytic activity than pure APO, NFO and P25 TiO₂ as evident from photocatalytic activity study for the degradation of MB under visible light irradiation. MB dye degradation activity of APO/NFO composite was monitored by UV-Vis spectra (see Supporting Information, Figure S5). Introduction of NFO in the composite significantly improves the photocatalytic activities of APO. However, an excess addition of NFO showed decrease in photocatalytic efficiencies. The apparent rate constant values were calculated from the slope of plot of $\ln(C_0/C_t)$ versus irradiation time (Figure 8), where C_0 is initial MB concentration and C_t is the concentration at time t . The rate constant (k) value i.e. 0.532 min^{-1} was estimated for the APO/NFO5 sample which is higher than APO/NFO10 (0.302 min^{-1}), APO/NFO15 (0.086 min^{-1}) and pure APO (0.293 min^{-1}) and NFO (0.003 min^{-1}) samples. From the observed results it was evident that the photocatalytic activity deteriorates with increasing NFO content ($>10\%$), showing that the loading percentage and intimate contact between two materials play an important role in determining photocatalytic efficiency. This means that with higher content of NFO the number of the active photocatalytic reaction sites decreases and cause a negative influence on the photocatalytic processes. Introduction of large amount of NFO leads to shield the incident light, thus preventing the generation of charge carriers in APO. Excessive amount of NFO may cover the active sites at the surface of APO and also could hinder the contact with MB.⁴¹ It could be further confirmed from the photocatalytic activity results that the low optimal molar ratio of APO/NFO is good for increasing surface active sites and increasing photocatalytic performance. The highest photocatalytic performance of APO/NFO5 composite can be attributed to intimate contact between APO and NFO which facilitates the electron-hole separation. Moreover, the presence of NFO in composite avoids the photocorrosion of APO; which usually occurs by photo-induced electrons during photocatalytic reactions. Due to photocorrosion problem, APO photocatalysts tend to suffer poor stability however coupling with NFO to construct a heterojunction structure can increase the stability of APO if transferring photogenerated electrons on APO to reduce O₂ (ORR) instead of reducing Ag⁺ ions in APO to Ag metal.⁴² This effect is a result of modification of surface properties, such as surface potential by combining with NFO.⁴² In addition to photocatalytic activity, the stability of photocatalysts is another important issue for their practical applications. The stability of as synthesized composite photocatalyst was checked by performing three consecutive cycles (Supporting Information, Table S1). There was no noticeable deactivation of photocatalyst was observed, indicating that the present hybrid photocatalysts are stable enough during the repeated experiments without exhibiting any significant loss of photocatalytic activity. Therefore, the as-prepared APO/NFO composites can work as an effective photocatalysts for MB degradation with good stability.

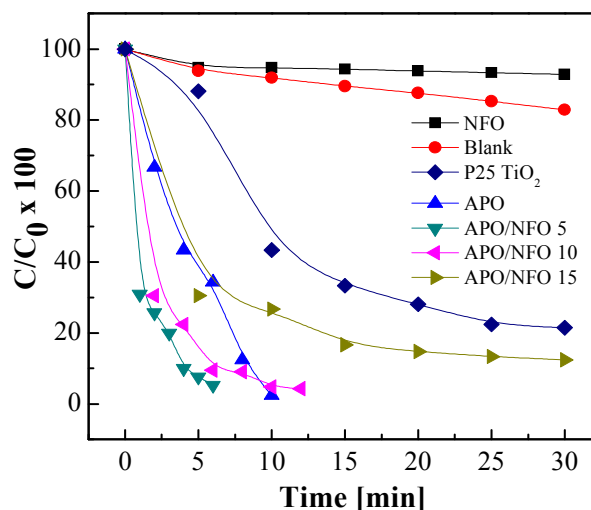


Figure 7: Graph of amount of MB remained with irradiation time using APO, APO/NFO5, APO/NFO10, APO/NFO15 samples

