Ti3C2-MXene/Bismuth Ferrite Nanohybrids for Efficient Degradation of Organic Dye and Colorless Pollutant

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Ti$_3$C$_2$-MXene/Bismuth Ferrite Nanohybrids for Efficient Degradation of Organic Dye and Colorless Pollutant

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Abstract Nanohybrids, made up of Bismuth ferrites/Carbon allotropes, are extensively used in photocatalytic applications nowadays. Our work proposes a nanohybrid system composed of Bismuth ferrite nanoparticles with two-dimensional (2D) MXene sheets namely, the BiFeO$_3$ (BFO)/Ti$_3$C$_2$ (MXene) nanohybrid for enhanced photocatalytic activity. We have fabricated the BFO/MXene nanohybrid using simple and low cost double solvent solvothermal method. The SEM and TEM images show that the BFO nanoparticles were attached onto the MXene surface and in the inter-layers of two-dimensional (2D) MXene sheets. The photocatalytic application is tested for the visible light irradiation which showed the highest efficiency among all pure-BFO based photocatalysts, i.e. 100% degradation in 42 min for organic dye (Congo Red) and colorless aqueous pollutant (acetophenone) in 150 min, respectively. The present BFO-based hybrid system exhibited the large surface area of 147 m$^2$g$^{-1}$ measured via Brunauer-Emmett-Teller (BET) sorption-desorption technique, and is found to be largest among BFO and its derivatives. Also, the photoluminescence (PL) spectra indicate large electron-hole pair generation. Fast and efficient degradation of organic molecules is supported by both factors; larger surface area and lower electron-hole recombination rate. The BFO/MXene nanohybrid presented here is a highly efficient photocatalyst compared to other nanostructures based on pure BiFeO$_3$ which makes it a promising candidate for many future applications.

Keywords: BiFeO$_3$/MXene, nanohybrids, photocatalysis, chemical etching, organic pollutants

1 Background
Photocatalysis is a low cost and environment-friendly technique to purify the wastewater from pollutants such as the organic dyes thus, splitting out the compounds to form water molecules and carbon monoxide. In the past, semiconductors have been widely used as the photocatalysts to degrade organic dye owing to the fact that they are not easily biodegradable. For the last decade, the TiO$_2$ used as a photocatalyst, however, its activity is limited to the ultra-violet (UV) light as it has wider band gap (~3.2 eV) and lower activity under visible light irradiation. As, the UV and visible lights form 4 % & 43 % of the solar spectrum respectively, therefore it is required to develop such materials that could be used under visible light spectrum. For this purpose, bismuth ferrites are the potential candidates under visible light irradiation having narrow band gap.

Bismuth ferrites (BiFeO$_3$ or BFO) are the family of transition metal oxides used in several applications. At room temperature it is a perovskite type material which manifests multiferroic behavior with 2.01 eV band gap. According to the recent studies, BFO compound showed photocatalytic activity to degrade the organic pollutants such as the dyes. In a recent report, thermally reduced graphene oxide is used in a solution to absorb the methyl orange dye. It has been shown in recent works that the nanocomposites of BiFeO$_3$/graphene and metal co-doped BiFeO$_3$ are highly efficient for the photocatalytic applications. The reported result shows that the two dimensional (2D) materials have better and extra ordinary properties for their enhanced effects therefore, they are taken as promising materials for many applications.
2D materials such as metal chalcogenides\textsuperscript{28-29}, boron nitride\textsuperscript{30}, oxides and hydroxides\textsuperscript{31-33} etc are prepared by exfoliating their three dimensional (3D) structures.

