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# Design and evaluation of a Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite for dye degradation under simulated solar light and charge storage

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A ternary photocatalyst, Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub>, was synthesized *via* simple calcination, where NiMnO<sub>3</sub> incorporation into the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> matrix formed a dual S-scheme heterojunction with g-C<sub>3</sub>N<sub>4</sub> acting as an electron mediator between Bi<sub>2</sub>O<sub>3</sub> and NiMnO<sub>3</sub>. This configuration enhanced charge transfer, promoted electron–hole separation, and improved redox activity, as confirmed by structural, morphological, and optical characterization. The Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite exhibited significantly improved photocatalytic activity toward the degradation of mixed organic dyes, cationic crystal violet (CV) and anionic Congo red (CR), under natural solar light irradiation. The optimized catalyst achieved approximately 99% degradation of crystal violet (CV), 94% of Congo red (CR), and 92% degradation of mixed dyes within 90 min under ambient conditions, using 40 mg of catalyst in 40 mL of dye solution at standard temperature and pressure. The pH values were adjusted to pH 7 for crystal violet (CV), pH 3 for Congo red (CR), and pH 6 for the mixed dye solution, based on the optimal stability and adsorption behaviour of the respective dyes in aqueous media. The photocatalytic degradation followed pseudo-first-order kinetics ( $R^2 = 0.98$ ) for the mixed dye, indicating efficient and reproducible reaction behaviour. Photoluminescence (PL) spectra confirmed the suppressed recombination of photo-induced charge carriers, consistent with the proposed dual S-scheme charge transfer mechanism. Radical scavenging identified •OH and •O<sub>2</sub><sup>−</sup> as key reactive species, and the photocatalyst retained good stability and reusability after four cycles. Electrochemical analysis verified efficient charge transport and stable semiconducting behaviour.

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## 1. Introduction

The generation of organic wastewater has increased significantly due to the rapid expansion of industrial and agricultural activities.<sup>1</sup> Accelerated industrialization has led to severe water pollution, with an estimated 10–15% of organic dyes being discharged into lakes, rivers, and groundwater, posing carcinogenic and mutagenic risks to human health.<sup>2</sup>

Conventional wastewater treatment methods, such as adsorption, coagulation, flocculation, and biological degradation, suffer from inherent limitations including incomplete mineralization, secondary pollution, and high operational costs. In contrast, photocatalytic processes represent sustainable and eco-friendly alternatives that utilize light energy to drive reactions such as water splitting and pollutant degradation through photon absorption, charge separation, carrier migration, and surface redox reactions.<sup>3,4</sup>

In recent years, numerous semiconductor photocatalysts, including TiO<sub>2</sub>,<sup>4</sup> ZnO,<sup>5</sup> Ag<sub>2</sub>CO<sub>3</sub>,<sup>6</sup> g-C<sub>3</sub>N<sub>4</sub>,<sup>7</sup> Bi<sub>2</sub>O<sub>3</sub>,<sup>8</sup> and MoS<sub>2</sub>,<sup>9</sup> have been extensively investigated. However, single-component semiconductors often exhibit limited visible-light activity due to wide band gaps and rapid recombination of photogenerated charge carriers.<sup>10</sup>

Among these materials, perovskite-type oxides (ABO<sub>3</sub>), containing alkaline earth or rare-earth metals at the A-site and transition metals at the B-site, have attracted considerable attention owing to their favourable electronic structures and photocatalytic properties. Perovskites such as LaFeO<sub>3</sub>, NiMnO<sub>3</sub>, BaTiO<sub>3</sub>, BiFeO<sub>3</sub>, and SrTiO<sub>3</sub> have been widely studied for photocatalytic applications.<sup>11,12</sup>

Among these, nickel manganese oxide (NiMnO<sub>3</sub>), a mixed-metal perovskite oxide, is notable for its low cost, good specific capacity, and high electrical conductivity, making it an attractive candidate for energy-storage applications.<sup>13</sup> NiMnO<sub>3</sub> exhibits excellent chemical and physical stability and is synthesized from abundant and nontoxic elements, rendering it environmentally benign and sustainable. Consequently, NiMnO<sub>3</sub> has

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been explored for diverse applications, including photocatalysis, water splitting for hydrogen production, electrocatalysis, and supercapacitors.<sup>14,15</sup> The synergistic redox activity of Ni<sup>3+</sup>/Ni<sup>2+</sup> and Mn<sup>4+</sup>/Mn<sup>3+</sup> ions enhances charge transfer and catalytic efficiency while mitigating the limitations of single-metal oxides. Nevertheless, the wide bandgap of NiMnO<sub>3</sub> (3.0–3.5 eV) restricts its photoresponse primarily to the UV region, resulting in poor visible-light utilization and limited photocatalytic efficiency.<sup>16,17</sup> Therefore, bandgap engineering is essential to improve its solar-light activity.

To overcome these limitations, coupling NiMnO<sub>3</sub> with narrow bandgap semiconductors such as Bi<sub>2</sub>O<sub>3</sub> and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) provides a promising strategy for constructing efficient heterostructures with enhanced light absorption and improved charge separation. Bi<sub>2</sub>O<sub>3</sub> is a nontoxic and chemically stable semiconductor with a relatively narrow bandgap (2.1–2.8 eV), high surface area, strong oxidation ability of valence-band holes (+3.13 V vs. NHE), and excellent visible-light activity. These properties make Bi<sub>2</sub>O<sub>3</sub> suitable for applications in photocatalysis, sensors, fuel cells, coatings, and gas detection, although its performance is limited by rapid charge recombination.<sup>18,19</sup> Similarly, g-C<sub>3</sub>N<sub>4</sub> is a low-cost, metal-free, and environmentally friendly photocatalyst that exhibits visible-light activity and has been applied in pollutant degradation, water splitting, CO<sub>2</sub> reduction, and organic synthesis. However, its photocatalytic efficiency is constrained by low surface area, limited light absorption, and fast charge recombination, which can be mitigated through heterostructure engineering or elemental modification.<sup>20</sup>

To achieve synergistic functionality, heterostructure engineering has emerged as a promising approach to combine the complementary advantages of individual semiconductors. When Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and NiMnO<sub>3</sub> are integrated, a ternary heterojunction is formed, which not only facilitates efficient charge migration but also broadens the light absorption spectrum across UV-visible regions. The combination of these materials enhances the redox potential, suppresses charge recombination, and provides abundant active sites for surface reactions.

Heterostructure construction has emerged as an effective approach to integrate the complementary advantages of individual semiconductors. The integration of Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and NiMnO<sub>3</sub> into a ternary heterojunction facilitates efficient interfacial charge transfer, broadens the solar-light absorption range, suppresses electron-hole recombination, and enhances redox activity by providing abundant surface-active sites. Various synthesis methods have been reported for NiMnO<sub>3</sub>-based heterostructures, including co-precipitation,<sup>21</sup> thermal treatment,<sup>22</sup> the sol-gel auto combustion route,<sup>23</sup> hydrothermal,<sup>24</sup> microwave-assisted,<sup>25</sup> and precipitation.<sup>26</sup> Previous studies on NiMnO<sub>3</sub>-based systems have primarily focused on binary composites, such as mixed dyes. Krishna Chandar Nagamuthu Rajaa *et al.* developed a NiMnO<sub>3</sub>/NiMn<sub>2</sub>O<sub>4</sub>-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene (20 wt%) photocatalyst that can photodegrade 90%, 72%, and 100% of rhodamine B (RhB), methyl orange (MO), and methylene blue (MB) after 50 min under visible light

illumination.<sup>27</sup> Krishna Chandar Nagamuthu Raja *et al.* and his colleagues created NiMnO<sub>3</sub>/NiMn<sub>2</sub>O<sub>4</sub>-graphene nanocomposites and they found that the NiMnO<sub>3</sub>/NiMn<sub>2</sub>O<sub>4</sub>-graphene nanocomposite demonstrated superior photocatalytic performance higher than that of NiMnO<sub>3</sub>, as it degrades methylene blue (MB) dye with 100% efficiency in 30 min under visible light absorption.<sup>28</sup>

Beyond photocatalysis, NiMnO<sub>3</sub> and its composites have gained increasing attention for supercapacitor applications due to the pseudo capacitive behaviour arising from the reversible redox reactions of Ni and Mn ions. The incorporation of Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> further improves electron and ion transport, increases the electrochemically active surface area, and stabilizes the electrode structure, enabling high-performance energy-storage devices. Although perovskite oxides, Bi-based oxides, and g-C<sub>3</sub>N<sub>4</sub> have been widely explored individually or in binary combinations, reports on their rational integration into a Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> ternary heterostructure remain scarce. In particular, NiMnO<sub>3</sub>-based systems have largely been limited to binary composites and single-function studies. In this work, the ternary heterostructure enables effective bandgap engineering, enhanced solar-light absorption, and accelerated interfacial charge transfer, leading to suppressed charge recombination. Moreover, this study demonstrates the dual functionality of the synthesized material for solar light-driven mixed dye degradation and supercapacitor energy storage, supported by systematic parameter optimization and density functional theory (DFT)-assisted mechanistic insights.