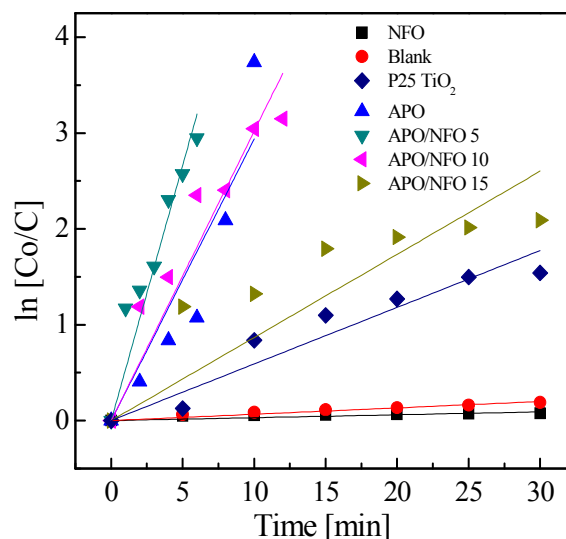


Figure 8: Chemical kinetics study of photocatalytic MB degradation using (a) APO (b) APO/NFO5, (c) APO/NFO10, (d) APO/NFO15 samples.

On the basis of experimental results, we have proposed photocatalytic reaction mechanism for high efficiency of APO/NFO photocatalyst based on the alignment of their energy levels. The schematic representation of band diagram for the n-n type NFO–APO heterojunction at equilibrium is shown in Figure 9. According to the energy band structure of n-n heterojunction, the photogenerated electron–hole pairs could be effectively separated through the heterojunction interface between n-type Ag₃PO₄ and n-type NiFe₂O₄. The n-n heterojunction formed between two semiconductors establishes an internal electrostatic field directed from the NFO region to the APO region, creating an energy barrier for the electron transfer from conduction band (CB) of NFO to CB of APO. Under visible-light irradiation, both APO and NFO can absorb

the photon energy and produce the electron-hole pairs. Since, the flat band potential of NFO is more negative than that of APO, the electrons keep transferring from NFO to APO until the Fermi level equilibrium of both is attained. Meanwhile, photoexcited holes from valence band (VB) of APO would be immigrated to the less positive VB of NFO and further reacted with the absorbed H₂O molecules to form active oxidants such as hydroxyl radicals (•OH). At the same time, the accumulated electrons on the surface of APO reacts with absorbed oxygen to form oxidants such as superoxide ions (•O²⁻). Thus, the generated reactive oxidants (•OH and •O²⁻) degrade MB.

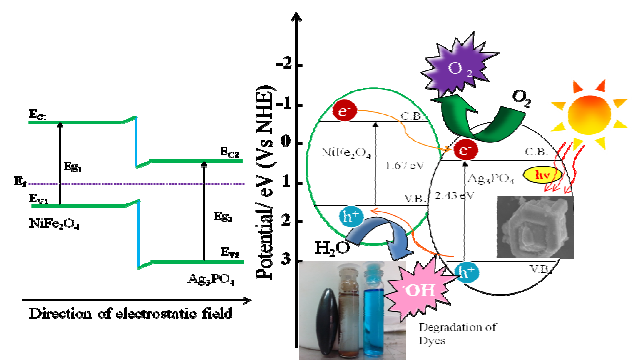


Figure 9: Photocatalytic mechanism for degradation of MB using AP/NFO composite photocatalyst.

Furthermore, it is important to note that due to strong magnetic properties of the NFO, the APO/NFO photocatalyst can be magnetically separable from a suspension by virtue of their magnetic properties. As seen from the inset of Figure 8, the as-formed APO/NFO nanoparticles were well-dispersed in suspension, and the suspended nanoparticles could be easily drawn to the side wall of the vial with a magnet implying good magnet-controlled properties and recyclability.