Recently, well-synthesized reported 2D layered materials such as transition elements, with carbide and nitride, also called MXene, have attracted considerable attraction for their carbon-based 2D layered structures.\textsuperscript{33-39} They are characterized by the formula M\textsubscript{n+1}X\textsubscript{n}Tx (n=1,2,3) whereas, M corresponds to various transition metals like Titanium, chromium etc X shows the carbon, nitrogen etc and the functional groups of MXenes are represented by T\textsubscript{x} (OH, O, F).\textsuperscript{40} The first MXene compound reported was Ti\textsubscript{3}C\textsubscript{2}Tx and till today, there are 19 more such compounds from MXene family being synthesized and many of them have been predicted for various applications using first principle calculations.\textsuperscript{34, 37, 39, 41-42} Recently, T. Soltani et al studied the photodegradation of BiFeO\textsubscript{3}/reduced graphene oxide (rGO) nanocomposites and have found that it degrades completely the aqueous bisphenol A in 70 minutes under visible light irradiation.\textsuperscript{20} X. F. Wang et al reported the 100% degradation efficiency for the Bi\textsubscript{25}FeO\textsubscript{40}/rGO nanocomposites in 180 minutes under visible light irradiation for methyl orange.\textsuperscript{12} Also, J. F. Dai et al have found only 50% degradation of methyl orange in 6 hours which shows very poor photocatalytic efficiency of the BiFeO\textsubscript{3}/GO nanohybrid.\textsuperscript{43} S. Irfan reported the 17% photodegradation of acetophenone using La\textsuperscript{3+} and Se \textsuperscript{4+} doped BFO nanostructures.\textsuperscript{44} Many researchers are working on various metal-doped BiFeO\textsubscript{3} and their hybrids with graphene to be used as photocatalysts since the pure BiFeO\textsubscript{3}/graphene photocatalysts reached to its efficiency limit. Therefore, there is a dire need of finding highly efficient pure-BiFeO\textsubscript{3} based 2D nanohybrid
structures. In such an effort, we have presented here a very highly efficient BiFeO$_3$/Ti$_3$C$_2$Tx-MXene nanohybrid structure which showed 100% photocatalytic activity within only 42 minutes for Congo Red dye removal at room-temperature. But no research found on doped BiFeO$_3$/Ti$_3$C$_2$Tx-MXene nanohybrid or composites showing the photocatalytic degradation of acetophenone because of its difficulty in degrading from the solution. Moreover, this work reports the band gap tuning of the proposed nanohybrid structure upto1.96 eV having the largest BET surface area of 147 m$^2$g$^{-1}$ for any BiFeO$_3$ structure or its derivative reported till date.

