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Highly sensitive electrochemical detection of hazardous 2,4-dinitrophenylhydrazine using MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites

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In this study, MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites were successfully synthesized for the electrochemical detection of 2,4-dinitrophenylhydrazine. The MgCo-TiO₂/C₃N₄ heterostructure nanocomposites were synthesized by preparing bimetal (Mg-Co)-doped TiO₂ via a microwave-assisted sol gel method, followed by a thermal approach to coat it onto g-C₃N₄ nanosheets. The morphology, structure, composition and optical and electrochemical properties of the fabricated heterostructure nanocomposites were characterized by various analytical techniques including PXRD, UV-DRS, VB-XPS, PL, HRTEM, FESEM-EDX, FT-IR, EIS and CV. To develop an electrochemical sensor for 2,4-dinitrophenylhydrazine (2,4-DNPH), the MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites were coated onto a glassy carbon electrode (GCE) by a drop-casting method. MgCo-TiO₂/g-C₃N₄/GCE showed an excellent electroanalytical response for the oxidation of 2,4-DNPH in a lower pH environment. MgCo-TiO₂/g-C₃N₄/GCE exhibited excellent selectivity, sensitivity (589.13 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$), and a lower limit of detection (0.06 μM) in a wide linear range (0.1–0.9 μM) under optimized conditions. Furthermore, the sensor exhibited high repeatability (RSD 1.38%), reproducibility (RSD 3.57%), stability and recovery in real sample analysis.

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1. Introduction

The widespread industrial use of aromatic compounds has led to their increasing environmental emissions, raising serious concerns due to their toxicity, persistence, and bioaccumulation. Among these compounds, 2,4-dinitrophenylhydrazine (2,4-DNPH) is an aromatic compound containing both nitro and hydrazine functional groups. It is widely used as a raw material in the industrial production of explosives, pharmaceuticals, pesticides, metal plating agents, blowing agents, and photographic materials.^{1,2} In laboratories, 2,4-DNPH is commonly employed in analytical chemistry for the detection of aldehyde and ketone carbonyl groups through derivatization reactions^{3,4} as well as in the synthesis of aryl

hydrazones with potential antifungal activity.⁵ 2,4-DNPH is an environmentally hazardous and poorly degradable compound because of its stable nitro and toxic hydrazine groups. Its major source of environmental contamination is untreated industrial and laboratory effluents, which can penetrate soil and groundwater² or enter surface water bodies through erosion and runoff. Long-term exposure to 2,4-DNPH can lead to hepatotoxicity, skin disorders, central nervous system impairments, cardiovascular complications, and carcinogenic and mutagenic risks in humans.^{6,7}

Therefore, the accurate detection and continuous monitoring of 2,4-DNPH in environmental matrices are essential to assess its levels and ecological risks. However, only a limited number of detection methods have been reported to date, including spectrometry,^{8,9} potentiometric titration,¹⁰ gas chromatography-mass spectrometry,¹¹ chemiluminescence,¹² and fluorescence sensing.¹³ Furthermore, these techniques are often expensive, non-portable, reagent-intensive, and time-consuming for real-sample analysis. In recent years, electroanalytical approaches using nanomaterial-modified electrode surfaces have gained increasing attention for the detection of 2,4-dinitrophenylhydrazine. The reported examples include poly-*para*-aminobenzoic acid-manganese oxide (P-*p*ABA-MnO₂)

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composite-modified glassy carbon electrodes (GCEs),² (P₈W₄₈/PDDA)₇-modified ITO electrodes,¹⁴ PDDA/(Cu₄P₄W₃₀/PDDAGO)_n assemblies,¹⁵ Zn,N-doped γ -cyclodextrin/GCE,¹⁶ and m-TiO₂/FeTiO₃@NCF/GCE.¹⁷ These sensors demonstrate excellent electroanalytical performances with low limits of detection, high electron transfer rates, sensitivity, selectivity, wide linear concentration ranges, and good reproducibility, primarily due to the synergistic effects of the composite materials on the modified electrode surface.