Table 1. The apparent rate constant (Kapp) values for photocatalytic MB degradation and magnetization data of APO/NFO composites

Sr. No.	Catalyst	Rate constant (Kapp) for MB degradation [min ⁻¹]	Standard Err.	Ms (emu/gm)	Mr (emu/gm)
1	APO	0.29	0.03484	-	-
3	APO/NFO5	0.53	0.03298	0.58	0.13
4	APO/NFO10	0.30	0.02076	1.81	0.32
5	APO/NFO15	0.086	0.0098	2.47	0.45
2	NFO	0.003	0.00040	9.05	1.14
6	P25 TiO ₂	0.059	0.0037	-	-
7	Blank	0.006	0.00033	-	-

The experimental results and mechanism proposed above imply that NiFe₂O₄ can serve as co-catalyst for an efficient photocatalytic MB degradation, which not only provides active sites for the photocatalytic reaction but also inhibits recombination by promoting charge separation. Moreover, this photocatalyst could be recovered easily by external magnet and

can be reused for replicate experiment of photocatalytic degradation.

Current–Voltage characteristic

In order to check the photo-stability of the APO/NFO composites, we have studied photoconductivity of the APO, NFO and APO/NFO5 composites. Furthermore, the high efficiency of APO/NFO photocatalyst was correlated with the conductivity of the composites. Figure 10 represents I-V characteristic of APO, NFO and APO/NFO5 samples measured using two probe techniques with the applied bias from -10 V to +10 V under both dark and light irradiation. Pure APO and NFO sample do not show photoconducting behavior which is evident from their noisy I-V characteristics. The resistance of both the samples is found to be in the order of 10¹⁰ Ω. Upon illumination of light, not much change is observed in the photoconductivity. Similarly, APO/NFO composite also did not show large change in photoconductivity upon illumination of light, however, their photoconductivity is very stable which is evident from its linear and stable I-V response. Although, APO/NFO samples showed weak photo-response, their overall resistance is drastically decreased by 5 orders i.e. from 10¹¹ Ω to 10⁶ Ω, which suggest the improved conductivity of the samples. As mentioned earlier, when the n-n type heterojunction is formed between APO and NFO semiconductors, an intermediate energy gap between valence band and conduction band becomes more active, which facilitate the electron-hole pairs separation by band gap alignment through the co-catalytic effect of NFO, thereby allowing the better the electrical conductivity. So it is concluded that the enhancement in photocatalytic activity for APO/NFO composites is attributed to the excellent electrical conductivity of APO/NFO composite.

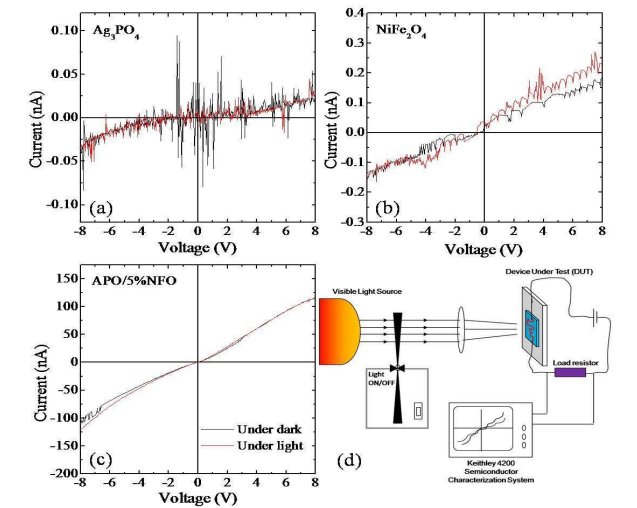


Figure 10: I-V curves of the sample (a) APO (b) NFO and (c) APO/NFO5 samples without (dark) and with illumination (1000 Lux) of light intensity (d) Schematic of experimental setup of photoconductivity measurement.

Conclusions

An efficient magnetically separable and stable photocatalyst for the degradation of organic pollutant was fabricated by loading a small amount of NiFe_2O_4 onto Ag_3PO_4 through a facile precipitation method. APO/NFO composite photocatalysts showed enhanced photocatalytic activity as compared to that of their individual counterparts. The enhanced photocatalytic activity is ascribed to the increasing electrical conductivity of the composites through the co-catalytic effect of NiFe_2O_4 providing accelerated charge separation by band gap alignment. The conductivity of the photocatalysts gives direct experimental evidence for improved photocatalytic activity as well as stability and provides useful guidance for developing an efficient photocatalyst.