2 Results & Discussion

2.1 Structure of doped BFO nanoparticles and BFO/MXene nanohybrid

The structural analysis was done by Cu-Kα radiations in X-ray diffraction (XRD) (XRD, Rigaku 2500, Japan). The scan angle range was 2θ ~ (5–65) degree using Cu-Ka radiation are operating at the voltage of 40 kV and 20 mA. The Figure 1(a) shows the XRD pattern of MAX phase (Ti$_3$AlC$_2$) in red, and etched MAX phase (MXene, Ti$_3$C$_2$Tx) in black, whereas the “Tx” is the surface terminations (O-, OH- and F-) on MXene sheet [40]. In Figure 1(b) the closer view of MXene peaks is shown, three characteristic peaks are observed at 2θ ≈ 9.7°, 2θ ≈ 19.1° and 2θ ~ 39° corresponding to (002), (004) and (104) planes respectively, represent etched MAX; the decrease in peak intensity showed the crystallinity loss after the removal of aluminium from the MAX phase, as shown in SEM images. [38-39] The most intense peak in (Ti$_3$C$_2$Tx) is at 2θ ~ 39°, which corresponds to (104) plane as shown in Figure 1(b), indicating the etching of Al from the structure. [45-46] In Figure 1(c) the X-ray diffraction pattern of pure BFO nanoparticles is given in
blue and BFO/MXene nanohybrid structure is given in black. The diffraction peaks confirm the perovskite crystalline structure of pristine BFO, distorted rhombohedral structure with the space group of R3c. All the diffraction peaks of BFO and indexing is same as reported in literature (JCPDS 71-1518). Along the characteristics peaks of BFO, a small amount of secondary phase also occurs at 2θ ~ 27°-28°. In non-stoichiometry, the Bi2O3 volatilization results are well known and also the secondary phase formation in BFO. The XRD peaks of impurity phase in this BFO structure matches with Bi2Fe4O9 phase as shown in Figure 1(c). The effect of addition of BFO on MXene sheet can be seen by suppressed behavior of peaks, broadened, less intense as well as slightly shifting towards higher diffraction angles as shown in Figure 1(d). The little shifting of XRD peaks of BFO/MXene nanohybrid along (2θ) towards right as compared to pure BFO, might be termed as one of the lattice’s compression of the unit cell happening by the addition of BFO on MXene sheet. The doublet sharp peaks (104) and (110) at 2θ ≈ 32° of BFO shifted to higher angle which may be due to the fact that there is a stress on the unit cell that causes the decrease of lattice constant and interplanar distance as a result contraction of unit cell volume occurs. However, the structure of the BFO nanoparticles remain same which is rhombohedral distorted space group R3c as the doublet peaks are clearly separated even after the nanohybrid formation. The particle size of BFO and BFO/MXene was calculated by Scherrer’s formula and it seems to be 45 nm and 43 nm, respectively. The grain size decreases due to the decrease of lattice constant or lattice distortion that takes place upon doping or by hybrid formation, which ever happens. This reduction in grain size causes to enhance the surface to
volume ratio of the prepared nanohybrid. During lattice parameters calculation similar decreasing trend was observed for BFO/MXene nanohybrid compared to pure BFO particles. The calculated values of lattice parameters “a” and “c” were decreased from 4.58Å to 4.55Å, and 7.31Å to 7.29Å, respectively. The measured values of BFO/MXene have slight difference over the actual calculated values of BFO, this small difference in lattice parameters is due to the presence of minute content of secondary phase. The grain size was calculated using Scherrer’s formula whereas, the reduction in grain size of BFO/MXene compared to BFO is due to the attachment of the BFO nanoparticles onto the Ti3C2Tx surfaces.
Figure 1. XRD spectra of (a) MAX (Ti$_3$AlC$_2$) and MXene (Ti$_3$C$_2$Tx), (b) closer view of MXene curve, (c) BFO, BFO/MXene nanohybrid, (d) the zoomed image of peak shifting.

2.2 Morphological Analysis

The surface morphology including the shape and size of MXene and BFO/MXene nanohybrid was studied using field emission scanning electron microscope and tunneling electron microscope as shown in Figure 2(a-f) and Figure 2(g, h) respectively. The Ti$_3$C$_2$Tx-MXene sheets
after etching shows partial splitting due to the Aluminium removal from its parent Ti$_3$AlC$_2$
compound as seen in Figure 2(a,b), forming a multilayer stack of MXene sheets.$^{38,39}$ The BFO
nanoparticles seem to attach on the MXene surface indicating a good nanohybrid formation as
shown in (Figure 2c-2f) taken at different zooming scales i.e. 2µm, 300 nm, 200nm and 100nm
respectively. The closer view at 100nm shows the BFO particles are in non-uniform round
clusters attached at MXene sheet forming a porous network of BFO/MXene. The TEM analysis
of the BFO/MXene nanohybrid shown in (Figure 2g and 2h). It can be clearly seen that the BFO
nanoparticles penetrate into the MXene layers and adsorbed onto the surface of the MXene
sheets, which are in good agreement of SEM results. The multilayer MXene sheets can be seen
clearly providing smooth surface to the BFO nanoparticles. The particle size estimation from
TEM images is estimated using ImageJ software$^{40}$ which is ~ 25 nm - 50 nm.
Figure 2. Surface morphology of MXene sheets, BFO/MXene nanohybrids. (a) & (b) show the morphology of exfoliated-MXene sheets (c-f) shows BFO/MXene nanohybrids (g-h) show the TEM images of BFO/MXene nanohybrids.
2.3 X-ray photoelectron spectroscopy (XPS)