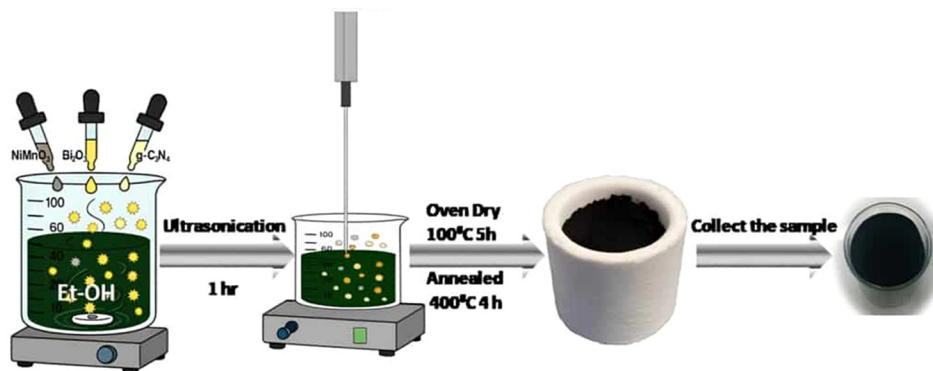
To the best of our knowledge, the photocatalytic performance of a Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> ternary nanocomposite for the degradation of mixed organic dyes under solar illumination has not been previously reported. Accordingly, a novel ternary nanocomposite was synthesized using a simple and effective approach, and its structural, optical, morphological, and electrochemical properties were thoroughly characterized using XRD, Raman, FTIR, UV-vis spectroscopy, FESEM-EDX, BET surface area analysis, TEM, photoluminescence, and cyclic voltammetry. The photocatalytic activity was evaluated using a mixture of Congo red and crystal violet dyes, and the degradation mechanism was systematically elucidated, while the electrochemical performance confirmed its potential as a high-performance supercapacitor electrode.

## 2. Experimental details

### 2.1 Chemicals

The chemicals used in this study include nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Merck, 99.9% purity), manganese nitrate hexahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Merck, 99.9% purity), bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Merck, 99.9% purity), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, Merck, 99.9% purity), sodium bicarbonate (NaHCO<sub>3</sub>, Merck, 99.9% purity), sodium hydroxide (NaOH, Merck, 99.9% purity), melamine, and crystal violet and Congo red dye (Merck, 99% purity). The solutions were prepared using deionized, double-distilled water (DI) and





Scheme 1 Schematic diagram of the synthesis of  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  by the co-precipitation method.

analytical-grade ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Fisher Chem., 99%). All other reagents used in both the synthesis and experimental procedures were of laboratory-grade purity and quality.

## 2.2 Synthesis of the $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$ and their characterization

The  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  composite was produced by a calcination method (Scheme 1). At first, a fixed amount of as-prepared  $\text{NiMnO}_3$ ,<sup>29</sup>  $\text{Bi}_2\text{O}_3$ ,<sup>30</sup> and  $\text{g-C}_3\text{N}_4$ <sup>31</sup> powders was taken in a molar ratio of 4 : 3 : 2 and dispersed in a mixture of 50 mL ethanol and distilled water. The suspension was subjected to ultrasonication for 1 h to obtain a homogeneous mixture. The resulting slurry was dried in an oven at 100 °C for 5 h, followed by annealing at 400 °C for 4 h in an electric muffle furnace (JSMF-30T). The final product was denoted as BGN, representing the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  composite.

## 2.3 Material characterization

The crystallographic structure of the synthesized materials was analyzed by X-ray diffraction (XRD) using a PANalytical diffractometer (PW 1830, Philips, Japan) with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), operated at 40 kV and 30 mA, over a  $2\theta$  range of 10–80° with a step size of 0.02°, and phases were identified using standard JCPDS files. Elemental composition and distribution were examined by energy-dispersive X-ray spectroscopy (EDS) attached to a field-emission scanning electron microscope (FESEM, ZEISS SUPRA 55), which was also used to study the surface morphology at accelerating voltages of 5–15 kV, while detailed microstructural and lattice information was obtained by high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100) operated at 200 kV. Functional groups and bond vibrations were identified using Fourier-transform infrared (FTIR) spectroscopy (PerkinElmer Spectrum, version 10.4.3) in the range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ , and Raman spectra were recorded at 312 K using a Renishaw (UK) spectrometer with a 785 nm diode laser. Optical properties were evaluated by UV-visible diffuse reflectance spectroscopy (UV-DRS, PerkinElmer Lambda 365), and band gap energies were estimated using the Kubelka–Munk function and Tauc plots, while photoluminescence spectroscopy was employed to assess charge-carrier recombination behaviour. Electrochemical

characteristics were studied by cyclic voltammetry using a PGSTAT 204 workstation in a three-electrode configuration, and the specific surface area and pore size distribution were determined by Brunauer Emmett Teller (BET) nitrogen adsorption–desorption analysis using a Quantachrome Instruments analyzer (v11.05) after prior degassing of the samples. Dye concentrations before and after photocatalytic degradation were measured using a UV-vis spectrophotometer (Systronics 2202), and surface chemical composition and oxidation states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCA+ Omicron Nano Technology) using Al  $\text{K}\alpha$  radiation with binding energies calibrated to the C 1s peak at 284.8 eV.

## 2.4 Photocatalytic study setup

The photocatalytic performance of the synthesized nanocomposites was evaluated through the degradation of crystal violet (CV), Congo red (CR), and their mixed dye solution under natural sunlight irradiation. In a typical experiment, 25 mL of aqueous dye solution (crystal violet (CV):  $\lambda_{\text{max}} = 590 \text{ nm}$ , Congo red (CR):  $\lambda_{\text{max}} = 497 \text{ nm}$ , and mixed dye:  $\lambda_{\text{max}} = 530 \text{ nm}$ ) with a fixed initial concentration was mixed with 0.04 g of the photocatalyst in a 250 mL beaker. Prior to light irradiation, the suspension was magnetically stirred in the dark for 30 min to establish adsorption–desorption equilibrium; dark control experiments were conducted under identical conditions of dye concentration, catalyst dosage, volume, and pH, but without light exposure. After equilibration, the reaction mixture was exposed to sunlight to initiate photocatalysis. At regular time intervals, 2.5 mL aliquots were withdrawn, centrifuged to remove the catalyst, and the residual dye concentration was determined using a UV-vis spectrophotometer. The photocatalytic degradation efficiency was calculated using the dye concentration at time  $t$  ( $C$ ) and the equilibrium concentration at time  $t$  ( $C_0$ ).

$$\% \text{ Degradation} = 1 - \frac{C}{C_0} \times 100 \quad (1)$$

## 2.5 Scavenger test

To identify the key active species in the degradation process, scavenger tests were performed on the crystal violet (CV), Congo red (CR) and mix dye solution before the reaction. IPA, EDTA,



and BQ were used to trap hydroxyl radicals ( $\cdot\text{OH}$ ), superoxide radicals ( $\cdot\text{O}_2^-$ ), and holes ( $h^+$ ), respectively. This trapping analysis helped evaluate the photocatalytic activity under consistent conditions.

## 2.6 Theoretical analysis using density functional theory (DFT)

Density functional theory (DFT) calculations were performed using ORCA 5.0 with the B3LYP/g hybrid functional and def2/J basis set to optimize the molecular geometries of the mixed dye (Congo red (CR) + crystal violet (CV)) and  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$ . The ground-state structures and frontier molecular orbitals (HOMO and LUMO) were visualized using Avogadro 1.2.0. The interaction energy between the mixed dye (Congo red (CR) + crystal violet (CV)) and  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  ( $E_{\text{inter}}$ ) was calculated at the same level of theory using:

$$E_{\text{inter}} = E_{\text{mix dye-Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3} - (E_{\text{mix dye}} + E_{\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3}) \quad (2)$$

where  $E_{\text{mix dye-Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3}$ ,  $E_{\text{mix dye}}$  and  $E_{\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3}$  correspond to the total energies of the mixed dye- $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  complex, isolated mixed dye, and isolated  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  respectively.

## 3. Results and discussion

### 3.1 Structural analysis

The XRD patterns of the synthesized nanocomposites are presented in Fig. 1, illustrating the crystalline phases of each component. Nickel manganese oxide belongs to the perovskite oxide family having JCPDS No: 75-2089, which also indicates that the pure phase  $\text{NiMnO}_3$  has been successfully prepared. The  $\text{NiMnO}_3$  crystal structure is constructed by  $\text{NiO}_6$  octahedra and  $\text{MnO}_6$  octahedra. They are linked together by sharing oxygen vertices.<sup>32,33</sup> Strong diffraction peaks aligned with the (012), (104), (110), (113), (024), (116), (214), and (300) crystal planes of  $\text{NiMnO}_3$  were detected at  $24.2^\circ$ ,  $33.4^\circ$ ,  $36.9^\circ$ ,  $41.1^\circ$ ,  $50.9^\circ$ ,  $64.6^\circ$ , and  $65.2^\circ$ .<sup>34</sup> The XRD pattern of  $\text{Bi}_2\text{O}_3$  shows labelled peaks without other detectable phases. Peaks at  $28.6^\circ$ (201),  $31.2^\circ$ (002),  $32.2^\circ$ (220),  $46.7^\circ$ (222),  $47.4^\circ$ (400), and  $54.5^\circ$ (203) correspond to  $\beta\text{-Bi}_2\text{O}_3$  (JCPDS No. 27-0050), while the (201) plane also indicates  $\gamma\text{-Bi}_2\text{O}_3$ , revealing a mixed-phase composition dominated by  $\beta\text{-Bi}_2\text{O}_3$ .<sup>35,36</sup>  $\text{g-C}_3\text{N}_4$  has a modest peak at  $12.9^\circ$  associated with the (100) planes of tris-triazine units of JCPDS 87-1526 and a significant peak at  $27.7^\circ$  relating to the (002) planes of layered structures.<sup>37,38</sup> The absence of impurity peaks in the XRD pattern confirms the successful fabrication of the BGN heterojunction shown in Fig. 1 and indicates no reaction between the individual semiconductors.<sup>39</sup> The reflected crystallographic parameters of the synthesized materials are enlisted in Table 1.