In electrochemical sensors, modifying the electrode surface with carbon-based catalyst materials provides significant advantages by forming conductive interfaces that enhance their interactions with the target analyte. For instance, reduced graphene oxide (rGO) provides excellent electrical conductivity and a large surface area,¹⁸ while graphene oxide (GO) is valued for its high chemical stability, large surface area, and abundant electrochemically active sites.¹⁹ Similarly, graphitic carbon nitride (g-C₃N₄) exhibits a high surface area, rapid electron transfer, and strong chemical stability.²⁰ Among these materials, g-C₃N₄ has attracted considerable research interest owing to its simple preparation, medium band gap, low cost, wide availability, and chemical inertness.^{21–23} Furthermore, the presence of C–N bonds contribute improved catalytic electron transfer compared to other carbon-based materials due to the strong electronegativity and lone pair electrons on the nitrogen atoms, which offer abundant electrochemically active sites, enhance the electrode-analyte interactions, and facilitate rapid electron transfer through their conjugated structure.²⁴ Several studies have reported the modification of electrodes with g-C₃N₄ nanosheets for electrochemical detection using voltammetric techniques, including the detection of hydrogen peroxide,²⁵ oxalic acid,²⁶ and tryptophan.²³

However, g-C₃N₄ suffers from a relatively small surface area and rapid electron-hole recombination, which limit its electrocatalytic performance in electrochemical detection. Thus, to overcome these drawbacks, many researchers have focused on enhancing its surface area and electrical conductivity by forming heterostructures with various semiconductors. For instance, Co₃O₄ anchored g-C₃N₄ heterostructures exhibit improved electrical conductivity;²⁴ an g-C₃N₄/CuWO₄ nanocomposite-modified electrode exhibits excellent selectivity sensitivity for nitrofurazone detection;²⁷ a Pd/CeO₂/g-C₃N₄ nanocomposite demonstrates reduced electron-hole recombination and enhanced photocatalytic activity;²⁸ g-C₃N₄Ag₂ZrO₃ composites show a high surface area and superior ethanol gas sensing ability;²⁹ ZnO-modified g-C₃N₄ displays an enlarged specific surface area, narrowed band gap, and superior photocatalytic performance compared to pure g-C₃N₄;³⁰ and a g-C₃N₄/MnO₂/ZnO-modified GCE achieves faster electron transfer with greatly enhanced electrochemical sensing of metronidazole.³¹ Coupling g-C₃N₄ with transition metal oxide semiconductors noticeably enhances its surface area and electrical conductivity. Among these semiconductors, TiO₂ exhibits superior physicochemical properties such as high stability, large surface area, porosity, strong catalytic activity, efficient electron transfer, and enhanced hydroxyl radical adsorption capacity, which

collectively improve the electrochemical detection of organic compounds by increasing the electrode surface roughness.^{32–34}

Nevertheless, TiO₂ nanoparticles possess a wide band gap (3.2 eV), which leads to reduced electrical conductivity due to rapid electron-hole recombination. Thus, to address this limitation, researchers have explored doping TiO₂ with metals and nonmetals to narrow its band gap without altering its crystallographic structure. The choice of synthesis method and dopant concentration plays a crucial role in determining the particle size, surface area, band gap, and electrical conductivity of TiO₂. In our previous work, Ce–Ni co-doped TiO₂ synthesized *via* an Aloe vera gel-mediated sol-gel method exhibited a small particle size, high surface area, reduced band gap, and enhanced photocatalytic activity for binary dye degradation.³⁵ Furthermore, P. E. Imoisili and T. C. Jen reported that V-doped TiO₂ prepared using a microwave-assisted method showed improved particle quality, surface area, uniform particle distribution and a narrowed band gap,³⁶ which is attributed to its rapid nucleation and crystallization in a short irradiation time under microwave irradiation.³⁷

In this work, a synergistic, highly sensitive, selective, and stable electrochemical sensor based on MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites was developed for the detection of 2,4-dinitrophenylhydrazine (2,4-DNPH). Prior to the coupling of the MgCo-TiO₂ and g-C₃N₄ materials, TiO₂ was doped with Mg and Co *via* a microwave-assisted sol gel method with systematically optimized dopant concentrations and microwave powers to narrow its band gap and enhance its conductivity by promoting efficient charge separation. Integration of the TiO₂ nanoparticles with g-C₃N₄ nanosheets resulted in the formation of MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites. In this system, g-C₃N₄ provided strong interactions with 2,4-DNPH through hydrogen bonding and π – π stacking, while the MgCo-doped TiO₂ nanoparticles enhanced the conductivity of g-C₃N₄ by increasing its surface area, narrowing its band gap, and suppressing electron-hole recombination. The synergistic coupling of both materials significantly improved the electrochemical detection performance toward 2,4-DNPH. The fabricated MgCo-TiO₂/g-C₃N₄/GCE sensor demonstrated high selectivity, sensitivity, and stability toward the detection of 2,4-DNPH, emphasizing both the novelty and practical relevance of our approach.