Chemical composition and binding energies of the synthesized nanohybrid is confirmed using the X-ray photoelectron spectroscopy (XPS) technique. XPS analysis of the BFO/MXene nanohybrid is shown in Figure 3. (Figure 3a) shows the survey spectrum containing the peaks for the following elements bismuth, iron, oxygen, titanium and carbon and will be abbreviated here after as Bi, Fe, O, Ti and C elements in BFO/MXene nanohybrid with their respective binding energies. High-resolution scans were taken for Bi, Fe, O, Ti and C and are shown in Figure 3 (b-f). The high-resolution spectrum of Bi 4f is in Figure 3 (b), spreading from 157 eV to 166 eV having sharp peaks at 158.8 eV and 164.1 eV, shows the binding energies of two different states of Bi that are Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$, respectively. According to a report it implies that Bi has oxidation state of “+3”.\textsuperscript{57} In Figure 3(c), the high-resolution spectrum of Fe is discussed which spreads over a range 706 to 729 eV, the exact peaks are measured at 710.8 eV and 724.3 eV that show the binding energies of two states i.e. Fe 2p$^{3/2}$ and Fe 2p$^{1/2}$, respectively which relates to the Fe$^{2+}$ ions.\textsuperscript{57-59} The presence of Fe ion causes to form more oxygen vacancies on BFO’s surface, which further increases the chances of adsorption of organic species on the surface.\textsuperscript{60-61} High-resolution spectrum of the oxygen O1s is given in Figure 3d. The binding energy of oxygen ranges from 527 eV to 534 eV; deconvolution of the oxygen peak was done and fitted with Lorentzian-gaussian curve to further observe the bonding of oxygen atom. Three different peaks were found from the curve deconvolution, the energy peaks are found at (529.7 eV, 531.1 eV and 532.8 eV) which are attributed to lattice oxygen atoms, hydroxyl oxygen, and surface adsorbed oxygen species.\textsuperscript{62-63} These results of XPS confirms the presence of species oxygen and hydroxyl on the surface BFO/MXene nanohybrid, which helps in the Photocatalytic degradation mechanism; it is a series of redox reactions that occurs on the surface of the materials.\textsuperscript{64} Figure 3 (e) shows the high-resolution spectrum of Ti 2p, the peak spreads over 454 to 470 eV, showing Ti bond; the binding energy for Ti 2p lies at sharper ends of 459.7 eV and 465.6 eV for the Ti(IV) 2p$^{3/2}$ and Ti(IV) 2p$^{1/2}$, respectively. The evidence of Ti-O and Ti-C bonding can be seen from both
of the peaks. High-resolution spectrum of the carbon C 1s is shown in Figure 3 (f); it is a single peak at 284.7 eV as seen which can be deconvoluted if required into two peaks for C-C and C-O bonds. Thus, elemental bonds present in the synthesized nanohybrid structure at specific binding energies confirms the successful formation of the BFO/MXene nanohybrid.
Figure 3. XPS analysis (a) survey scan of BFO/MXene nanohybrid and high resolution scans of (b) Bi 4f (c) Fe 2p (d) O 1s (e) Ti 2p (f) C 1s.

2.4 Band gap engineering

The absorption spectra of pure BFO nanoparticles and BFO-MXene nanohybrid was calculated using UV-vis spectrophotometer. The well-established Kubelka-Munk technique is used to estimate the absorption spectra of both samples.\(^{67-68}\) It is well known from this theory that the relation between the absorption coefficient \(\alpha\) and the photon energy \(h\nu\) for the allowed transitions is:

\[
(\alpha h\nu) = A (h\nu - E_g)^{n/2}
\]

Whereas, \(A\) is a constant function, \(E_g\) shows the band gap energy, \(h\nu\) shows the frequency times the Planck’s constant, and \(n\) is a positive integer.

The optical absorption spectra for pure BFO nanoparticles and BFO-MXene nanohybrid is measured at room temperature between the wavelength range of 350-700 nm as shown in (Figure 4a). A sudden characteristic peak of pure BFO nanoparticles is observed at around 599 nm.\(^68\) To calculate the band gap for pure BFO nanoparticles and BFO/MXene nanohybrid, Tauc’s plot method is used as shown in (Figure 4b).\(^{69-70}\) A clear red shift is observed in the absorption spectra for BFO/MXene nanohybrid, compared to the pure BFO nanoparticles. The calculated band-gap from tauc’s plot for pure BFO nanoparticles at direct band transition is 2.01 eV which agreed
well with the previous reports.71,72 The calculated band gap for BFO/MXene is 1.96 eV, there is slight reduction in band-gap, as shown in (Figure 4b) which indicates that the produced nanohybrid is better suitable for photocatalytic application compared to its pure BFO counterpart.