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Supporting Information

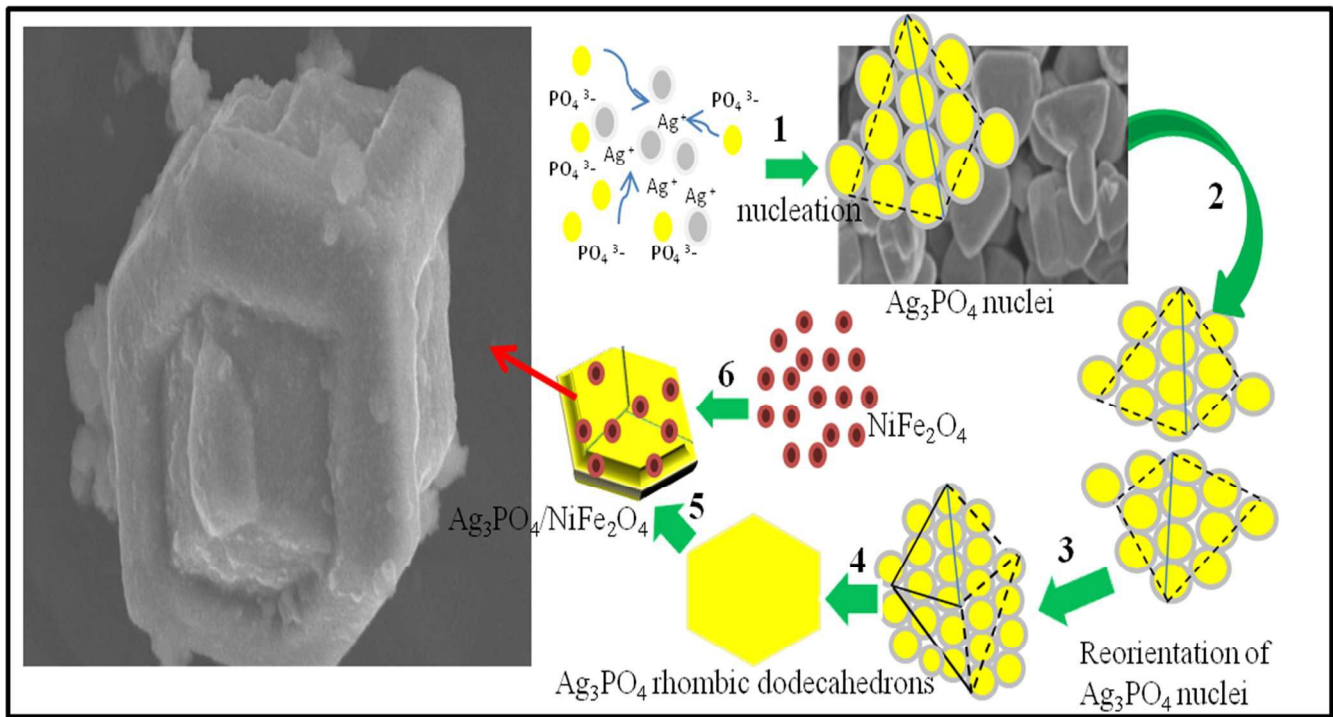
Electronic Supplementary Information (ESI) available: [FESEM images of pure APO and APO/NFO composites, results of photocatalytic recyclability study, UV-Vis spectra of photocatalytic MB degradation using APO/NFO5 composite]. See DOI: 10.1039/x0xx00000x

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Table of Content

Growth mechanism of APO/NFO composite



Scheme 1. Schematic representation of growth process of APO/NFO composite

Scheme 1 represents the formation mechanism of APO/NFO composite. A step wise growth process of APO nuclei leads to develop interesting morphologies of APO/NFO composite. Magnetically separable APO/NFO heterojunction photocatalyst with co-catalytic effect of NFO onto APO have been demonstrated.