2. Experiment

2.1. Chemicals and reagents

The precursors used for the synthesizing magnesium (Mg²⁺) and cobalt (Co²⁺)-doped titanium oxide nanoparticles coated with graphitic carbon nitride (g-C₃N₄) were magnesium nitrate hydrate (Mg(NO₃)₂·6H₂O, 99%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 98%), tetra-*n*-butyl orthotitanate (Ti(OBu)₄, 98%) and urea (NH₂CONH₂). 2,4-Dinitrophenylhydrazine (97%) was used for electrocatalytic detection applications. All chemicals were procured from Sigma-Aldrich. Ethanol (C₂H₅OH, 100%) from Hayman (UK) served as the solvent during the synthesis, while nitric acid (HNO₃) from Merck (Germany) was used for surface modification during the synthesis of the TiO₂



nanoparticles. All chemicals were analytical reagent (AR) grade and used without further purification.

2.2. Synthesis of MgCo co-doped TiO₂ nanoparticles

The MgCo co-doped TiO₂ nanoparticles were synthesized *via* the microwave-assisted sol gel method in two steps. Firstly, dopants with five different weight percentages were synthesized *via* the sol gel method. Among them, the one with the smallest crystalline particle size and lowest band gap was selected and further subjected to microwave irradiation to further decrease the crystalline particle size and band gap, while enhancing the specific surface area of MgCo-TiO₂.

2.2.1 .Using sol gel method. To optimize the dopant weight percentage, five different weight percentages of each dopant ratio to titanium was synthesized using the sol-gel method. Solution 1 was prepared by mixing 20 mL of tetra-*n*-butyl orthotitanate [Ti(Obu)₄] with 40 mL of ethanol in a 250 mL Pyrex beaker. Ethanol enhanced the miscibility between the organic and aqueous phases, facilitating better interaction of Ti(Obu)₄ with water. After stirring the mixture for 30 min, 3.2 mL of HNO₃ was added under continuous stirring to catalyze and control the hydrolysis and condensation reactions, thus stabilizing the sol formation. The second dopant solution was prepared by dissolving 0.25 wt% (0.073 g) of Mg(NO₃)₂·6H₂O and 0.75 wt% (0.0475 g) of (Co(NO₃)₂·6H₂O) in a separate 250 mL Pyrex glass beaker containing 40 mL of ethanol and 7.2 mL of Milli-Q water with continuous stirring. After stirring solution 1 for 1 h, solution 2 was added dropwise into solution 1, and the mixture was stirred for an additional one hour until a sol was formed. The sol was kept in the dark for 48 h to allow gel formation. Subsequently, the gel was dried in a hot oven at 72 °C for 24 h to obtain controlled solvent removal and structural integrity before high-temperature treatment, which was ground repeatedly to obtain a fine powder. The resulting fine powder was calcined in a muffle furnace at 450 °C for 5 h to promote crystallization into the anatase TiO₂ phase and remove residual organic components, yielding pure and finely structured TiO₂ nanoparticles. The calcined sample was collected, cooled, ground and labeled as MgCo-TiO₂ nanoparticles (MCT1). Using the same procedure, other samples with varying dopant weight percentages of 0.5 wt% Mg and 0.5 wt% Co (MCT2), 0.75 wt% Mg and 0.25 wt% Co (MCT3), 1 wt% Mg and 0.25 wt% Co (MCT4), and 0.25 wt% Mg and 1 wt% Co (MCT5) were prepared. Bare TiO₂ was also prepared using the same procedure without adding dopants.

2.2.2 .By microwave-assisted sol gel method. Based on PXRD and UV-Vis DRS characterization, the sample with 0.25 wt% Mg and 1 wt% Co (MCT5) exhibited the smallest crystallite size (7.28 nm) and the lowest band gap (2.67 eV) among the five synthesized samples (MCT1, MCT2, MCT3, MCT4 and MCT5). To further reduce the crystallite size and band gap, while enhancing the specific surface area of the MgCo-TiO₂ nanoparticles, using the MCT5 composition, the synthesis was carried out to the sol stage and divided into five equal portions, each placed in a 150 mL Pyrex beaker. The sols were kept in the dark for 48 h to form gels, and then irradiated

Table 1 Power level, irradiation time and labelled names for catalysts

Power level	Output	Irradiation time (min)	Catalyst name
Low	180 W	20	MCT5M1
Medium low	300 W	8	MCT5M2
Medium	450 W	7	MCT5M3
Medium high	600 W	3	MCT5M4
High	900 W	2.5	MCT5M5

at 180, 300, 450, 600, and 900 W, with the corresponding irradiation times of 20, 8, 7, 3, and 2.5 min (Table 1), producing samples labeled MCT5M1, MCT5M2, MCT5M3, MCT5M4 and MCT5M5, respectively. All samples were subsequently collected, ground, calcined at 450 °C for 5 h, cooled, and reground for further characterization (Scheme 1). The microwave-assisted method yielded higher-quality products with smaller crystallites with a uniform particle distribution.