Figure 4(c) shows that the photoluminescence spectra (PL) of pure BFO nanoparticles, and BFO/MXene nanohybrid. PL intensity shows the recombination rate of the charge carries, as BFO shows a higher peak compared to BFO/MXene nanohybrid, which means the charge recombination rate for BFO is much higher compared to the BFO/MXene nanohybrid.
Once the light falls on the nanohybrid producing electron-hole pairs, which in case of attached MXene surfaces are allowed to spread on MXene surfaces quickly, that may cause delay for recombination of charge carriers.

The phenomena of excitation occur for the BFO nanoparticles when light falls, the valence band (VB) electrons from low energy level jumps to conduction band (CB). The CB in semiconductors have more than one energy bands as explained in detail by J. Liqiang et al due to which the photoluminescence mechanism in the semiconductors is complex and their work also relates the PL intensity with the photocatalytic activity.\textsuperscript{24} The nanohybrid when activated with light produces electron-hole pairs, and in the presence of aqueous media the electron-hole pairs react to form radicals on the surface of BFO/MXene nanohybrid.

In Figure 5 (a), Brunauer-Emmett-Teller surface area calculation is made using multi-point BET method. It confirms that the material is mesoporous in nature.\textsuperscript{25} The pore sizes are found to be about 1.68 nm-2.47 nm using the Barret-Joyner-Halender method, as shown in the Figure 5 (b).\textsuperscript{26} The BFO/MXene nanohybrid in produced system showed the highest reported BET surface area of about 147 m\textsuperscript{2}g\textsuperscript{-1}. So understanding the effect of larger surface area, it can be concluded that the generated charge carriers reside over the surface of MXene sheets, thus causing lower recombination rate for BFO/MXene nanohybrid as compared to the bare BFO nanoparticles.
Figure 5. (a) \( N_2 \) gas isotherm for BFO/Ti\(_3\)C\(_2\)Tx, measured at 77 K. (b) Pore volume vs pore diameter.

2.5 Photocatalytic activity of pure BFO and BFO-MXene

Figure 6 (a) shows the absorbance spectra of BFO/MXene nanohybrid. Figure 6 (b) shows the photocatalytic degradation capacity of the bare BFO and BFO/MXene nanohybrid. It can be observed that only 33% of Congo Red (CR) was degraded by pure BFO under visible light irradiation in 42 mins. It shows that the pure BFO is very stable and not suitable for degradation. Previously reported photocatalytic degradation of the CR using pure MXene (Ti\(_3\)C\(_2\)) was 12% in 120 minutes.\(^{22}\) Crystal clear water was obtained only in 42 minutes by using BFO/MXene as a photocatalyst using visible light irradiation. From Figure 6 (c) it was observed that only 21% of Congo Red dye was degraded from catalytic solution under dark experiment, which shows that BFO/MXene is a better photocatalyst rather than catalyst in dark conditions. The degradation of the dye can be achieved in two conditions, dark and light induced condition, its a combination of
surface adsorption and degradation mechanism. Degradation mechanism is explained in the later section.

The photocatalytic activity also depends upon the electron and hole recombination process as stated earlier, the BFO/MXene’s PL intensity is quite less than the BFO’s PL intensity, which also supports the face that lower PL intensity means higher photocatalytic activity of the system. Previous reports on BFO/graphene hybrids shown higher surface area and higher photogeneration rate and in turn providing the higher photocatalytic activity.\textsuperscript{12, 16, 19, 43} Here, the produced system has higher BET surface area of 147 m\(^2\)g\(^{-1}\), in comparison with previously reported bare BFO, BFO/graphene hybrids and its other derivatives, thus causing higher production of charge carries for the redox reactions and hence, providing more effective photodegradation of organic dye (CR). Thus, the improved photocatalytic activity should be attributed to following factors as stated earlier, the higher charge carrier generation of BFO, large separation time of electrons and holes, slight reduction in crystallite size, higher BFO/MXene surface area which provides more activate sites in number as compared to bare BFO nanoparticles, and the higher surface area of BFO/MXene nanohybrid provides quick transfer of excited charges from BFO to MXene sheets.

