La- and Mn-Codoped Bismuth Ferrite/Ti$_3$C$_2$ MXene Composites for Efficient Photocatalytic Degradation of Congo Red Dye

M. Abdullah Iqbal, S. Irfan Ali, Faheem Amin, Ayesha Tariq, Muhammad Z. Iqbal, and Syed Rizwan

ABSTRACT: Over the years, scarcity of fresh potable water has increased the demand for clean water. Meanwhile, with the advent of nanotechnology, the use of nanomaterials for photocatalytic degradation of pollutants in wastewaters has increased. Herein, a new type of nanohybrids of La- and Mn-codoped bismuth ferrite (BFO) nanoparticles embedded into transition-metal carbide sheets (MXene—Ti$_3$C$_2$) were prepared by a low-cost double-solvent sol–gel method and investigated for their catalytic activity in dark and photoinduced conditions. The photoluminescence results showed that pure BFO has the highest electron hole recombination rate as compared to all the codoped BFO/Ti$_3$C$_2$ nanohybrids. The higher electron–hole pair generation rate of the nanohybrids provides a suitable environment for fast degradation of organic dye molecules. The band gap of the prepared nanohybrid was tuned to 1.73 eV. Moreover, the BLFO/Ti$_3$C$_2$ and BLFMO-5/Ti$_3$C$_2$ degraded 92 and 93% of the organic pollutant, respectively, from water in dark and remaining in the light spectrum. Therefore, these synthesized nanohybrids could be a promising candidate for catalytic and photocatalytic applications in future.

1. INTRODUCTION

With increasing population and global industrialization, potential risks associated with contaminating potable water streams have increased tremendously. Different coloring industries discharge various kinds of organic dyes into the freshwater streams, consequently generating wastewaters. With the increasing demand of potable water, these organic coloring substances must be treated in order to make water safe to drink. Congo red (CR) is a sodium salt of benzidine-bis-1-naphthylamine-4-sulfonic acid. In this study, CR has been selected because of its anionic structure and severe environmental issues. A large number of industries such as textiles, printing, dyeing, paper, and plastic produce CR effluents which can contaminate the freshwater supply. If metabolized, CR can turn into benzide, a well-known human carcinogen. The treatment of CR-contaminated wastewater may also be complicated because of the complex aromatic structure, which resists degradation.

Several physical, chemical, and biological methods qualify for the treatment of colored waters. These methods include adsorption, reverse osmosis, coagulation, biological and photochemical degradation of organic dyes in water. Photocatalysis (photochemical degradation) is a low-cost treatment method that uses catalysts in order to accelerate degradation of organic dyes using sunlight. A class of photocatalysts called semiconductor photocatalysts have also been reported for effective degradation of organic compounds in water. Over the years, several semiconductor particles such as TiO$_2$ and ZnO were reported for photocatalysis. However, these materials exhibited lower photocatalytic activity attributed to wide band gaps (~3.2 eV for TiO$_2$ under visible light). Many heterogeneous and hierarchical photocatalysts were reported previously for degradation of different dyes such as CR, methyl orange (MO), cyanide, rhodamine B (RhB), p-chlorophenol, norfloxacin, and phenol. As the UV and visible lights constitute 3–5 and 43% of the solar light spectrum, respectively, developing new catalysts for visible light photocatalysis are of great interests.

In semiconducting materials, bismuth ferrites, BiFeO$_3$ (called BFO hereafter), have shown promising results for photocatalysis using visible light irradiation attributed to their narrow band gap (~2.2 eV). The band gap in BFOs can be further improved by doping with other ions, which alternatively improves its photocatalytic activity under the visible light irradiation. At room temperature, BFOs exhibit rhombohedrally distorted perovskite structure (R3c), with...
MXenes are considered significant but diﬃcult to synthesize further, leading to the synthesis of additional 19 potentially valuable nanohybrids. The morphology and electronic properties of these nanohybrids were studied using photoluminescence (PL), XPS, respectively. The charge carrier recombination rate of nanohybrids was measured using photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS), respectively. The charge carrier recombination rate of nanohybrids was measured using photoluminescence (PL) technique. The MXene−Ti₃C₂ attachment and codoping of BFOs provided a suitable environment for fast degradation of CR. A high degradation rate of CR (~92%) was observed.