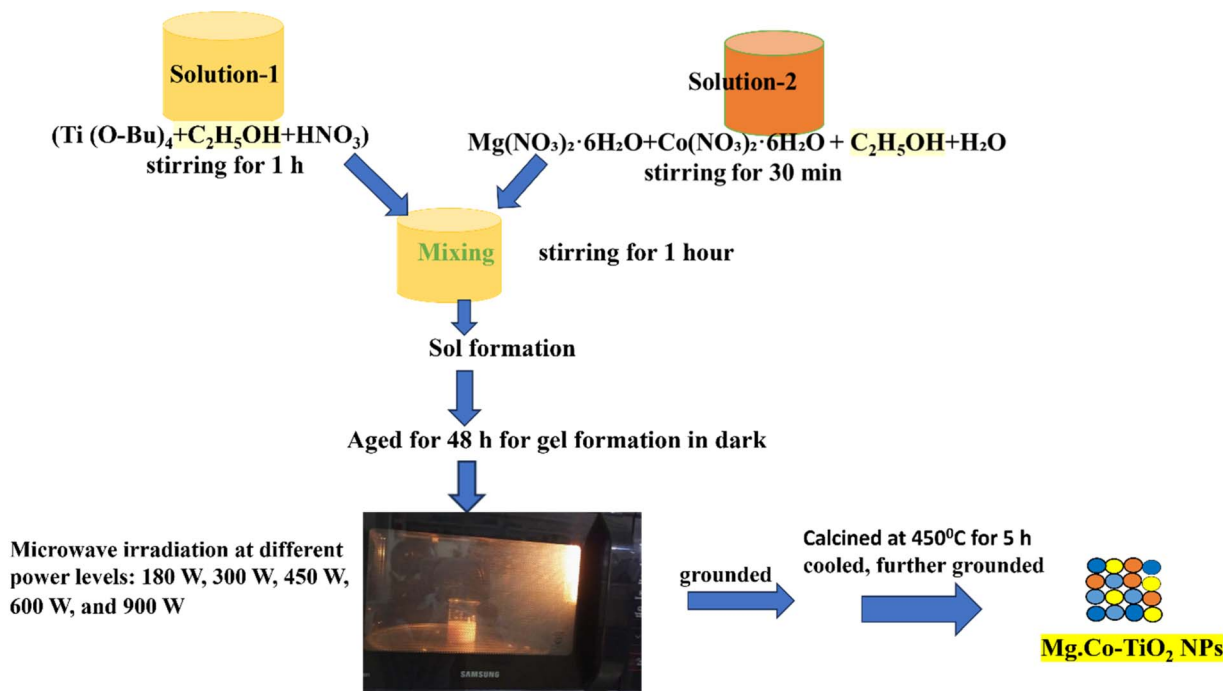
2.3. Fabrication of MgCo-TiO₂/g-C₃N₄ heterostructure composites

Using the optimized TiO₂ sample (MCT5M3), prepared with 0.25 wt% Mg and 1 wt% Co dopants under 450 W irradiation power, MgCo-TiO₂/g-C₃N₄ heterostructure composites were synthesized following a reported method with minor modifications.³⁸ In a typical procedure, 5 g of urea was placed in a crucible and heated in a muffle furnace at 600 °C for 3 h, then allowed to cool, and finely ground, obtaining a yellow nano-sheet powder. A 1 : 3 mass ratio of MgCo-TiO₂ to g-C₃N₄ was dispersed in 20 mL of distilled water by continuous stirring, followed by ultrasonication for 30 min to achieve a uniform dispersion. The resulting suspension was transferred into a ceramic crucible and heated at 72 °C for 6 h. The product was cooled, ground, and further calcined at 400 °C for 2 h in a muffle furnace. After cooling, the material was finely ground again and collected as MgCo-TiO₂/g-C₃N₄ heterostructure composites.

2.4. Preparation of MgCo-TiO₂/g-C₃N₄-modified glassy carbon electrode

Prior to modification, a bare glassy carbon (GC) electrode was sequentially polished with 1.0, 0.3, and 0.05 μm alumina powders, rinsed with distilled water, ultrasonicated in ethanol and deionized water, and finally dried at room temperature. For electrode modification, 2 mg of MgCo-TiO₂/g-C₃N₄ was dispersed in 2 mL of ethanol and ultrasonicated for 10 min to obtain a uniform suspension. A 5 μL aliquot of the suspension without binder was drop-casted onto the pretreated GC electrode surface and air-dried for 30 min prior to use. Three identical electrodes were prepared following the same procedure for reproducibility evaluation. The actual loading on GCE was calculated using the suspension concentration (2 mg/2 mL = 1 mg/mL), volume drop-cast (5 μL = 0.005 mL), and GCE diameter (3 mm = 0.3 cm), corresponding to a geometric area of





Scheme 1 Schematic of the microwave-assisted sol gel synthesis of MgCo-TiO₂ NPs.