The stability of a photocatalyst is a key factor for their practical applications. From Figure 6 (d,e), it can be seen that after four cyclic runs, the crystal structure of BFO/MXene remains same before and after the photocatalytic degradation reactions, which makes BFO/MXene a stable visible light induced catalyst and thus, is suitable for commercial applications.
Figure 6. (a) The absorbance spectra of BFO/MXene nanohybrid (b) Photocatalytic degradation of CR by BFO and BFO/MXene nanohybrid against the time taken using light (c) Degradation of CR by BFO/MXene nanohybrid against the time taken under dark conditions experiment (d) 4 cycles repetition of the degradation process (e) BFO/MXene XRD curve before and after irradiation.

2.6 Photocatalytic degradation mechanism
The visible light irradiation produces electron-hole pairs in the material, electrons combines with O$_2$ and holes combine with OH$^-$ to produce super oxide and free hydroxyl radicals, respectively. These radicals are highly active species that degrade the organic pollutants and produced some harmless by-products (CO$_2$ and H$_2$O). Figure 7 explains the photocatalytic degradation mechanism. The photo-excited BFO/MXene produces electron-hole paired charge carriers (Equation. 1). The MXene sheets quickly trap the electrons reducing the chances of recombination, as shown by lower PL intensity of the BFO/MXene earlier. In the presence of aqueous media, electrons on combining with O$_2$ produces superoxide anion radicals •O$_2^-$, on the other hand holes interact with OH$^-$ to produce free hydroxyl radicals •OH$^-$. The •O$_2^-$ and •OH$^-$ radicals are highly reactive towards the degradation of organic pollutants, so degrades CR into harmless products (CO$_2$ and H$_2$O). Previously reported dye degradation reports show the degradation mechanism as shown here.\textsuperscript{44, 78-82}
Following equations express the whole photodegradation mechanism:

\[ \text{BFO-MXene} + h\nu \rightarrow h^+ + e^- \quad (1) \]

\[ e^- + \text{MXene} \rightarrow e^- \text{ (MXene trapping sites)} \quad (2) \]

\[ e^- \text{ (MXene trapping sites)} + \text{O}_2 \rightarrow \cdot \text{O}_2^- \quad (3) \]

\[ h^+ + \text{H}_2\text{O} \rightarrow \cdot \text{OH}^- \quad (4) \]

\[ \cdot \text{OH}^- + \text{CR} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degradation by-products) } \quad (5) \]

\[ \cdot \text{O}_2^- + \text{CR} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degradation by-products) } \quad (6) \]

The improved photocatalytic activity of BFO/MXene is due to the higher electron-hole pair generation, lower recombination rate of charge carriers, wider absorption of photons and enhanced redox reactions on the photocatalyst surface.