2. RESULTS AND DISCUSSIONS

2.1. Structure and Morphology of Nanohybrids. X-ray diﬀractometry was used to study the phase morphology of the synthesized nanohybrids. The doped BFO nanohybrids defined as, Bi₀.⁹La₀.¹Fe₀.₇₅Mn₀.₂₅O₃ (BLFMO-5), Bi₀.⁹La₀.¹Fe₀.₉₅Mn₀.₀₅O₃ (BLFMO-10), Bi₀.⁹La₀.¹Fe₀.₈₅Mn₀.₂₀O₃ (BLFMO-20), and Bi₀.⁹La₀.¹Fe₀.₇₅Mn₀.₂₂O₃ (BLFMO-25) with Ti₃C₂−MXene, were synthesized. The microstructure of nanohybrids was studied using XRD (Figure 1). The pure BFO matches the JCPSD card no. 20-0169 for BiFeO₃ structure. All diﬀraction peaks were indexed as rhombohedral, corresponding to (012), (104), (110), (006), (202), (024), (116), (112), (018), and (214) reflections. The doublet peak at 32° merged into a single peak showing structural transformation from rhombohedral to orthorhombic. La and Mn doping causes the diﬀraction peaks to vanish, related to planes (006) and (018). Overall, the peaks shifted toward right for Bi₁−ₓLaₓFe₁−ₓMnₓO₃ compared to that in pure BFO. However, the dual diﬀraction peaks of planes (104) and (110) occurring at 2θ = 31.6° and 32.01° were reduced in intensity and merged as the concentration of Mn was increased in BLFO as shown in Figure 1b, a similar trend was observed elsewhere.⁴⁸ The average particle sizes were calculated using Scherrer’s formula

\[
D = \frac{k \lambda}{β \cos θ}
\]

where k = Debye constant, λ = wavelength of X-ray, and β = fwhm. For pure BFO, BLFO, BLFMO-5, BLFMO-10, BLFMO-20, and BLFMO-25, the average particle sizes are 46.32, 33.89, 27.68, 26.65, 22.96, and 30.15 nm, respectively. There was a reduction in average particle size from pure BFO up to BLFMO-20 as Mn doping increased; however, larger particles were observed for BLFMO-25.

The surface morphology of hybrids (Bi₁−ₓLaₓFe₁−ₓMnₓO₃/Ti₃C₂) was studied using SEM (Figure 2). In BLFO/Ti₃C₂ nanohybrids (Figure 2a), the only dopant is the La, where the dopants are La and Mn as in BLFMO (Figure 2b–c). MXene (Ti₃C₂) showed a sheetlike structure observed in all micro-images where the sheets were ~1–1.5 μm wide and 2–3 μm in the lateral dimensions. The nanoparticles (codoped BFO particles (Bi₁−ₓLaₓFe₁−ₓMnₓO₃)) were embedded on the surfaces of Ti₃C₂ sheets. Despite improved catalytic activity (later), there was no regular pattern of the distribution of nanoparticles on Ti₃C₂ sheets observed in SEM images. Briefly,
the BLFO particles (Figure 1a) formed a coagulated structure on the Ti$_3$C$_2$ sheets with approximately 0.8 $\mu$m cluster size. In BLFMO/Ti$_3$C$_2$ nanohybrids, Mn concentration was increased, which further reduced the distribution of BLFMO particles on Ti$_3$C$_2$ sheets, and some sheets had lesser attached particles.

In addition, the average nanoparticle size (from XRD) ranged 22–33 nm, whereas SEM showed large clustering of the nanoparticles. There were a few grains which were not nucleated and observed distributed over the sheets. The BLFMO/Ti$_3$C$_2$ nanohybrid exhibited a uniform growth of the BFO nanoparticles compared to the BLFMO/Ti$_3$C$_2$ samples with Mn doping (Figure 2b–e).

Figure 3 shows the PL spectra of the Bi$_{1-x}$La$_x$Fe$_{1-y}$Mn$_y$O$_3$/Ti$_3$C$_2$ nanohybrids. All the samples of pure BFO, Bi$_{1-x}$La$_x$Fe$_{1-y}$Mn$_y$O$_3$/Ti$_3$C$_2$, were tested for the PL spectra. Considering the PL peaks showing the recombination rate of the separated charge carriers, the pure BFO showed the highest electron–hole recombination rate as compared to all the codoped BFO/Ti$_3$C$_2$ nanohybrids. A low-intensity peak in the PL spectrum indicates a lower electron–hole recombination rate and consequently high photocatalytic activity of the material. The opposite is true for the high-intensity peak observed in PL spectra. A very low PL peak was observed for BLFO/Ti$_3$C$_2$ nanohybrids. Also, the electron–hole recombination rate was lower for all BLFMO/Ti$_3$C$_2$ nanohybrids compared to that of pure BFO particles, which is attributed to enhanced surface area and larger active points present on Ti$_3$C$_2$ sheets. Increasing the concentration of Mn doping lowered the recombination rate significantly, bringing it almost similar to that of the BLFMO/Ti$_3$C$_2$ nanohybrid level.