0.07 cm². Based on these parameters, the calculated loading on the GCE electrode was approximately 70.7 μg cm⁻².

2.5. Characterization instruments

The crystallite sizes of the fabricated catalysts were determined based on FWHM and diffraction angle data using PXRD (Ultima IV Rigaku, 40 kV/30 mA) with Cu Kα radiation, scanned at 2° min⁻¹ over the 2θ range of 2–80° at room temperature. Optical band gaps and absorption edges were measured using a Shimadzu 3600 UV-Vis DRS NIR spectrophotometer in the range of 200–800 nm with BaSO₄ as a reference. Elemental composition and surface morphology were examined by energy-dispersive X-ray spectroscopy (EDX) coupled with field-emission SEM (FESEM) operating at 20 kV. High-resolution transmission electron microscopy (HRTEM) was employed to analyze the surface morphology and nanostructure of the heterostructure composites. The surface area, pore size, pore volume, and pore distribution of the synthesized catalysts were analyzed using a BET surface area analyzer (Gemini VII 2390, Micromeritics). X-ray photoelectron spectroscopy (XPS) was employed to determine the oxidation states, elemental composition, and binding energies. The functional groups in the metal oxides were characterized by FTIR (Bruker Hyperion 3000 with Vertex 80) in the range of 400–4000 cm⁻¹. Photoluminescence (PL) spectroscopy was carried out using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer equipped with a PMT (50 V) to study electron-hole recombination. Excitation and emission monochromators were set at 2.5 nm slit widths, and samples were measured in a four-sided quartz cuvette suitable for excitation and emission detection. The electrochemical behavior of the catalyst-modified electrodes was evaluated using cyclic voltammetry

(CV), electrochemical impedance spectroscopy (EIS), chronocoulometry, and linear sweep voltammetry (LSV). All measurements were performed on a CHI6005E electrochemical analyzer (CHI Inc., USA) in a three-electrode system, employing a glassy carbon electrode (GCE) as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode.

2.6. Optimization and electrochemical detection of 2,4-dinitrophenylhydrazine

The optimization was performed by evaluating the effects of pH, 2,4-dinitrophenylhydrazine concentration, and scan rate on the electrochemical response of a MgCo-TiO₂/g-C₃N₄-modified GCE using the cyclic voltammetry technique. Experiments were conducted in 0.1 M phosphate buffer solution containing 0.1 M KCl as the supporting electrolyte. The pH of the buffer was varied from 3.0 to 11.0, while the concentration of 2,4-dinitrophenylhydrazine ranged from 0.1 μM to 0.9 μM. The scan rate effect was tested in the range of 20 mV s⁻¹ to 90 mV s⁻¹. The detection of 2,4-dinitrophenylhydrazine was carried out using the linear sweep voltammetry (LSV) technique across a range of concentrations from 0.1 μM to 0.9 μM (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 μM).

3. Results

3.1. Structural, morphological and optical characterization

3.1.1. XRD analysis. The crystalline phases and composition of the prepared samples of undoped (pure TiO₂), five different percentage weight ratios of Mg to Co co-doped TiO₂ nanoparticles, which were synthesized *via* the sol-gel and



microwave-assisted sol-gel methods, g-C₃N₄ and Mg-Co-TiO₂/g-C₃N₄ heterostructure composites were characterized by PXRD. The PXRD peaks of the undoped TiO₂ nanoparticles were observed at 2θ values of 25.43°, 37°, 48°, 54.32°, 62.6°, 69.72°, and 75.5°, corresponding to the anatase phase diffraction planes of (101), (004), (200), (105), (204), (220), and (215), respectively. After Mg and Co co-doping at various weight ratios *via* the sol-gel method, no new peaks appeared; however, the slight shift in the main peak from 25.43° to 24.58° indicated the successful incorporation of the dopant into the TiO₂ lattice (Fig. 1a). All the synthesized samples remained in the anatase phase, as the low dopant concentrations did not alter their crystallographic structure. Similarly, in the microwave-assisted sol gel method (Fig. 1b), no additional peaks were detected, though slight peak shifts were observed. The PXRD pattern of the synthesized g-C₃N₄ showed two characteristic peaks at 2θ = 12.82° (100), attributed to tri-s-triazine units, and 26.74° (002), corresponding to the conjugated aromatic structure. In the case of the MgCo-TiO₂ particles coated with g-C₃N₄ synthesized *via* the microwave-assisted sol gel method, their diffraction peaks

appeared at 2θ = 24.58°, 37°, 47.2°, 53.9°, 62°, 69.62°, and 74.77°, indexed to the anatase TiO₂ planes of (101), (004), (200), (105), (204), (220), and (215), respectively (Fig. 1c).