2.7 Catalytic and Photocatalytic Degradation of Acetophenone

Figure 8 shows the degradation of acetophenone under dark and light conditions. The BFO/MXene nanohybrid was also studied for dark and photo degradation of acetophenone. In-order to prepare the pollutant solution, 100 mg of prepared BFO/MXene photocatalyst added into 30 ppm acetophenone solution having concentration of 100 mL. After 2 h stirring we get a homogenous saturated solution of pollutant and catalyst. In the first experiment the solution was put under light and its degradation concentration was check for every 30 mins for upto 150 min, until the solution was clear and pollutant was completely degraded. To check remaining pollutant concentration, every 30 mins 5 ml amount of prepared sample was taken out and centrifuged at 7000 rpm, and the supernatant was characterized by a UV-visible spectrophotometer to check the
absorbance which relates to remaining pollutant concentration in the solution. Figure 8 (b) shows the degradation of acetophenone under light, the pollutant was degraded completely in 150 minutes. In the second experiment the homogenous mixture of pollutant and catalyst was kept in dark condition for 2 hours and then under light. Same method was repeated as stated above for checking the remaining pollutant concentration, BFO/MXene nanohybrid degraded the same pollutant in 150 minutes but with less efficiency, only 60% of acetophenone was degraded in similar time as shown in Figure 8 (c). In the second experiment with dark phase, the adsorption of the acetophenone on catalyst’s surface reaches the equilibrium point. Although the large surface area of (BFO/MXene) allows more adsorption of organic molecules on catalyst surface in the process of achieving the homogenous mixture of catalyst and organic pollutant, as a result light may not interact completely with catalyst, it might be the reason for less efficient degradation of the pollutant by the catalyst, which is supported by the first experiment in comparison from Figure 8 (b). It is difficult to degrade the pollutant “Acetophenone” as compared to other organic pollutants such as organic dyes Congo Red (CR) and Methyl Violet etc due to the highly stable benzene ring in its structure. But the degradation rate of Acetophenone and Congo Red (CR) by the newly produced nanohybrid was almost same due to the enhanced properties of BFO/MXene nanohybrid. In a word BFO/MXene are highly efficient to degrade colored compounds, such as CR, as well as colorless compounds, like acetophenone because of its good physical and chemical properties.44
Figure 8. (a) The absorbance spectra of BFO/MXene shows the degradation efficiency of organic pollutant from solution at different time (b) Catalytic and photocatalytic degradation of Acetophenone in the presence of BFO/MXene (c) Photocatalytic degradation of Acetophenone in the presence of BFO/MXene in light induced experiment.

3 Methods

3.1 Materials

Bismuth nitrate pentahydrate (Bi (NO$_3$)$_3$.5H$_2$O) (99% pure), Iron nitrate (Fe (NO$_3$)$_3$.9H$_2$O) (98.5% pure), Ethylene glycol (C$_2$H$_6$O$_2$) (99%), Acetic acid (C$_2$H$_4$O$_2$) (99.5%), Ti$_3$AlC$_2$ (Max Phase) and Hydrofluoric Acid (39 wt%) were used as received.

3.2 Synthesis of MXene sheets

Exfoliated sheets of Ti$_3$C$_2$Tx were fabricated from pure MAX phase (Ti$_3$AlC$_2$) using chemical etching technique with Hydrofluoric acid (HF, 39 wt%) at room temperature for 60 hours with magnetic stirring; washed it through de-ionized (DI) water and kept it in oven at 60 °C for 6 h to dry the water molecules in the sample.
3.3 Synthesis of BiFeO$_3$ nanoparticles

The double-solvent sol-gel method was used to synthesize BiFeO$_3$ (BFO) nanoparticles. Bismuth nitrate pentahydrate (99% pure) and iron nitrate non-hydrate (98.5% pure) were mixed with equal ratio in ethylene glycol and acetic acid solution followed by stirring for 180 min. The detailed synthesis method is given somewhere else.\textsuperscript{83}

3.4 Synthesis of BiFeO$_3$-MXene nanohybrid

The BiFeO$_3$/MXene (BFO/MXene) nanohybrid was fabricated using double solvent solvothermal technique. MXene solution was made in DI water with the molarity of (0.5 mg/ml), followed by ultrasonication for 10 minutes. The BFO nanoparticles were dissolved in a mixture of acetic acid and ethylene glycol with a 1:1 ratio and (0.01 M) molarity. The BFO solution was ultrasonicated for 1 hour at 60 °C; after that both the prepared solutions were mixed and were transferred to Teflon-lined steel autoclave for solvothermal synthesis at 160 °C for 2 h. The final product washed many times with deionized (DI) water several times and then dried it at 80 °C for 3 h.