The radicals produced in BLFMO/Ti$_3$C$_2$ nanohybrids are due to activation of nanoparticles. The generation of electron–hole pairs, as the light falls, at first excites the electrons from valence band to the conduction band (CB). The CB of semiconductors has more than one energy band. Liqiang et al. explained the dependence of photocatalytic activity on the PL spectra of semiconductor materials. The working mechanism of hybrid is such that the charge carriers produced are suddenly spread over the Ti$_3$C$_2$ sheets occupying the larger areas of the Ti$_3$C$_2$ sheets. The charge carriers spread on the sheets further significantly enhance the surface redox reactions of the Ti$_3$C$_2$ sheets. The BLFMO/Ti$_3$C$_2$ nanohybrids have higher surface areas compared to neat BFO nanoparticles. Attaching BFO particles on MXene surface along with doping has significantly lowered the recombination rate of charge carriers and a higher surface area of the nanohybrids is expected. These results are in agreement with previous reports on BFO/graphene nanohybrids where higher surface area and higher photogeneration/lower recombination rate were observed, providing the higher photocatalytic activity.

2.2. X-ray Photoelectron Spectroscopy. XPS analysis is used to check the chemical composition and binding energies of different elements present in the synthesized hybrid structure. Figure 4 shows the XPS analysis of the prepared nanohybrid (BLFMO-5/Ti$_3$C$_2$). In order to confirm the newly proposed nanohybrids, the XPS survey scans were conducted on a represented sample of BLFMO-5/Ti$_3$C$_2$ containing La and Mn doping. Survey scans (Figure 4a) indicated the presence of Bi, Fe, O, Ti, La, Mn, and C with their respective binding energies in the synthesized BLFMO-5/Ti$_3$C$_2$ nanohybrid. A very small signal attributed to La was detected at about binding energy (BE) 840 eV. Mn peak is attributed to BE 682 eV, while Bi and O shows intense peaks at 159 and 531 eV, respectively, which are explained in the discussion later.

The high-resolution scans were also performed for Bi, Fe, O, and C in codoped nanohybrids shown in Figure 4b–e. The high-resolution XPS scan for Bi 4f was in the BE range of 156–167 eV (Figure 4b). Two sharp peaks were observed: BE $\approx$ 158.9 and 164.2 eV, representing Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively. Further stating, Bi is in the Bi$^{3+}$ oxidation state. Figure 4c shows the high-resolution spectrum for Fe over BE range of 707–728 eV. Similar to Bi spectrum, two peaks were observed at 710.7 and 724.4 eV, attributed to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ indicating the formation of Fe$^{2+}$ ions; in a previous report, Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ peaks of pure BFO were at 714.5 and 728 eV, respectively, and due to La doping Fe 2p$_{3/2}$ shifted to lower BE near to 710 eV. More oxygen vacancies should be produced because of the presence of Fe ions of such valence states on the surface of BFO, which enhances the surface adsorption of the organic and oxygen species on the BFO surface. Figure 4d represents high-resolution O1s spectrum. The photocatalytic mechanism is a series of redox...
reactions that occur on the surface of the material, and oxygen species is an important part of the process. The O 1s high-resolution spectra were deconvoluted and fitted using the Lorentzian–Gaussian curves (Figure 4f). Three peaks were observed from the curve fitting: the peak at BE ≈ 529 eV (because of the lattice oxygen atoms), the peak at BE ≈ 531 eV is attributed to hydroxyl oxygen, and the third peak at BE ≈ 532 eV is attributed to the surface-adsorbed oxygen species.60,61 During photocatalytic reactions, higher content of hydroxyl species is required to produce reactive oxygen species such as hydroxyl radical $\cdot OH$.62 Figure 4e represents a high-resolution C1s spectrum. A sharp peak at BE ≈ 284.8 eV was further deconvoluted into two peaks for C$-\text{C}$ and C$-\text{O}$ bonds (not shown).50,63

2.3. Diffusive Reflectance Spectroscopy of Nano-hybrids. The light absorption properties of BLFMO/Ti$_3$C$_2$ nanohybrids were investigated via diffuse reflectance UV (DR-UV) spectroscopy. Band gap energies ($E_{BG}$) were calculated from the extrapolation of the linear range obtained from modified Kubelka–Munk function $[F(R)/h\nu]^{0.5}$ versus photon energy, $h\nu$.64 Significant band gap narrowing was observed for BLFMO/Ti$_3$C$_2$ nanohybrids in comparison to the bare BFO nanoparticles. $E_{BG}$ of bare BFO nanoparticles were given as 2.04 eV, in good agreement with literature values. 19,20 BLFMO/Ti$_3$C$_2$ composites showed band gaps between 1.3 and 1.5 eV. In particular, 1.30 eV was calculated for BLFO/Ti$_3$C$_2$, whereas for BLFMO-20/Ti$_3$C$_2$, the band gap was 1.48 eV (Figure 5).