According to the Scherrer equation, crystallite size,

$$D_c = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where  $\lambda$  is the wavelength of the Cu source,  $\beta$  is the full width at half maximum (in radians) and  $\theta$  is the diffraction angle (in

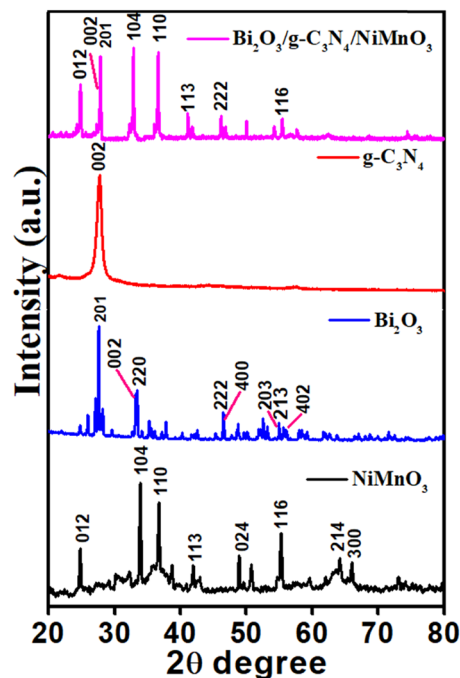


Fig. 1 XRD patterns of  $\text{NiMnO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$ , and the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  composite, confirming the successful formation and coexistence of all phases in the ternary heterostructure.

degrees). The calculated crystallite size of BGN is 33.74 nm. The significantly smaller crystallite size compared to the pure form of the catalysts supported the assumption that loading  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  effectively surpasses the grain growth of  $\text{NiMnO}_3$ , leading to the formation of smaller crystalline particles.<sup>40</sup>

It is important to note that  $\text{NiMnO}_3$  intrinsically forms small crystallites, whereas  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  typically have larger particle sizes. In the BGN composite, the small average crystallite size primarily reflects the intrinsic dimensions of  $\text{NiMnO}_3$  and its dispersion within the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$  matrices, which may hinder local agglomeration without implying direct “grain-size reduction” by the other components. This clarification provides a more accurate description of the interactions and structural features within the heterostructure.

### 3.2 Functional group analysis

In Fig. 2, the FTIR spectroscopy of the produced  $\text{NiMnO}_3$  nanoparticles was performed to identify functional groups and investigate their chemical structure. The spectrum showed absorption bands below  $1000\text{ cm}^{-1}$  at  $497\text{ cm}^{-1}$  and  $585\text{ cm}^{-1}$ , corresponding to the Ni-O and Mn-O metal-oxygen vibrations. The bands at  $1635\text{ cm}^{-1}$  and  $3413\text{ cm}^{-1}$  were attributed to the H-O-H bending and O-H stretching vibrations of adsorbed water.<sup>41</sup> For  $\text{Bi}_2\text{O}_3$ , the  $\text{BiO}_6$  octahedron peaks at  $424\text{ cm}^{-1}$  and  $503\text{ cm}^{-1}$  represented Bi-O bond vibrations, while the Bi-O-Bi stretching vibration appeared at  $845\text{ cm}^{-1}$ . The O-H stretching vibration of adsorbed water was detected at  $3425\text{ cm}^{-1}$ , and the characteristic nitrate group was observed at  $1380\text{ cm}^{-1}$ .<sup>42</sup> The weak band observed near  $1380\text{ cm}^{-1}$  is attributed to trace surface-adsorbed nitrate species originating from the bismuth



Table 1 Crystallographic parameters of the synthesized nanoparticles

Serial no	Sample name	Crystal phase	Space group	Crystal size (nm)	Lattice parameters
1	NiMnO <sub>3</sub>	Rhombohedral	R3 spatial symmetry	35.43	$a = 4.89 \text{ \AA}$ , $b = 4.89 \text{ \AA}$ , and $c = 13.60 \text{ \AA}$
2	Bi <sub>2</sub> O <sub>3</sub>	Tetragonal	$P4_2c$	46.98	$a = b = 7.749 \text{ \AA}$ , $c = 5.632 \text{ \AA}$
3	g-C <sub>3</sub> N <sub>4</sub>	Hexagonal	$P6_3cm$ (185)	46.87	$a = b = c = 0.67 \text{ \AA}$

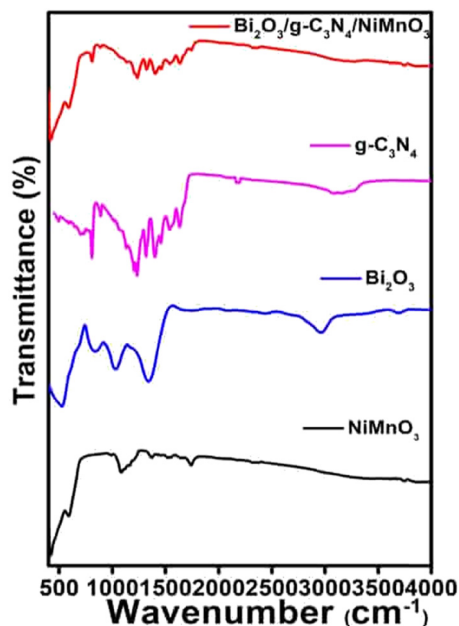


Fig. 2 FTIR spectra of NiMnO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub>, confirming the presence of functional groups from all components in the composite.

nitrate precursor used during synthesis. Since pure Bi<sub>2</sub>O<sub>3</sub> does not intrinsically contain nitrate groups in its crystal structure, this peak arises from residual surface species rather than structural nitrate. In g-C<sub>3</sub>N<sub>4</sub>, the peak at 801 cm<sup>-1</sup> was linked to the breathing mode of the triazine units, while strong bands in the 1200–1650 cm<sup>-1</sup> range corresponded to CN heterocycle stretching. NH stretching vibrations were observed around 3000 cm<sup>-1</sup>.<sup>43</sup> In the ternary composite of BGN, small shifts in the absorption peaks at 589 cm<sup>-1</sup>, 1375 cm<sup>-1</sup>, and 805 cm<sup>-1</sup> are observed, linked to Mn–O and N–O stretching vibrations. The signals at 497 cm<sup>-1</sup> and 503 cm<sup>-1</sup> correspond to Ni–O and Bi–O–Bi stretching vibrations, indicating BGN photocatalyst formation. The O–H stretching vibration signals are broader and weaker in BGN, with O–H groups playing a key role in photocatalytic activity by trapping holes to form OH<sup>•</sup> radicals, reducing electron–hole recombination and enhancing the photocatalytic process.<sup>44</sup>

### 3.3 Morphological analysis

**3.3.1 Scanning electron microscopy.** The morphology of the metal oxides observed by field emission scanning electron microscopy (FE-SEM) is shown in Fig. 3. In Fig. 3(a), NiMnO<sub>3</sub> exhibits spherical particles, indicating a *para*-phase structure.<sup>45</sup>

In Fig. 3b, Bi<sub>2</sub>O<sub>3</sub> exhibits ellipsoidal particles, along with smaller rounded ones and a few larger aggregates, possibly resulting from the fusion of smaller particles.<sup>46</sup> Pure g-C<sub>3</sub>N<sub>4</sub> (Fig. 3c) has a two-dimensional nanosheet structure, confirming its successful bulk formation.<sup>47</sup> Fig. 3d shows that in the BGN nanocomposite, g-C<sub>3</sub>N<sub>4</sub> nanosheets and ellipsoidal Bi<sub>2</sub>O<sub>3</sub> particles are well anchored on spherical NiMnO<sub>3</sub>. The composite exhibits a uniform morphology with consistent particle size, indicating its potential for applications such as photocatalysis. However, elemental mapping (Fig. 3e and f) indicates that g-C<sub>3</sub>N<sub>4</sub> is partially agglomerated rather than perfectly homogeneously distributed, while Ni, Mn, Bi, C, N, and O are overall well dispersed. This non-uniformity of g-C<sub>3</sub>N<sub>4</sub> may influence local charge separation and, consequently, photocatalytic activity.

**3.3.2 High-resolution transmission electron microscopy.** Spherical NiMnO<sub>3</sub> particles are evenly distributed and sandwiched between g-C<sub>3</sub>N<sub>4</sub> nanosheets and Bi<sub>2</sub>O<sub>3</sub> with little aggregation, according to TEM examination (Fig. 4a). Strong interactions can be shown in the magnified pictures, where NiMnO<sub>3</sub> is strongly bonded to both g-C<sub>3</sub>N<sub>4</sub> and Bi<sub>2</sub>O<sub>3</sub>. Lattice spacings of 0.14 nm, 0.13 nm, and 0.10 nm are seen in the HRTEM picture (Fig. 4b), which corresponds to g-C<sub>3</sub>N<sub>4</sub>, Bi<sub>2</sub>O<sub>3</sub>, and NiMnO<sub>3</sub>, respectively. These results demonstrate that g-C<sub>3</sub>N<sub>4</sub> facilitates effective interfacial charge transfer and supports the Bi<sub>2</sub>O<sub>3</sub>/NiMnO<sub>3</sub> composite. The existence of the nanocomposites is confirmed by the SAED pattern in Fig. 4c. It is anticipated that these interfacial structures would improve photoinduced charge transfer and, consequently, the photocatalytic activity of the composite.<sup>48</sup> In addition to the morphological examination by SEM, the surface area of the nanocomposites was evaluated using BET in S2.