The coupling of g-C₃N₄ with undoped TiO₂ and MgCo-TiO₂ did not significantly alter their anatase phase structure. However, a weak peak at 29.62° was observed in both TiO₂/g-C₃N₄ and MgCo-TiO₂/g-C₃N₄, while the peak for g-C₃N₄ at 12.82° disappeared and the peak at 26.74° shifted to 29.62°, likely due to interfacial interactions (Mg-O-N, Co-O-N, or Ti-O-N) in the heterostructure. The peaks for g-C₃N₄ were also masked by stronger anatase TiO₂ signals due to the shielding effect.³⁹ The crystallite sizes were calculated using the Debye-Scherrer equation ($D = k\lambda/\beta \cos \theta$, where β is the FWHM, $k = 0.9$, θ is the Bragg angle, and λ is the Cu K α wavelength). As dopants were introduced in the TiO₂ lattice, the crystallite size of TiO₂ increased. Among the doped samples, the MCT5 sample with a higher Co content (lower Mg : Co ratio) allows larger Co²⁺ ions (0.745 Å) to substitute Ti⁴⁺ (0.605 Å), leading to lattice distortion and the formation of oxygen vacancies for charge compensation. The Co dopants act as heterogeneous nucleation centers,

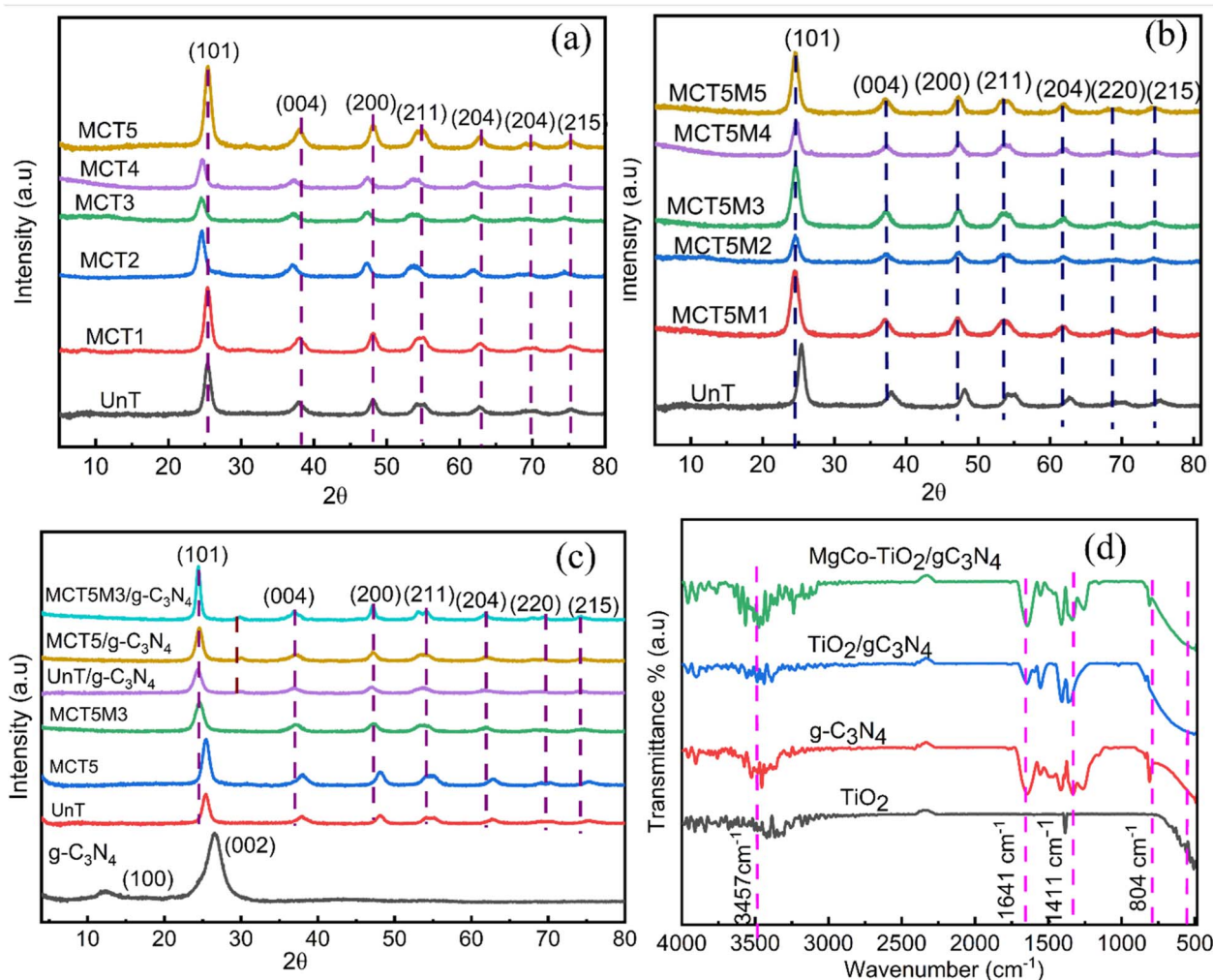


Fig. 1 PXRD patterns of sol gel-synthesized particles (a), microwave-assisted sol gel synthesized at different power levels (b) and g-C₃N₄ and coated heterostructure composites (c). FT-IR spectra of TiO₂, g-C₃N₄, TiO₂/g-C₃N₄ and MgCo-TiO₂/g-C₃N₄ (d).

Table 2 UV-DRS band gap and PXRD crystalline particle size results

Catalyst name	Average crystalline size (nm)	Band gap (eV)	Catalyst name	Average crystalline size (nm)	Bandgap (eV)
UnT	5.62	3.06	MCT5M2	9.21	2.68
MCT1	38.05	2.72	MCT5M3	6.28	2.58
MCT2	17.23	2.74	MCT5M4	9.53	2.77
MCT3	18.53	2.84	MCT5M5	8.38	2.79
MCT4	7.38	2.70	g-C ₃ N ₄	25.05	2.72
MCT5	7.28	2.67	TiO ₂ /g-C ₃ N ₄	11.39	2.84
MCT5M1	7.52	2.69	MgCo-TiO ₂ /g-C ₃ N ₄	6.52	2.41

enhancing nucleation, while the moderate amount of Mg introduces additional defect states that inhibit grain growth. Consequently, the MCT5 sample exhibits the smallest crystallite size of 7.28 nm among the ratios.