Precise $E_{BG}$ assessment of the rest of BLFMO/Ti$_3$C$_2$ series was not possible because of the difficulty in discerning the onset of the decrease, which may be attributed to a small amount of impurity phases.35

The narrowing of the band gap in nanohybrids in comparison with bare BFO nanoparticles can be explained through the formation of Fe$-\text{O}-\text{C}$ bonds at the surface of BLFM, which reduces the charge transfer from oxygen ion to Fe ions.35 Analogous band gap narrowing was observed in literature for graphene/BiFeO$_3$ nanohybrids.65 The superior band gap narrowing of BLFO/Ti$_3$C$_2$ is indicative of better coupling of the BLFO nanoparticles and Ti$_3$C$_2$ sheets, which was illustrated through SEM images.

2.4. Catalytic Degradation. O$_2$ and OH radicals on the organic matter help in the degradation of the organic pollutants. These highly active radicals start degrading the organic pollutants present in the water solution and in turn reduce to harmless byproducts (CO$_2$ and H$_2$O). The general mechanism of combining electrons ($e^-)$ with O$_2$ and holes ($h^+$) with OH$^-$ produces super oxides and free hydroxyl radicals, respectively, consequently removing dye from the liquid solution.66

Figure 6a shows the catalytic activity (under dark conditions) and photocatalytic activity of the Bi$_{1-x}$La$_x$Fe$_{1-y}$Mn$_y$O$_3$/Ti$_3$C$_2$ nanohybrids (irradiated). The

Figure 5. Tauc plot of BLFMO-20/Ti$_3$C$_2$–MXene from DR-UV spectroscopy.

Figure 6. (a) Photocatalytic degradation of CR by BLFO/Ti$_3$C$_2$–MXene, and BLFMO/Ti$_3$C$_2$–MXene nanohybrids against the time taken and (b) BLFO–Ti$_3$C$_2$ dye degradation curves for four cycles.
relative concentration of the CR dye versus the irradiation time for various nanohybrids is represented. All the nanohybrids showed improved dye degradation as compared to the neat BFO nanoparticles. Neat BFO nanoparticles exhibited 10% dye degradation under dark conditions, which reached to a maximum of 40% at 90 min of irradiation after which no change in dye concentration was observed. Pure MXene–Ti3C2 showed 12% dye degradation in 120 min reported previously. In Bi1−xLaxFex−yMnO3 nanocomposites, BLFMO-5/MXene showed the best degradation under dark conditions, which did not change much when irradiated. Here, the best catalytic activity was observed for BLF/O/Ti3C2 and BLFMO-5/Ti3C2 where BLF/O/Ti3C2 reduced the CR concentration to ~92% in dark whereas an ~93% reduction in CR concentration was observed for BLFMO-5/Ti3C2 in dark. Both nanohybrids reached to almost 100% degradation when irradiated within 30 min of irradiation. Both of these nanohybrids proved to be the best reducing catalysts of CR.

Most of the dye degradation was achieved under dark conditions, which might be attributed to the adsorption effect of CR on BLFMO/Ti3C2 nanohybrids. The enhanced catalytic effect was exhibited by the combined structure of the codoped BFO with MXene–Ti3C2 sheets. As stated earlier in the XPS discussion, the nanohybrid is enriched with oxygen species such as hydroxyl ions and adsorbed oxygen, which consequently enhances the photocatalytic activity on the surface of the material. Exfoliated MXene–Ti3C2 as reported earlier with a surface area of 39 m2 g−1 might have increased the active sites on the nanohybrid for reactive species for the adsorption effect as larger surface area provides more space to dye molecules to get adsorbed and degraded easily and quickly.

The produced nanohybrids showed better catalytic activity compared to previously reported hybrid systems. Previous research reported the BLFMO/GNP nanohybrids for CR removal in which the best catalyst in their report is BLF/O/GNP graphene nanoplatelet, which took 30 min to degrade the CR completely and another BLFMO-20/GNP nanohybrid degraded 76% CR dye in dark with complete degradation in about 120 min. Another report showed BLFMO/O nanohybrids for the CR dye degradation; the best catalyst BLFMO-15/GO degraded 96% CR dye in 30 min. In another report, researchers showed the photocatalysts for the degradation of RhB. Their best produced catalyst Au–CdS degraded the RhB in 90 min. Graphene-wrapped TiO2 (graphene-w-TiO2) was reported as the best photocatalyst for the degradation of methylene blue (MB) in 90 min. A system of MoS2/rGO aerogel was produced to photodegrade chromium(VI) in about 120 min. A Ag–CdS–TiO2 nanotube system was produced to degrade MB under ultra violet (UV) light, which degraded MB in 120 min.

Under photocatalytic conditions, the generation of electron–hole pairs by visible light irradiation produces O2 and OH radicals. These highly active radicals start degrading the organic pollutants present in the water solution and in turn reduce to harmless byproducts (CO2 and H2O). In the general mechanism, photoexcited BLF/O/Ti3C2 produces electron–hole paired charge carriers as in eq 1. Large surfaces may possibly have many active sites, which might increase the possibility of maximum interactions between the dye molecules and the nanohybrid. Once the process starts, the superoxide anion radicals •O2− can be produced, and meanwhile, "OH radicals can be produced by the reaction of OH− with holes.