### 3.4 Optical analysis

UV-Visible spectroscopy (Fig. 5a) reveals that NiMnO<sub>3</sub> has an absorption edge at 242 nm, while the BGN composite shows a red-shift into the visible region due to the addition of Bi<sub>2</sub>O<sub>3</sub>, indicating enhanced light absorption due to strong interfacial interactions. This bathochromic shift suggests improved charge carrier separation and extended lifetimes. The formation of heterojunctions introduces intermediate energy states, facilitating electron transitions and enhancing the material's optical and electronic performance.<sup>49,50</sup> Band gap values derived from Wood and Tauc plots (Fig. 5b) range from 2.7 to 1.8 eV. The band gap of the synthesized photocatalysts was estimated using a Tauc plot based on the classical method.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$



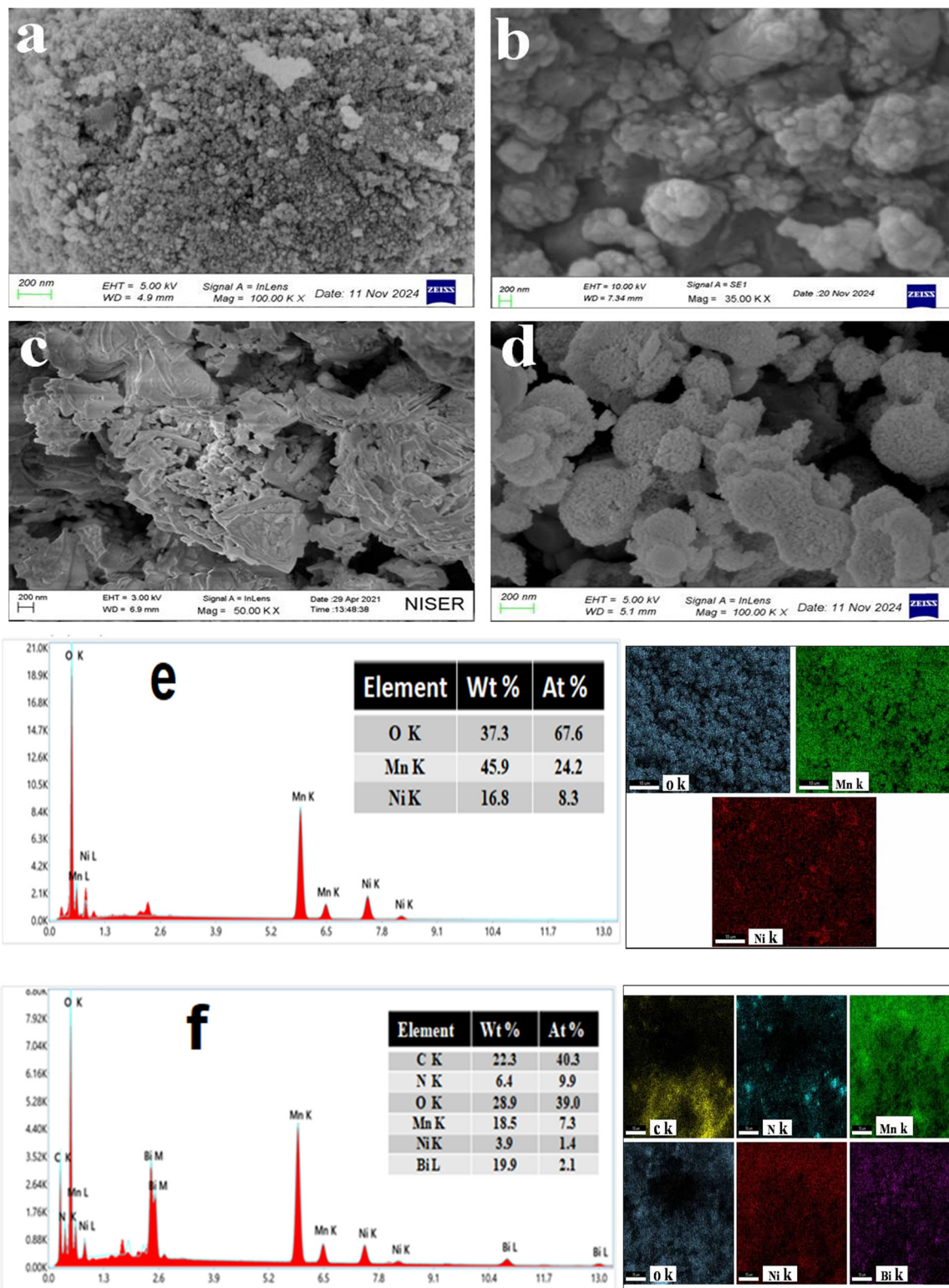


Fig. 3 FESEM images of (a) NiMnO<sub>3</sub>, (b) Bi<sub>2</sub>O<sub>3</sub>, (c) g-C<sub>3</sub>N<sub>4</sub>, and (d) the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> nanocomposite; EDX pattern and mapping images of (e) NiMnO<sub>3</sub> and (f) BiGN nanocomposites, illustrating the surface morphology and microstructural features of the individual components and the ternary heterostructure.

The absorption coefficient ( $\alpha$ ), band gap energy ( $E_g$ ), Planck's constant ( $h$ ), photon energy ( $h\nu$ ), and proportional constant ( $A$ )

are related through Tauc's equation, where  $n$  equals 0.5 for indirect and 2 for direct band-gap semiconductors. Bi<sub>2</sub>O<sub>3</sub> is a p-



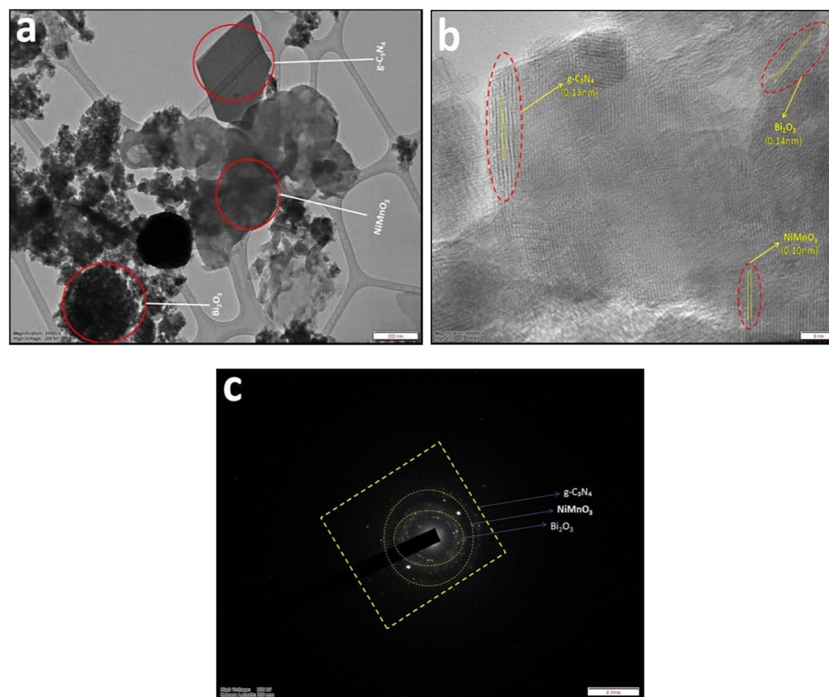


Fig. 4 TEM analyses of the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  (BGN) ternary nanocomposite: (a) magnified TEM image, (b) high-resolution TEM (HR-TEM) image showing lattice fringes, and (c) selected area electron diffraction (SAED) pattern confirming the polycrystalline nature.

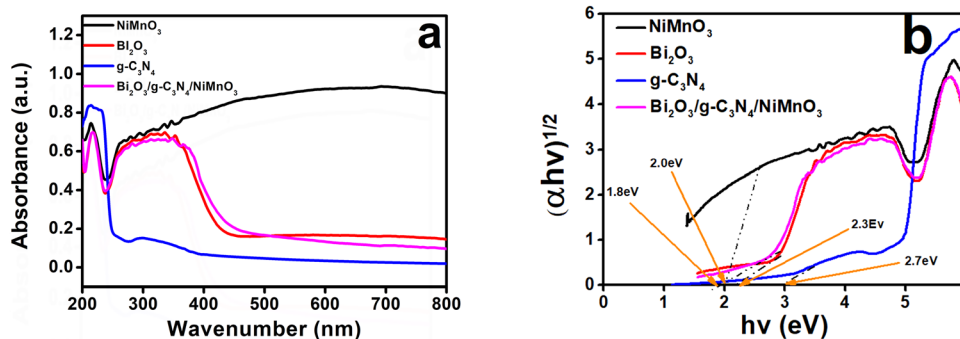


Fig. 5 (a) UV-Vis absorption spectra and (b) Tauc plots of  $\text{NiMnO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$ , and the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  nanocomposite, illustrating enhanced visible light absorption and reduced band gap in the ternary heterojunction.

type semiconductor and  $\text{g-C}_3\text{N}_4$  is an n-type semiconductor, while  $\text{NiMnO}_3$  is a p-type indirect band-gap semiconductor.

The BGN composite shows the narrowest band gap due to enhanced visible-light absorption from mid-gap energy levels introduced by  $\text{Bi}_2\text{O}_3$  and  $\text{g-C}_3\text{N}_4$  doping. Additionally, the conduction and valence band positions of the pristine materials, shown in Table 2, were analyzed for their influence on charge separation across heterojunctions. The band-edge positions of the nanocomposites were calculated using standard equations.

$$E_{\text{VB}} = X - E_0 + 0.5E_{\text{g}} \quad (5)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (6)$$

Table 2 Values of calculated  $E_{\text{CB}}$  and  $E_{\text{VB}}$  for  $\text{NiMnO}_3$ ,  $\text{g-C}_3\text{N}_4$ , and  $\text{Bi}_2\text{O}_3$

Semiconductor	Absolute electronegativity ( $X$ )	$E_{\text{CB}}$ (eV)	$E_{\text{VB}}$ (eV)	$E_{\text{g}}$ (eV)
$\text{NiMnO}_3$	3.1 eV	0.5	2.3	1.8
$\text{g-C}_3\text{N}_4$	4.25 eV	-1.1	1.6	2.7
$\text{Bi}_2\text{O}_3$	3.05 eV	0.3	2.6	2.3
$\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$	7.03 eV	1.53	3.53	2.0

The valence band edge potential ( $E_{\text{VB}}$ ) is calculated using the semiconductor's electronegativity ( $X$ ), which is the geometric mean of its constituent atoms' electronegativities.  $E_0$  represents the free electron energy on the hydrogen scale ( $\sim 4.5$  eV).