3.5 Characterization

The structural analysis was done by Cu-Kα radiations in X-ray diffraction (XRD) (XRD, Rigaku 2500, Japan). The scan angle range was 20 ~ (5–65) degree using Cu-Ka radiation are operating at the voltage of 40 kV and 20 mA. Surface morphology of the MXene and BFO/MXene nanohybrid were investigated using field emission scanning electron microscope (FESEM, JEOL7001F) and transmission electron microscope (TEM, Hitachi HT7700, 100 kV).
Platinum was sputter coated before characterization on the nanohybrid to avoid any charging effect. The ultra violet diffused reflectance spectra (UV-vis DRS) were observed using UV-vis spectrophotometer (Hitachi UV-3310, Japan) to calculate the band gap and photocatalytic activity of BFO/MXene nanohybrid. BET Surface area and porosity of the sample were investigated by Brunauer-Emmett-Teller (BET) using Quadrasorb-SI v. 5.06. by N₂ sorption/desorption isotherms at temperature 77.35 K. For adsorption measurements, the sample of BFO/MXene was degassed at 300 °C. The surface area was calculated using multi-point BET method and the Barret Joyner Halender (BJH) method was used to calculate the pore size. X-ray photoelectron spectroscopy (XPS) was used to study the binding energies of all the elements. Photoluminescence spectroscopy was used to observe the charge carrier’s generation/recombination rate.

3.5.1 Photocatalytic Characterization

The photocatalytic measurements of pure and hybrid BFO structures were analyzed by the degradation of organic compound Congo red (CR) under visible light illumination. The 100 mg/L aqueous solution of BFO and BFO/MXene samples were prepared. The 100 mg photocatalyst were dispersed into the dye solution and were stirred for nearly 2 hours under dark region to get equilibrium adsorption-desorption between the photocatalyst and the organic dye molecules. To keep the system's temperature moderate and also for avoiding any thermal contact during magnetic stirring, an ice bath was provided. For visible light source, a Xenon lamp of 300 W was used. The 3 ml solution was taken out after every 8 minutes during the whole
photocatalytic reaction. After centrifugation the supernatant was separated from the catalyst dye solution and further processed it through UV-vis spectroscopy. The photocatalytic degradation efficiency was estimated by the following formula:\textsuperscript{19, 44, 84-85}

\[
\text{Degradation}(\%) = \frac{o - \dot{C}_t}{C_0} \cdot 100
\]

Where, \( C_0 \) is the Initial concentration of CR, and \( C \) is the concentration of CR after time interval “\( t \)”. The visible light (420 nm < \( \lambda \) < 780 nm) was used to observe the photocatalytic efficiencies of pure BFO and BFO/MXene nanohybrid.

4 Conclusion

BiFeO\(_3\) (BFO) nanoparticles were prepared using sol-gel method. The two-dimensional (2D) MXene sheets were synthesized from their pure MAX phase (Ti\(_3\)AlC\(_2\)) by chemical etching of aluminium and used Hydrofluoric acid (HF) as etchant, the reaction was done at room-temperature. The BFO/MXene nanohybrid was fabricated using double solvent solvothermal technique. Nanohybrid was found to have the largest BET surface area of 147 m\(^2\)g\(^{-1}\), low band gap of 1.96 eV, large electron-hole pair generation and low recombination time. The nanohybrid was further tested for photocatalytic degradation of Congo Red and Acetophenone. It comes out to be a best photocatalyst under visible light irradiation which degraded the Congo Red dye in only 42 minutes. It can be seen that the degradation of the colorless pollutant Acetophenone was also achieved completely in about 150 mins. Whereas, the degradation for same pollutant under dark
effect was only 60% in the same time. This shows that present catalyst (BFO/MXene) is very efficient photocatalyst for colorless organic pollutant acetophenone. Although colorless organic pollutants are difficultly degraded but the highly efficient BFO/MXene nanohybrid makes it possible. The high photocatalytic activity attained here is unique in itself which makes it a potential candidate for commercial applications owing to its low-cost synthesis route.

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Author’s Contribution

Ayesha Tariq, Abdullah Iqbal carried out the experimentation and equally contributed to this work, S. Irfan Ali helped in characterization, Mohammad Z. Iqbal helped in analyzing the data, and Deji Akinwande helped in characterization, Deji Akinwande and Syed Rizwan conceived the idea and supervised the research project.
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