As the electrons react with the catalyst, the H2O molecules are converted into OH. The radicals produced in the process, that is, "O2− and "OH−, being highly reactive for the organic pollutants such as CR, degrade it to the harmless byproducts that are CO2 and H2O. The mechanism of degradation is given by the equations below

\[
\begin{align*}
\text{hv} + \text{Bi}_{1-x}\text{La},\text{Fe}_{x-1}\text{MnO}_3 - \rightarrow \text{e}^- + \text{h}^+ \\
\text{Ti}_3\text{C}_2 + \text{e}^- \rightarrow \text{e}^- \text{(trap sites Ti}_3\text{C}_2) \\
\text{e}^- \text{(trap sites Ti}_3\text{C}_2) + \text{O}_2 \rightarrow \text{"O}_2^- \\
\text{H}_2\text{O} + \text{"} \rightarrow \text{OH}^- \\
\text{CR} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degradation byproducts)} \\
\text{CR} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (degradation byproducts)}
\end{align*}
\]

The recycability of the nanohybrids was also investigated for one nanohybrid structure (BLF/O/MXene) as shown in Figure 6b. The nanohybrid was removed from the dye solution, washed, and reused in four consecutive cycles in order to show its potential regeneration in continuous applications. During each cycle, there was negligible reduction in the catalytic efficiency. This result further proves that the synthesized catalyst does not degrade itself, and it can be regenerated efficiently for extended applications. However, further experiments will be conducted later in order to understand the recyclability of these catalysts (a separate manuscript will be submitted later).

3. MATERIALS AND METHODS

Salts of bismuth nitrate pentahydrate (Bi(NO3)3·5H2O, 99% pure), iron nitrate (Fe(NO3)3·9H2O, 98.5% pure), ethylene glycol (C2H6O2, 99%), acetic acid (C2H4O2, 99.5%), and hydrofluoric acid (HF, 39 wt %) were used as received.

3.1. Synthesis of MXene–Ti3C2 Sheets. Multilayered sheets of Ti3C2Tx were fabricated from pure Ti3AlC2 (MAX phase) using the following procedure: approximately 3 g of Ti3AlC2 powder was dissolved in 70 mL of HF (39 wt %) in a closed Teflon bottle and stirred magnetically for 60 h at room temperature. Solids were removed from the Teflon bottle, filtered under vacuum, and subsequently washed with deionized (DI) water and ethanol until a pH ≈ 6 was reached. Finally, the washed residue was dried in a convection oven at 60 °C for 6 h. The residue obtained was MXene–Ti3C2 sheets with formula Ti3C2.

3.2. Synthesis of Doped BFO Nanoparticles. The Bi1−xLaxFex−yMnO3 (abbreviated as BLFMO, x = 0.1, y = 0.0, 0.05, 0.10, 0.20, and 0.25), named here as BLFO, BLFMO-S, BLFMO-10, BLFMO-20, and BLFMO-25, nanoparticles were synthesized using a double-solvent sol–gel method. Bismuth nitrate pentahydrate and lanthanum nitrate hexahydrate were stoichiometrically dissolved in equimolar acetic acid and ethylene glycol and magnetically stirred for 90 m at 40 °C. A mixture of iron nitrate nonhydrate powder and manganous nitrate solution (50%) was also dissolved in acetic acid and ethylene glycol (C2H6O2, 99%).
was produced. In order to compensate for Bi loss during the heating process, solutions containing 3% excess Bi were prepared. Ethylene glycol was used to maintain constant electronegativities of iron and bismuth during the chemical reaction, whereas acetic acid acted as a catalyst to maintain the solution concentration and for controlled chemical reaction during the synthesis process. The as-prepared solution was dried in a convection oven at 80 °C for 12 h to obtain a gel which was calcined in a furnace at 600 °C for 3 h. After calcination was completed, the powder was crushed to obtain a homogeneous fine powder.

3.3. Synthesis of MXene-Based Nanohybrids. The nanohybrids were fabricated using a double-solvent sol–gel technique. MXene–TiC3 solution was made in DI water with the molarity of 0.5 mg/mL, followed by ultrasonication for 10 min. The codoped BFO nanoparticles (Bi1−x−yLa−xFe1−yMn3O8) were dissolved in a mixture of ethylene glycol and acetic acid with a 1:1 ratio and 0.01 M molarity. The Bi1−x−yLa−xFe1−yMn3O8 solutions were ultrasonicated for 1 h at 60 °C; then, the solutions of Bi1−x−yLa−xFe1−yMn3O8 were mixed with TiC3 solutions separately for all hybrids, and then the Bi1−x−yLa−xFe1−yMn3O8/MXene−TiC3 solutions were stirred magnetically for 2 h at 80 °C for coprecipitation synthesis. The products were washed with DI water several times and dried at 60 °C for 3 h.