Consequently, MCT5 was further subjected to microwave irradiation at different power levels to obtain smaller crystallite sizes and improved particle-quality anatase TiO₂. Among them, the sample irradiated at 450 W showed the smallest crystallite size of 6.28 nm. Overall, Mg-Co co-doped TiO₂ prepared by microwave synthesis exhibited finer particles and superior quality due to its rapid nucleation, shorter reaction times, and lower activation energy, which minimize side reactions and phase transitions. The average crystallite size of pristine g-C₃N₄ was 25.05 nm, which decreased to 11.39 nm when coated with pure TiO₂ and further to 6.52 nm with MgCo-TiO₂ (Table 2).

3.1.2. UV-visible DRS analysis. The optical properties of the synthesized samples were examined using UV-Vis DRS in the range of 200–800 nm. Undoped TiO₂ (UnT) showed absorption only below 400 nm, confirming its UV-limited activity. In contrast, Mg-Co co-doped TiO₂ exhibited absorption in both the UV and visible regions (Fig. S1a), which is attributed to its dopant-induced intermediate energy states and electron traps, which shifted its absorption edge into the visible region. Among the doped samples, 0.25% Mg and 1% Co (MCT5) displayed the

strongest visible-light harvesting. Furthermore, microwave-assisted sol gel synthesized MCT5 at 450 W (MCT5M3) exhibited greater visible absorption than the other irradiation powers (180 W, 300 W, 450 W, 600 W, and 900 W) (Fig. S1c). Pristine g-C₃N₄ showed an absorption edge at 447.74 nm, indicating visible light activity, while coupling with MgCo-TiO₂ further shifted the absorption peak. Overall, the MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites demonstrated the highest visible light absorption compared to g-C₃N₄, TiO₂, and TiO₂/g-C₃N₄ (Fig. 2a).

The band gap (E_g) of all the fabricated samples was calculated from their Tauc plots using the Kubelka–Munk equation: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α is the absorption coefficient, h is Planck's constant, ν is the frequency of light, E_g is the band gap energy and A is a constant. All five percentages of Mg and Co-doped TiO₂ nanoparticles synthesized *via* the sol gel method showed a lower band gap compared to undoped TiO₂ (Fig. S1b). This reduction was observed due to the introduction of dopants atoms. Particularly, the 0.25% Mg and 1% Co-doped TiO₂ (MCT5) showed a significant reduction in the band gap of undoped TiO₂ by lowering it to 2.67 eV compared with other dopant concentration (Table 2). The higher concentration of Co dopant, with its d-orbitals might have a great interacting chance with TiO₂ electronic state, reducing the band gap. The co-