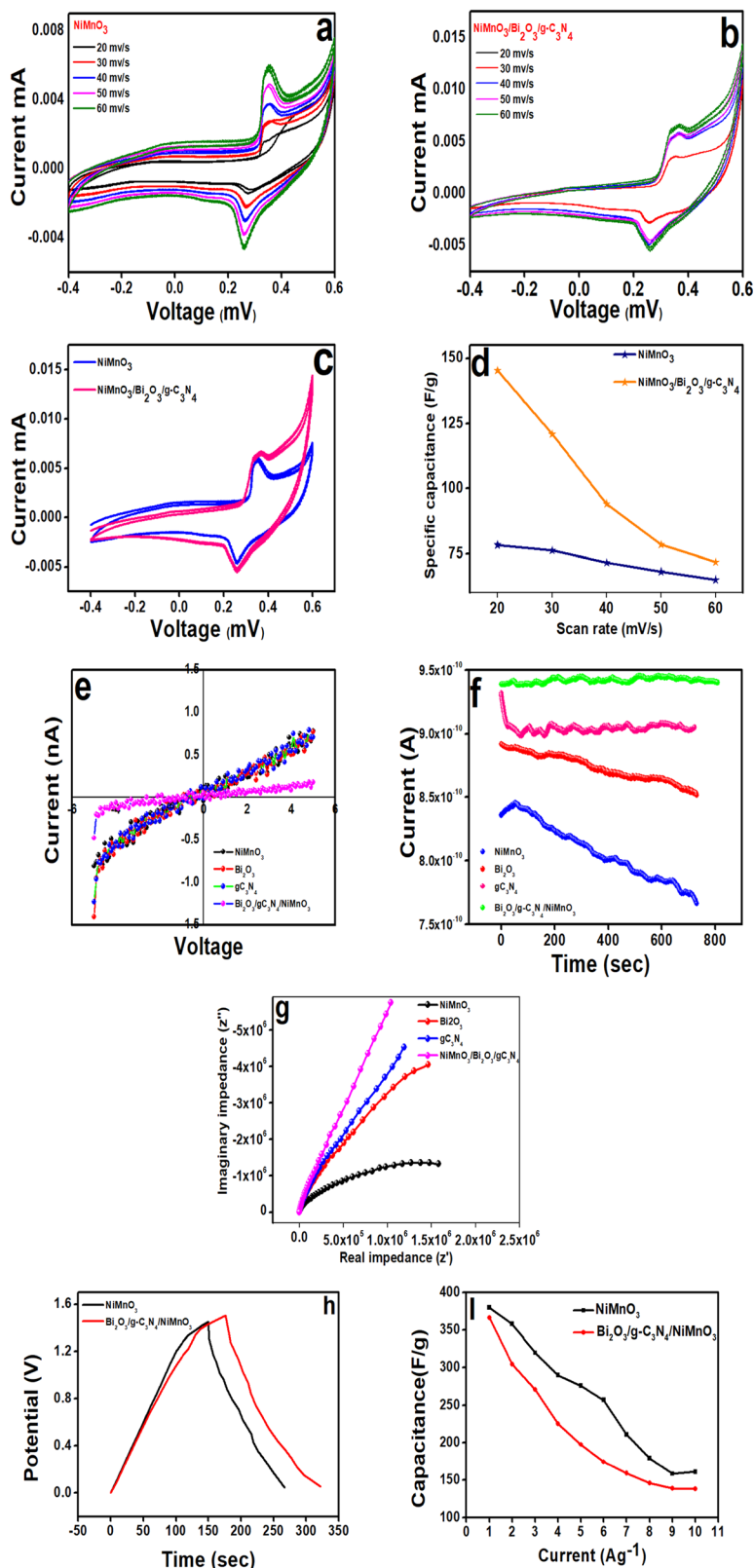


Fig. 6 Electrochemical analysis of NiMnO<sub>3</sub> and the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> (BGN) nanocomposite: (a) cyclic voltammetry (CV) curves of NiMnO<sub>3</sub> at different scan rates, (b) cyclic voltammetry (CV) curves of BGN at different scan rates, (c) comparative cyclic voltammetry (CV) curves of NiMnO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> at 50 mV s<sup>-1</sup>, and (d) variation of specific capacitance with scan rate for both electrodes, (e) *I*-*V* characteristics, (f) *I*-*t* response under light illumination, (g) Nyquist plot from electrochemical impedance spectroscopy (EIS) showing charge transfer resistance, (h) galvanostatic charge discharge (GCD) curves of NiMnO<sub>3</sub> and the BGN composite, and (i) variation of specific capacitance with current density for both electrodes.



### 3.5 Electrochemical analysis

**3.5.1 Cyclic voltammetry (CV) and measurement of specific capacitances.** The electrochemical performance of NiMnO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> was evaluated through cyclic voltammetry (CV) and specific capacitance analysis, as shown in the provided image. Fig. 6a and b depict the cyclic voltammetry (CV) curves of pure NiMnO<sub>3</sub> and the ternary Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite at various scan rates (20–60 mV s<sup>-1</sup>). While both materials exhibit redox peaks indicative of pseudo capacitive behaviour, the ternary composite shows significantly higher current responses, suggesting enhanced charge storage capacity and improved electrochemical activity.<sup>51,52</sup> In Fig. 6c, the direct comparison of both materials at the same scan rate reveals that Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> has a much larger cyclic voltammetry (CV) area, confirming superior capacitive performance due to the synergistic effect of the incorporated Bi<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. Furthermore, Fig. 6d shows that the specific capacitance of the composite is notably higher than that of NiMnO<sub>3</sub> alone, reaching up to ~150 F g<sup>-1</sup> at 20 mV s<sup>-1</sup>, and gradually decreasing with increased scan rate due to diffusion limitations. Overall, the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> nanocomposite demonstrates excellent potential for high-performance supercapacitor applications.

**3.5.2 Electrochemical impedance studies (EIS).** Fig. 6e shows the current–voltage (*I*–*V*) characteristics of NiMnO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite. All samples exhibit nearly linear and symmetric *I*–*V* curves, indicating ohmic contact between the electrode and electrolyte. The ternary composite displays a comparatively higher current response, suggesting facilitated charge transport across the heterointerfaces.

The photocurrent–time (*I*–*t*) responses recorded under continuous illumination are shown in Fig. 6f. The ternary composite exhibits the highest photocurrent density with relatively stable behaviour over the measurement duration, indicating efficient generation and transport of photoinduced charge carriers. Although a gradual decay is observed for all samples, the composite maintains a higher photocurrent level than the individual components, reflecting improved charge separation efficiency.

Nyquist plots obtained from electrochemical impedance spectroscopy are presented in Fig. 6g. The Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite shows a larger impedance response compared to the pristine materials, which can be attributed to enhanced interfacial polarization and charge accumulation at the multiple heterojunction interfaces. This increased impedance is indicative of suppressed charge recombination and effective charge trapping, which is beneficial for photocatalytic and photoelectrochemical processes. Overall, the electrochemical results suggest that the ternary heterostructure promotes efficient photoinduced charge separation rather than simple bulk conductivity enhancement.

**3.5.3 Galvanostatic charge/discharge studies (GCD).** Fig. 6h shows the galvanostatic charge–discharge (GCD) curves of pristine NiMnO<sub>3</sub> (black) and the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub>

composite (red) over 0–1.6 V and 0–50 s. Both electrodes display typical charge–discharge cycles, but the composite exhibits a longer discharge time, indicating higher specific capacitance. The gently sloped plateau suggests pseudo capacitive behaviour from redox reactions. In contrast, NiMnO<sub>3</sub> shows a shorter discharge period, reflecting lower energy storage. The enhanced performance of the composite arises from the synergistic interaction between Bi<sub>2</sub>O<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and NiMnO<sub>3</sub>, improving charge storage.<sup>53</sup>

Fig. 6i shows the variation of specific capacitance with current density for both electrodes. Capacitance decreases with increasing current due to limited ion diffusion, but the Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/NiMnO<sub>3</sub> composite maintains higher capacitance and better rate performance than NiMnO<sub>3</sub>. While NiMnO<sub>3</sub> shows higher capacitance at low currents, its cycling stability and rate capability are inferior. The specific capacitance (SC) values of the electrodes were calculated from the galvanostatic charge discharge (GCD) curves using the following equation:

$$\text{Specific capacitance (F g}^{-1}\text{)} = \frac{I \times t_d}{m \times \Delta V} \quad (7)$$

where *I* is the constant discharge current (A), *t<sub>d</sub>* is the discharge time (s),  $\Delta V$  is the potential window during discharge (V), and *m* is the mass of the electroactive material in the electrode (g). These results highlight the superior energy storage performance of the heterojunction composite.

### 3.6 XPS

The XPS survey spectra (Fig. 7) display distinct signals corresponding to C 1s, O 1s, N 1s, Mn 2p, Bi 4f, and Ni 2p, confirming the successful formation and elemental composition of the BGN nanocomposite. The high-resolution Ni 2p spectrum exhibits characteristic 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks at 854.11 and 871.58 eV, respectively. Peak deconvolution reveals the coexistence of Ni<sup>2+</sup> species at 854.20 and 871.63 eV and Ni<sup>3+</sup> species at 855.88 and 872.97 eV, indicating mixed-valence nickel states that can facilitate efficient interfacial charge transfer. The Mn 2p peaks at 641.37 and 653.12 eV correspond to Mn 2p<sub>1/2</sub> and Mn 2p<sub>3/2</sub> orbitals, suggesting redox-active behaviour of Mn centers capable of participating in electron-transfer processes during photocatalysis. The Bi 4f spectrum presents two well-defined peaks at 158.7 (4f<sub>7/2</sub>) and 164.0 (4f<sub>5/2</sub>) eV, consistent with the Bi<sup>3+</sup> oxidation state in Bi–O bonding environments. The C 1s spectrum shows peaks at 284.6 eV (sp<sup>2</sup> C–C), 286.0 eV (C–O), and 286.4 eV (surface carbon). N 1s peaks at 398.3 and 399.9 eV are attributed to C–N=C and N–H groups in heptazine units, respectively. The O 1s spectrum reveals a main peak at 529.7 eV for metal–oxygen bonds and a secondary peak at 531.0 eV due to lattice oxygen.<sup>54–57</sup> These spectral features confirm strong chemical interaction and the presence of multiple oxidation states, which are beneficial for photocatalytic applications.