4. CHARACTERIZATION

Samples were analyzed for their structure using the XRD, Cu Kα radiation source (Rigaku 2500, Japan). The samples were analyzed for a range of 10°–70°. Surface and morphology of hybrids were investigated using field-emission SEM (FESEM, JEOL7001F). To avoid the charging effect, platinum was sputter-coated on the nanohybrid before FESEM exposition. PL spectroscopy was performed to calculate the generation/recombination rate of the carrier. Binding energies of elements present in the hybrid were checked using XPS. The solid-state diffuse reflectance UV/vis spectra of the La-, Mn-codoped BFO nanoparticles were recorded with a double-beam UV/vis–NIR spectrophotometer (Cary 5000, Varian) equipped with a diffuse reflection accessory (Praying Mantis, Harrick). Baseline correction was achieved using a BaSO4 standard. Approximately, 50 mg of each sample was dispersed in 150 mg of BaSO4 for the measurement. The reflectance was converted to the Kubelka Munk function \(F(R)\) with Cary WinUV software.

4.1. Photocatalytic Characterization. The codoped nanohybrids were tested for their photocatalytic dye degradation application. The apparatus detailed as Hitachi (UV-3310) UV–vis spectrophotometer is used to test the photocatalytic property of the nanohybrids. An amount of 100 mg of nanohybrids was used to be tested in the prepared solution of 100 mL of CR so that the concentration of the dye solution is taken as 100 mg L\(^{-1}\) and the solution is put into stirring in dark condition for about 120 min. As to ignore the thermal degradation activity, the solution is put in the ice bath under constant stirring.\(^{12,30}\) Visible light is taken from the xenon lamp (300 W), a 5 W light-emitting diode was used for UV (ultraviolet) source. Every 30 min, an amount of 3 mL of the solution is taken out from the main solution during the complete process; the taken amount was centrifuged at 7000 rpm to get the supernatant. The supernatant is then used to check the concentration of CR using the Hitachi UV-3310 UV–vis spectroscope, and the curve is measured at a specific wavelength of 496 nm.\(^{30}\) The efficiency of the degradation can be measured using the formula

\[
\text{Degradation (\%) = } \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

Here, \(C_0\) shows the initial concentration of the dye and \(C_t\) shows the concentration of the dye at specific times.\(^{31}\)

5. CONCLUSIONS

La- and Mn-codoped BFO nanohybrids with various doping concentrations were successfully synthesized using a double-solvent sol–gel method. The 2D MXene–TiC3 sheets were synthesized from their pure MAX phase via selective etching of aluminum. The Bi1−x−yLa−xFe1−yMn3O8/TiC3 nanohybrids were fabricated using the double-solvent sol–gel technique. Nanohybrids showed large electron–hole pair generation and low recombination time compared to pure BFO nanoparticles. The nanohybrids were further tested for catalytic and photocatalytic degradation of CR. The best catalytic activity was observed under dark conditions where >90% CR degradation was observed; BLFO/TiC3 and BLFMO-5/TiC3 degraded the 92 and 93% dye in dark, respectively, and further complete (100%) degradation within 20 min of irradiation. Furthermore, these nanohybrid catalysts are regenerative and work efficiently without losing their catalytic activity up to four cycles. The hybrids reported are novel and best candidates for catalytic activities, which makes them potential candidates for commercial applications owing to its low-cost synthesis route.

■ AUTHOR INFORMATION

Corresponding Author
E-mail: syedrizwan83@gmail.com. Phone: +92-51-9085-5599.

ORCID
S. Irfan Ali: 0000-0002-6015-2415
Syed Rizwan: 0000-0002-6934-0949

Author Contributions
M.A.I., S.I.A., and A.T. carried out the experimentation; F.A. and M.Z.I. assisted in manuscript writing and data analysis; and S.R. designed and supervised the project.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful to the Higher Education Commission (HEC) of Pakistan for providing research funding under the project no. 6040/Federal/NRPU/R&D/HEC/2016 and HEC/USAID and financial support under the project no. HEC/R&D/PAKUS/2017/783. The author also thanks the School of Natural Sciences (SNS) at the National University of Science & Technology (NUST), Islamabad, Pakistan, for partial financial support. Special thanks to DAAD, Germany, for providing financial assistance under the project no. 57345771.

■ REFERENCES

(1) Walker, G. M.; Hansen, L.; Hanna, J.-A.; Allen, S. J. Kinetics of a reactive dye adsorption onto dolomitic sorbents. Water Res. 2003, 37, 2081–2089.
(2) Pavan, F. A.; Dias, S. L. P.; Lima, E. C.; Benvenuti, E. V. Removal of Congo red from aqueous solution by anilinepropylsilica xerogel. Dyes Pigm. 2008, 76, 64–69.
24. Wood, S. A. The aqueous geochemistry of the rare-earth elements and yttrium. Chem. Geol. 1990, 82, 159–186.