### 3.7 Theoretical analysis

In Fig. 8a–j, the DFT-derived HOMO–LUMO energy gaps (Table 3), obtained using molecular cluster models, are in the



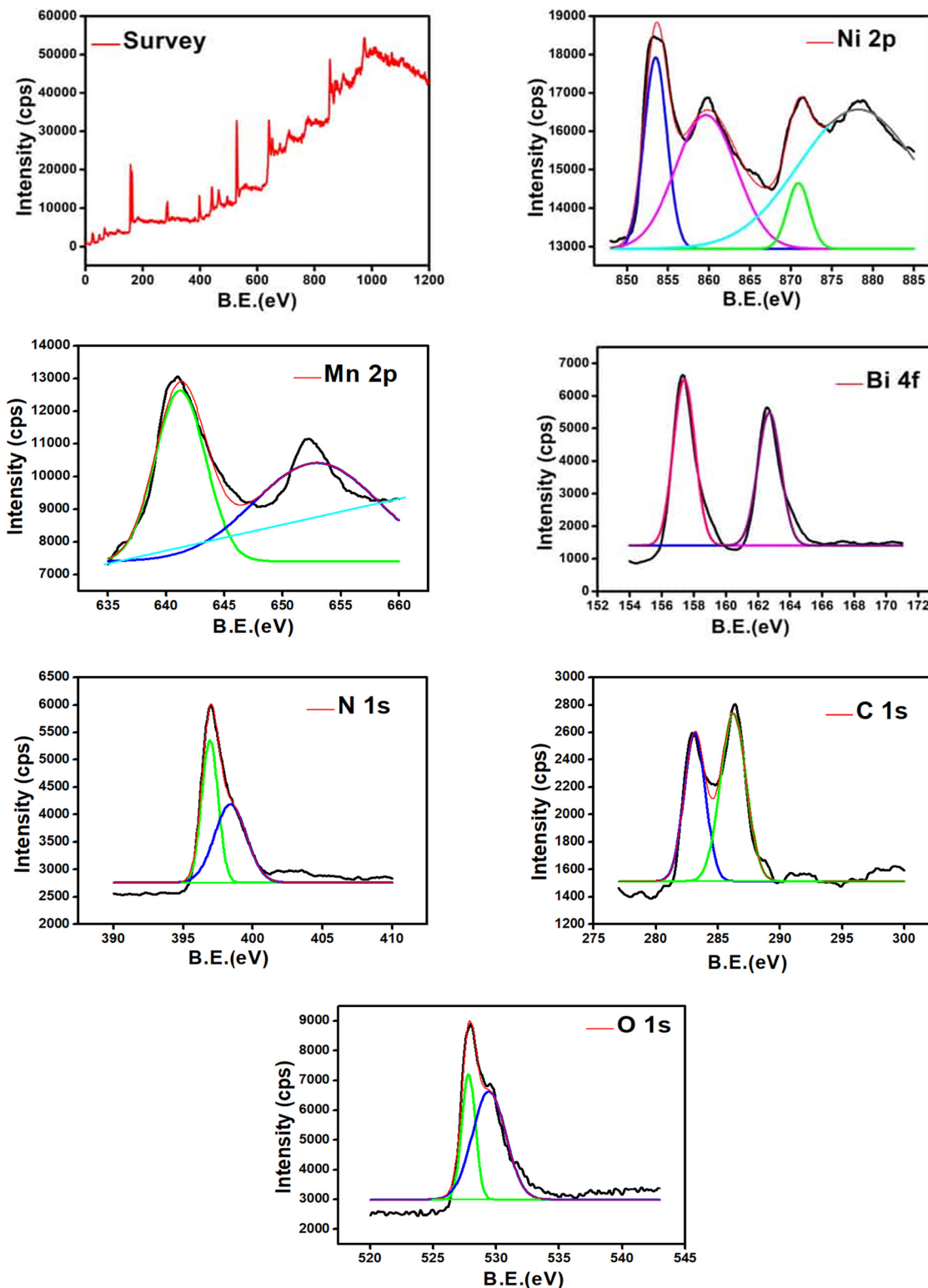


Fig. 7 XPS spectra of BGN materials: a survey spectrum of Ni 2p, Mn 2p, Bi 4f, C 1s, N 1s and O 1s.

same order of magnitude as the experimentally measured optical band gaps from UV-DRS (Table 2), with deviations of 0.2–0.3 eV for the individual oxides. Such differences are expected because cluster-based DFT describes localized

electronic states and frontier orbital separations, whereas UV-DRS-derived band gaps reflect bulk solid state effects, including excitonic contributions, particle size, defects, and long-range periodicity. Moreover, the use of molecular models instead of



periodic boundary conditions introduces systematic shifts arising from finite-size effects and the choice of functional and basis set.

Despite these limitations, the cluster approach reliably captures relative trends in electronic structure and interfacial charge redistribution, which are most relevant for understanding charge-transfer processes in complex heterostructures. The very small HOMO–LUMO gap obtained for crystal violet (0.19 eV) originates from the highly delocalized  $\pi$ -electron system and the specific charge and multiplicity used in the molecular model. This value is not representative of a solid-state band gap and is intended only for qualitative comparison of charge-transfer propensity rather than quantitative evaluation.

Overall, the combined experimental and computational results consistently indicate that the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  heterostructure exhibits a reduced effective electronic gap (2.0 eV), enabling efficient visible-light absorption and supporting the proposed photocatalytic mechanism.

## 4. Photocatalytic study

When anionic (Congo red, CR) and cationic (crystal violet, CV) dyes are combined, donor–acceptor interactions can lead to the formation of a charge-transfer (CT) complex, producing a new absorption band rather than merely shifting the individual dye peaks. This new band, characteristic of supramolecular assembly or ground state complexation, is absent in the individual dyes.<sup>52</sup> The UV-vis absorption spectra of the individual dyes and their mixture are shown in Fig. 8c, while their chemical structures are presented in Fig. 9a and b.

### 4.1 Degradation of the mixed dye

The photocatalytic degradation efficiency of the synthesized photocatalysts was evaluated by monitoring the degradation rate of a mixed dye solution (crystal violet and Congo red) under natural sunlight irradiation. The photocatalytic activity of the synthesized nanocomposites was evaluated using a binary mixture of CV and CR ( $40 \text{ mg L}^{-1}$  each) under natural sunlight irradiation at room temperature ( $27^\circ\text{C}$ ) and neutral pH 6. For the mixed dye system (CV + CR), the photocatalytic experiments were performed at a total dye concentration of 40 ppm and a photocatalyst dosage of  $0.6 \text{ g L}^{-1}$  (60 mg), and the degradation efficiency was evaluated over a 90 min sunlight irradiation period. A fixed amount of photocatalyst (80 mg) was used in all experiments. Control tests without photocatalyst confirmed the high photostability of the dyes, with negligible degradation observed over 30 min under sunlight. The absorption spectra recorded during photocatalysis (Fig. 10a) show a gradual decrease in the characteristic peak at 530 nm, indicating simultaneous degradation of both dyes. Among the tested materials, the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  (BGN) ternary composite exhibited the highest photocatalytic efficiency (92%), outperforming  $\text{NiMnO}_3$  (70.2%),  $\text{Bi}_2\text{O}_3$  (79.5%), and  $\text{g-C}_3\text{N}_4$  (88.7%). This enhanced performance is attributed to improved visible-light absorption, abundant reactive sites, efficient charge

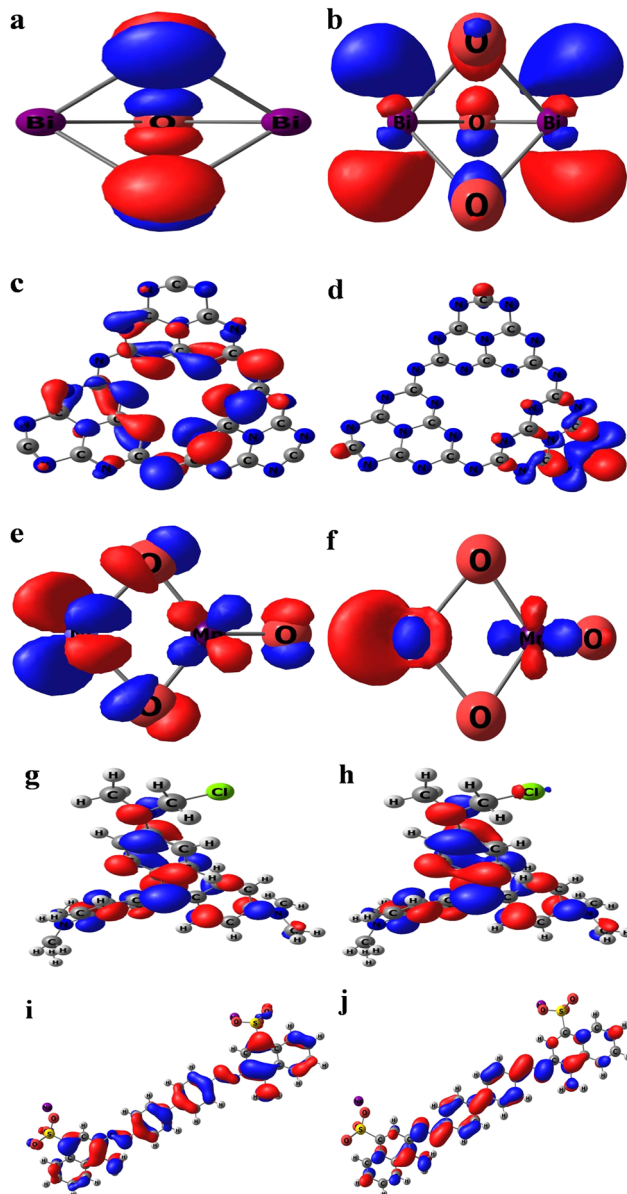


Fig. 8 Optimized molecular structures of (a)  $\text{Bi}_2\text{O}_3$  (HOMO), (b)  $\text{Bi}_2\text{O}_3$  (LUMO), (c)  $\text{g-C}_3\text{N}_4$  (HOMO), (d)  $\text{g-C}_3\text{N}_4$  (LUMO), (e)  $\text{NiMnO}_3$  (HOMO), (f)  $\text{NiMnO}_3$  (LUMO), (g) crystal violet (HOMO), (h) crystal violet (LUMO), (i) Congo red (HOMO) and (j) Congo red (LUMO).