25. Kothari, D.; Reddy, V. R.; Gupta, A.; Phase, D. M.; Lakshmi, N.; Deshpande, S. K.; Awasthi, A. M. Study of the effect of Mn doping on the BiFeO3 system. J. Phys.: Condens. Matter 2007, 19, 136202.

26. Zheng, X.; Xu, Q.; Wen, Z.; Lang, X.; Wu, D.; Qiu, T.; Xu, M. X. The magnetic properties of La doped and codoped BiFeO3. J. Alloys Compd. 2010, 499, 108–112.

27. Li, M.; Mi, M.; Ma, Y.; Wu, Q.; Ong, C. K. Room temperature ferroelectric, ferromagnetic and magnetoelectric properties of Ba-doped BiFeO3 thin films. J. Phys. D: Appl. Phys. 2007, 40, 1603.

28. Bartkowska, J. A. Dynamical magnetoelectric coupling in multiferroic BiFeO3. Int. J. Thermophys. 2011, 32, 739–745.

29. Arya, G. S.; Negi, N. S. Effect of In and Mn co-doping on structural, magnetic and dielectric properties of BiFeO3 nanoparticles. J. Phys. D: Appl. Phys. 2013, 46, 095004.

30. Irfan, S.; Rizwan, S.; Shen, Y.; Li, L.; Asfandiyar, A.; Butt, S.; Nan, C.-W. The Gadolinium (Gd3+) and Tin (Sn4+) Co-doped BiFeO3 Nanoparticles as New Solar Light Active Photocatalyst. ACS Omega 2017, 2, 3906–3924.

31. Wang, H.-C.; Hu, R.; Yang, J.; Du, Y.; Li, J.; Wang. H. Influence of lanthanum-doping on photocatalytic properties of BiFeO3 for phenol degradation. Chin. J. Catal. 2016, 37, 1283–1292.

32. Wang, H.-C.; Lin, Y.-H.; Feng, Y.-N.; Shen, Y. Photocatalytic behaviors observed in Ba and Mn doped BiFeO3 nanofibers. J. Electroceramics 2013, 31, 271–274.

33. Zhang, Z.; Liu, H.; Lin, Y.; Wei, Y.; Nan, C.-W.; Deng, X. Influence of La doping on magnetic and optical properties of bismuth ferrite nanofibers. J. Nanomater. 2012, 2012, 238605.

34. Kanhere, P.; Chen, Z. A review on visible light active perovskite-based photocatalysts. Molecules 2014, 19, 20095–20022.

35. Li, Z.; Shen, Y.; Yang, C.; Lei, Y.; Guan, Y.; Lin, Y.; Liu, D.; Nan, C.-W. Significant enhancement in the visible light photocatalytic properties of BiFeO3/graphene nanohybrids. J. Mater. Chem. A 2013, 1, 823–829.

36. Gupta, A.; Sakthivel, T.; Seal, S. Recent development in 2D materials beyond graphene. Prog. Mater. Sci. 2015, 73, 44–126.

37. Mas-Ballesté, R.; Gómez-Narváro, C.; Gómez-Herrero, J.; Zamora, F. 2D materials: to graphene and beyond. Nanoscale 2011, 3, 20–30.

38. Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-dimensional atomic crystals. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 10451–10453.

39. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Sui, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and graphene oxide: synthesis, properties, and applications. Adv. Mater. 2010, 22, 3906–3924.

40. Geim, A. K. Graphene: status and prospects. Science 2009, 324, 1530–1534.

41. Song, L.; Ci, L.; Hu, L.; Sorokin, P. B.; Jin, C.; Ni, J.; Kvatshin, A. G.; Kvatshin, D. G.; Lou, J.; Yakobson, B. I.; Ajayan, P. M. Large scale growth and characterization of atomic hexagonal boron nitride layers. Nano Lett. 2010, 10, 3209–3215.

42. Watanabe, K.; Taniguchi, T.; Kanda, H.; Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal. Nat. Mater. 2004, 3, 404.

43. Chopra, N. G.; Lukyen, R. J.; Cherrey, K.; Crespi, V. H.; Cohen, M. L.; Louie, S. G.; Zettl, A. Boron nitride nanotubes. Science 1995, 269, 966–967.

44. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides. ACS Nano 2014, 8, 1102–1120.

45. Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 2012, 7, 699.

46. Anasori, B.; Xie, Y.; Beidagh, M.; Lu, J.; Hosler, B. C.; Hultman, L.; Kent, P. R. C.; Gogotsi, Y.; Barsoum, M. W. Two-
dimensional, ordered, double transition metals carbides (MXenes). *ACS Nano* **2015**, 9, 9507−9516.

(47) Ghidhiu, M.; Naguib, M.; Shi, C.; Mashtalir, O.; Pan, L. M.; Zhang, B.; Yang, J.; Gogotsi, Y.; Billinge, S. J. L.; Barsoum, M. W. Synthesis and characterization of two-dimensional Nb<sub>2</sub>C<sub>3</sub> (MXene). *Chem. Commun.* **2014**, 50, 9517−9520.

(48) Naguib, M.; Halim, J.; Lu, J.; Cook, K. M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J. Am. Chem. Soc.* **2013**, 135, 15966−15969.

(49) Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional transition metal carbides. *ACS Nano* **2016**, 10, 13222−13311.

(50) Soltani, T.; Lee, B.-K. Sono-synthesis of nanocrystallized BiFeO<sub>3</sub>/reduced graphene oxide composites for visible photocatalytic degradation improvement of bisphenol A. *Chem. Eng. J.* **2016**, 306, 204−213.

(51) Wang, X.; Mao, W.; Wang, Q.; Zhu, Y.; Min, Y.; Zhang, J.; Yang, T.; Yang, J.; Li, X. a.; Huang, W. Low-temperature fabrication of Bi<sub>2</sub>FeO<sub>3</sub>/rGO nanocomposites with efficient photocatalytic performance under visible light irradiation. *RSC Adv.* **2017**, 7, 10064−10069.

(52) Dai, J. F.; Xian, T.; Di, L. J.; Yang, H. Preparation of BiFeO<sub>3</sub>-graphene nanocomposites and their enhanced photocatalytic activities. *J. Nanomater.* **2013**, 2013, 1.

(53) Asuha, S.; Zhou, X. G.; Zhao, S. Adsorption of methyl orange and Cr (VI) on mesoporous TiO<sub>2</sub> prepared by hydrothermal method. *J. Hazard. Mater.* **2010**, 181, 204−210.

(54) Liqiang, J.; Yichun, Q.; Baiqi, W.; Shudan, L.; Baojiang, J.; Libin, Y.; Wei, F.; Honggang, F.; Jiazhong, S. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Sol. Energy Mater. Sol. Cells* **2006**, 90, 1773−1787.

(55) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2. *Adv. Mater.* **2011**, 23, 4248−4253.

(56) Ballirano, P.; Pacella, A.; Nardi, E.; Fantauzzi, M.; Atzei, D.; Rossi, A.; Cametti, G. Fe (II) segregation at a specific crystallographic site of fibrous erionite: A first step toward the understanding of the mechanisms inducing its carcinogenicity. *Microporous Mesoporous Mater.* **2015**, 211, 49−63.

(57) Mullet, M.; Khare, V.; Ruby, C. XPS study of Fe(II)–Fe(III) (oxygen)hydroxycarbonate green rust compounds. *Surf. Inter. Anal.* **2008**, 40, 323−328.

(58) Chuai, H.; Zhou, D.; Zhu, X.; Li, Z.; Huang, W. Characterization of V<sub>2</sub>O<sub>5</sub>/MoO<sub>3</sub> composite photocatalysts prepared via electropinning and their photodegradation activity for dimethyl phthalate. *Chin. J. Catal.* **2015**, 36, 2194−2202.

(59) Ke, S.; Lin, P.; Zeng, X.; Huang, H.; Zhou, L. M.; Mai, Y. W. Tuning of dielectric and ferroelectric properties in single phase BiFeO<sub>3</sub> ceramics with controlled Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio. *Ceram. Int.* **2014**, 40, 5261−5268.

(60) Da Silva, L. F.; Lopes, O. F.; Catto, A. C.; Avansi, W.; Bernardi, M. I. B.; Li, M. S.; Ribeiro, C.; Longo, E. Hierarchical growth of ZnO nanorods over SnO<sub>2</sub> seed layer: insights into electronic properties from photocatalytic activity. *RSC Adv.* **2016**, 6, 2112−2118.

(61) Wang, T.; Lang, J.; Zhao, Y.; Su, Y.; Zhao, Y.; Wang, X. Simultaneous doping and heterojunction of silver on Sn<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub> nanoparticles for visible light driven photocatalysis: the relationship between tunable optical absorption, defect chemistry and photocatalytic activity. *CrystEngComm* **2015**, 17, 6651−6660.

(62) Li, H.; Zhou, Y.; Tu, W.; Ye, J.; Zou, Z. State-of-the-Art Progress in Diverse Heterostructured Photocatalysts toward Promoting Photocatalytic Performance. *Adv. Funct. Mater.* **2015**, 25, 998−1013.

(63) Myhra, S.; Crossley, J. A. A.; Barsoum, M. W. Crystal-chemistry of the Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>3</sub>AlN<sub>3</sub> layered carbide/nitride phases—characterization by XPS. *J. Phys. Chem. Solids* **2001**, 62, 811−817.