separation, and rapid interfacial charge transfer across the ternary heterojunction. Minimal dye removal in the dark confirmed that adsorption was negligible, and the observed

Table 3 Data interpretation from DFT calculations

Specimen	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E_{\text{gap}}$
$\text{Bi}_2\text{O}_3$	−5.3973	−2.7962	2.600937328
$\text{NiMnO}_3$	0.0378	2.0406	2.00277376
$\text{g-C}_3\text{N}_4$	−6.6424	−4.1672	2.475167136
Congo red	−5.0266	−2.3010	2.725513856
Crystal violet	−4.0550	−3.8620	0.192930244



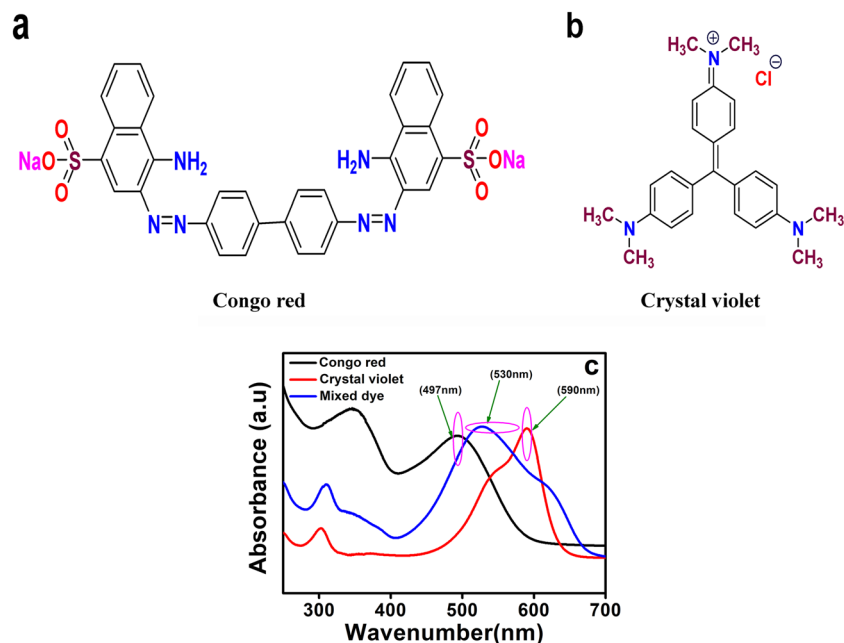


Fig. 9 Chemical structures of (a) Congo red and (b) crystal violet, and (c) UV-vis absorption spectra of the dyes.

photocatalytic activity was primarily due to reactive radicals ( $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$ ) generated under light.

#### 4.2 Kinetics, scavenger and reusability study

The photocatalytic degradation kinetics of Congo red (CR), crystal violet (CV) and mixed dyes by the synthesized samples were analyzed using the Langmuir–Hinshelwood kinetic model. The degradation behaviour was found to conform to a pseudo-first-order reaction mechanism. To better understand the kinetics of the process, the Langmuir–Hinshelwood model was applied using the equation:<sup>58</sup>

$$\ln(C/C_0) = k \times t \quad (8)$$

where  $C_0$  and  $C$  are the initial and remaining dye concentrations and  $t$  is the time. The linear plots obtained from Fig. S3c, S4c, and Fig. 10c yielded the apparent rate constant ( $k$ ), confirming that the ternary nanocomposite exhibits superior photocatalytic activity. This enhancement is attributed to enhanced light harvesting and efficient separation of charge carriers.

Fig. S3d, S4d, and Fig. 10d compare the degradation performance of various catalysts, clearly showing that the BGN composite outperformed both pristine and binary systems. To elucidate the reaction mechanism at the surface level, radical trapping experiments were conducted during dye degradation. Specific scavengers, namely isopropanol (IPA) for hydroxyl radicals ( $\cdot\text{OH}$ ), benzoquinone (BQ) for superoxide radicals ( $\cdot\text{O}_2^-$ ), and EDTA for photogenerated holes ( $h^+$ ), were introduced into the reaction system.<sup>59</sup> The outcomes, shown in S3e, S4e, and Fig. 10e demonstrate that both hydroxyl and superoxide radicals play key roles in the degradation process, confirming that these reactive species significantly contribute to the overall photocatalytic activity of the ternary

nanocomposites, thereby supporting the proposed heterojunction mechanism.

Reusability is a critical parameter for evaluating the practical applicability of photocatalysts in environmental remediation. The durability and recyclability of the BGN ternary nanocomposite were investigated by recovering the photocatalyst from Congo red (CR), crystal violet (CV), and mixed dye solutions after each photocatalytic cycle using a previously reported purification procedure. As shown in Fig. S3f, S4f, and Fig. 10f, the photocatalytic efficiency of BGN exhibited a gradual decrease over four successive cycles, while maintaining high degradation efficiency relative to the initial cycle. The slight decline in performance may be attributed to partial surface fouling by reaction intermediates and mild particle agglomeration during repeated use.

These findings confirm that the BGN ternary nanocomposites maintain high stability and reusability under prolonged photocatalytic conditions. Light alone had a significant effect, but the nanocomposites significantly reduced the dye concentration, and the photocatalytic efficiency ranked as:  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3 > \text{g-C}_3\text{N}_4 > \text{Bi}_2\text{O}_3 > \text{NiMnO}_3$ . A comparison was made between this work and previously reported ternary heterojunctions as shown in a tabular form in Table 4.

#### 4.3 Photocatalytic degradation mechanism

Under solar light irradiation, the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  (BGN) ternary heterojunction is effectively photoactivated due to its well-aligned band structure and enhanced visible-light absorption capability. Upon illumination, all three semiconductor components absorb incident photons ( $h\nu$ ), generating electron–hole pairs by promoting electrons ( $e^-$ ) from their valence bands (VB) to the conduction bands (CB), and leaving holes ( $h^+$ ) behind in the VB:



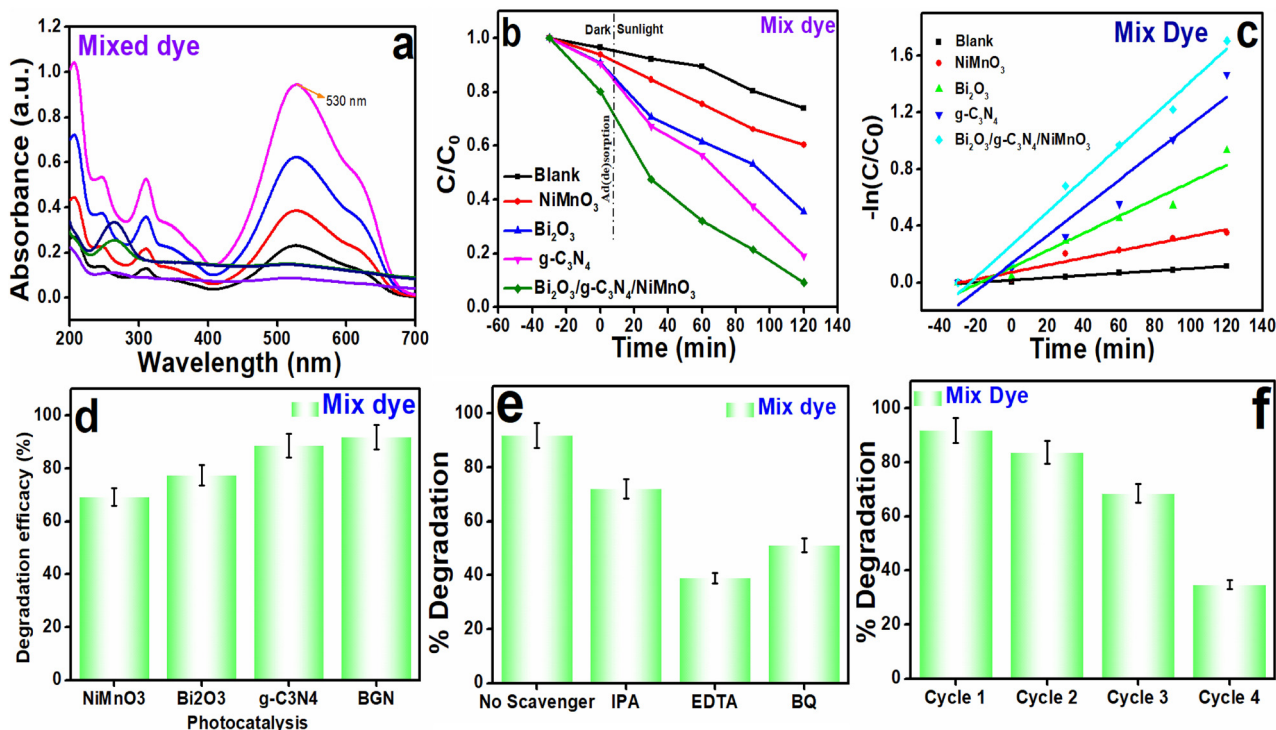
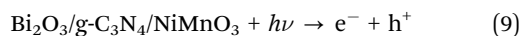
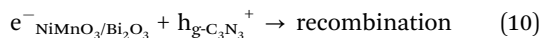


Fig. 10 UV-Visible absorption analysis of the photocatalytic activity of the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  ternary nanocomposites for a binary mixed dye (Congo red and crystal violet): (a) absorption spectra under visible light, (b)  $C/C_0$  vs. time plot, (c) pseudo-first-order kinetic fit, (d) degradation efficiency, (e) scavenger study revealing active species, and (f) recyclability over multiple cycles.



At the interface, electrons in the CBs of  $\text{NiMnO}_3$  (+0.5 V) and  $\text{Bi}_2\text{O}_3$  (+0.3 V) recombine with holes in the VB of  $\text{g-C}_3\text{N}_4$  (+1.6 V), following an S-scheme mechanism:



This selective recombination preserves the highly reducing electrons in the CB of  $\text{g-C}_3\text{N}_4$  (-1.1 V) and the strongly oxidizing holes in the VB of  $\text{Bi}_2\text{O}_3$  (+2.6 V). The  $\text{g-C}_3\text{N}_4$

CB electrons efficiently reduce  $\text{O}_2$  to superoxide radicals, since -1.1 V is more negative than the  $\text{O}_2/\cdot\text{O}_2^-$  potential (-0.33 V):



Meanwhile, the  $\text{Bi}_2\text{O}_3$  VB holes (+2.6 V) oxidize  $\text{OH}^-/\text{H}_2\text{O}$  to hydroxyl radicals, as the potential is more positive than the  $\text{OH}^-/\cdot\text{OH}$  level (+2.38 V):



Table 4 Comparative overview of photocatalytic performance based on synthesis methods, light sources, and degradation efficiencies

Sl. no.	Photo-catalysis	Synthesis method	Time (min)	Pollutants	Light source	%D efficiency	Ref.
1	RGO/ $\gamma$ - $\text{Fe}_2\text{O}_3$ / ZnO	Microwave synthesis	12, 21, 21	Malachite green (MG), methyl orange (MO), rhodamine B (RhB)	UV irradiation	100	60
2	SrTiO <sub>3</sub> /TiO <sub>2</sub> / Cu <sub>2</sub> O	Reflux method	120	Methylene blue (MB), rhodamine B (RhB), methyl orange (MO)	LED light source ( $\lambda > 400$ nm, intensity 46.1 W cm <sup>-2</sup> ) Sunlight	85	61
3	NiO/Ag/TiO <sub>2</sub>	Deposition coprecipitation	60	Methylene blue (MB)	Sunlight	93.15	62
4	V <sub>2</sub> O <sub>5</sub> -Fe <sub>3</sub> O <sub>4</sub> /rGO	One-pot solvothermal process	100, 110	Methylene blue (MB)	UV/visible light	89.2 and 76	63
5	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub> / chitosan	Sol-gel method	120	Eosin (EO) and erythrosine (ER)	Osram lamp (400 W)	84.2 and 96.5	64
6	RGO/ $\gamma$ - $\text{Fe}_2\text{O}_3$ / ZnO	Rapid microwave irradiation route	21	Malachite green (MG), methyl orange (MO), rhodamine B (RhB)	UV irradiation	100	65
7	MoS <sub>2</sub> -NiO-CuO	Hydrothermal process	80, 100	Crystal violet (CV), methyl orange (MO)	UV-Visible light irradiation	95 and 93	66
8	This study	Precipitation	90	Congo red (CR), CV (crystal violet), binary mix	Sunlight	94, 99 and 91	—



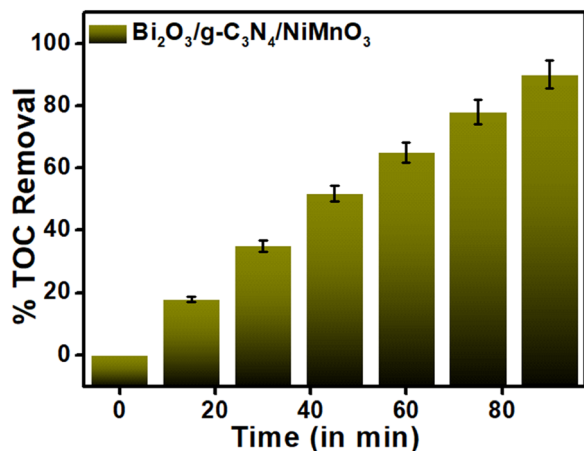
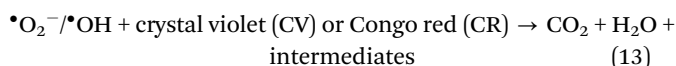


Fig. 11 TOC removal of mixed dyes under solar light using the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  photocatalyst.

These reactive oxygen species ( $\cdot\text{O}_2^-$  and  $\cdot\text{OH}$ ) synergistically degrade both cationic (crystal violet) and anionic (Congo red) dye pollutants through oxidative cleavage, hydrogen abstraction, and ring-opening, ultimately leading to complete mineralization:

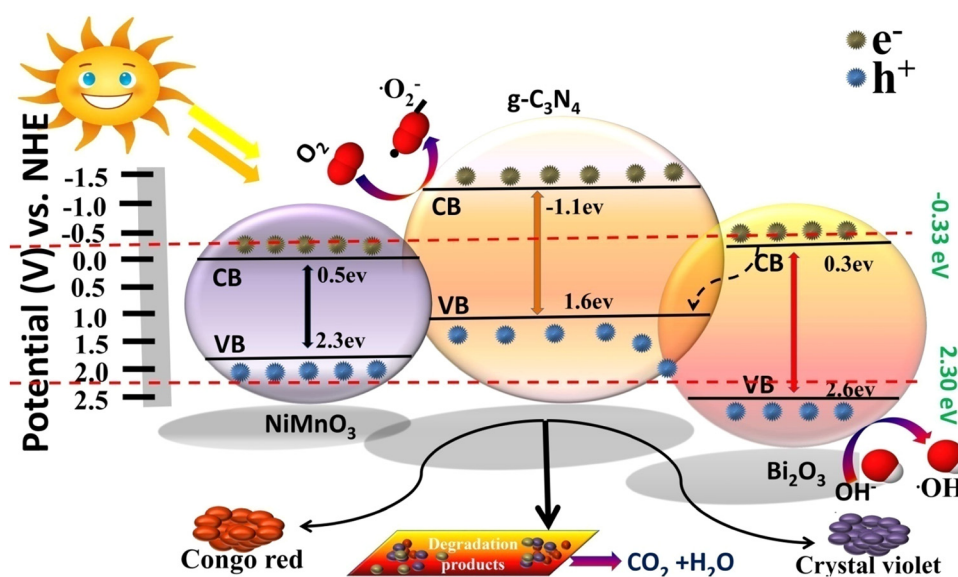


Furthermore, the progressive decrease in total organic carbon (TOC) with irradiation time (Fig. 11) provides direct evidence of effective mineralization rather than mere dye decolorization. As shown in Fig. 11, TOC removal increases steadily, reaching nearly 90% after prolonged solar irradiation, indicating continuous oxidation of intermediate organic fragments into inorganic end products. The slightly slower TOC removal compared to UV-vis decolorization confirms the

stepwise degradation pathway, wherein complex dye molecules are first transformed into smaller intermediates before complete mineralization. The intimate interfacial contact among  $\text{Bi}_2\text{O}_3$ ,  $\text{g-C}_3\text{N}_4$ , and  $\text{NiMnO}_3$ , together with the built-in electric field of the S-scheme heterojunction, ensures efficient charge separation and sustained generation of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  radicals, ultimately accounting for the high photocatalytic efficiency and mineralization capability of the BGN system under visible-light irradiation (Scheme 2).

## 5. Conclusion

In this study,  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  (BGN) ternary nanocomposites were successfully fabricated *via* a facile precipitation strategy and applied for the visible-light-driven degradation of individual (Congo red and crystal violet) as well as mixed organic dyes. Comprehensive physicochemical and optical characterizations confirmed the formation of an integrated heterostructure, with high-resolution TEM revealing intimate interfacial contact among the constituent phases, indicative of strong electronic coupling. Electrochemical investigations, including EIS (electrochemical impedance spectroscopy) and CV (cyclic voltammetry), provided insights into the enhanced charge transfer kinetics and redox activity of the photocatalyst, affirming its superior interfacial conductivity and electrochemical responsiveness. The optimized nanocomposite exhibited remarkable photocatalytic efficiency, durability, and recyclability under visible-light irradiation. Notably, the generation of reactive oxygen species, primarily hydroxyl ( $\cdot\text{OH}$ ) and superoxide ( $\text{O}_2^{\cdot-}$ ) radicals, was found to be the dominant pathway for dye decomposition, leading to complete mineralization. Stability assessments over multiple photocatalytic cycles confirmed the structural integrity and reusability of the catalyst. Overall, the BGN ternary heterojunction emerges as a



Scheme 2 Proposed S-scheme charge transfer mechanism in  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  under visible light, promoting efficient dye degradation (Congo red, crystal violet) *via* reactive oxygen species ( $\cdot\text{O}_2^-$ ,  $\cdot\text{OH}$ ).



promising candidate for sustainable wastewater remediation owing to its synergistically enhanced photocatalytic activity and operational robustness.

$\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  nanocomposites demonstrate strong potential for wastewater treatment, but key challenges remain for real-world use. Long-term stability under varying conditions, green and scalable synthesis methods, and deeper mechanistic understanding *via in situ* spectroscopy are crucial. Enhancing the heterojunction *via* doping or surface modifications could boost visible-light performance. Finally, integrating these materials into continuous-flow systems will be vital for industrial applications. Continued innovation in design, mechanisms, and integration is essential for sustainable environmental remediation.

Although conventional synthesis and characterization techniques were employed, their combined use with experimental–theoretical analysis provides new insight into the structure–property–performance relationship of the  $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4/\text{NiMnO}_3$  ternary system.

## Author contributions

Rasmirekha Pattanaik: investigation, methodology, formal analysis, data curation, visualization, and writing – original draft. Rishabh Kamal and Debapriya Pradhan: investigation, resources, and writing – review and editing. Suresh Kumar Dash: conceptualization, methodology, supervision, writing – review and editing, resources, and funding acquisition.

## Conflicts of interest

The authors declare that they have no competing financial interests or personal relationships that could have affected the objectivity or integrity of the work reported in this article.

## Data availability

All data supporting the findings of this study are included within the main article and its supplementary information (SI). The supplementary information file includes detailed data on BET surface area, PL spectroscopy, Raman spectroscopy, and individual dye degradation experiments. See DOI: <https://doi.org/10.1039/d6nj00220j>.

No computational code was used in this study. Additional data can be provided by the corresponding author upon reasonable request.

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