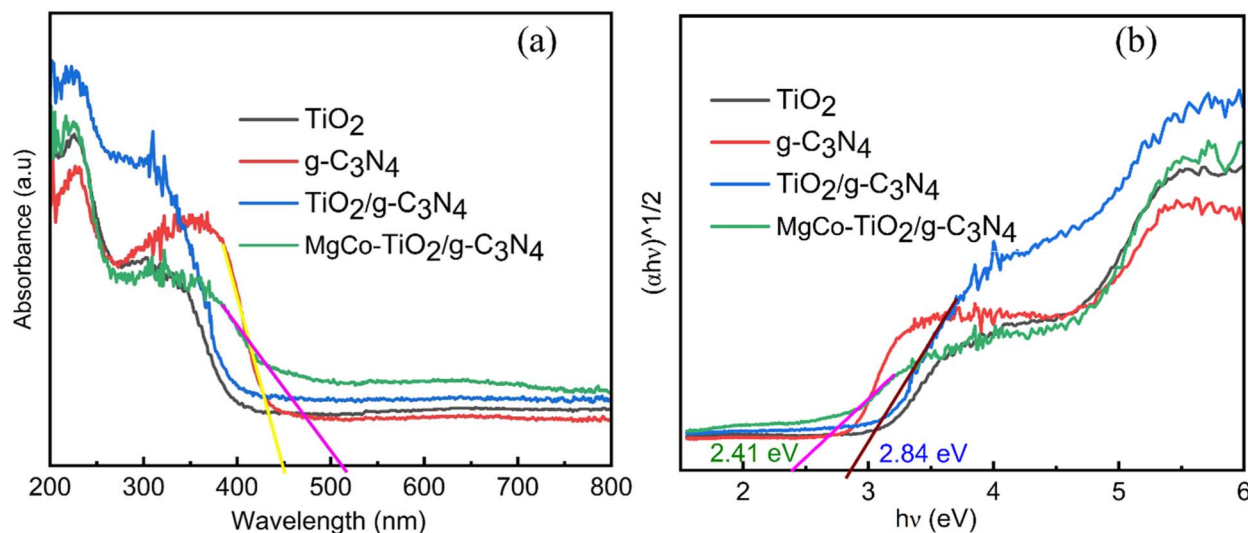


Fig. 2 UV-Vis DRS absorbance spectra of TiO₂, g-C₃N₄, TiO₂/g-C₃N₄ and MgCo-TiO₂/g-C₃N₄ (a) and square root of their Kubelka–Munk functions (b).



doping with Mg also enhances the formation of defect states and oxygen vacancies in the TiO_2 lattice.

Microwave-assisted sol gel synthesis further reduced the band gap by promoting rapid nucleation, controlled crystallization, and suppression of side reactions, yielding uniform, high-quality nanoparticles. Among the samples, MCT5 irradiated at 450 W (MCT5M3) exhibited the lowest band gap of 2.58 eV (Fig. S1d). Pure $\text{g-C}_3\text{N}_4$ showed a band gap of 2.72 eV, consistent with reported values,³⁸ confirming its successful synthesis. Coating TiO_2 and MgCo-TiO_2 onto $\text{g-C}_3\text{N}_4$ resulted in the formation of heterostructure nanocomposites with band gaps of 2.84 eV and 2.41 eV, respectively (Fig. 2d). In the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ heterostructure nanocomposites, Mg and Co facilitated efficient charge transfer and separation, enhancing the electronic state overlap. Notably, the microwave-synthesized $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ exhibited the lowest band gap, suggesting its superior electrocatalytic potential.

3.1.3. XPS. XPS analysis was conducted to investigate the chemical environments for each element in $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$. As shown in Fig. 3a in the XPS survey, no impurities were seen and all the elements in the samples were present (Mg, Co, Ti, O, C, and N). The fitted peak components, corresponding areas, FWHM, and quantitative atomic% of each element are listed in Table 3. Each element was verified in its XPS spectrum including Mg 1s state, Co 2p state, Ti 2p state, O 1s state, C 1s state and N 1s state. The Mg 1s spectrum exhibited various binding energies, showing the multiple chemical environments of magnesium within the composites. The main intensity band at the binding energy of 1304.26 eV and the second peak at 1304.76 eV corresponded to the substitution of Mg^{2+} into the TiO_2 lattice (Ti–O–Mg) by doping. The other two peaks at 1303.78 eV and 1303.4 eV are ascribed to the defect region with oxygen or interaction interface with $\text{g-C}_3\text{N}_4$ in the heterostructure composite (Fig. 3b). The main photoelectron Co 2p core-level peaks in Fig. 3c are observed at binding energies of

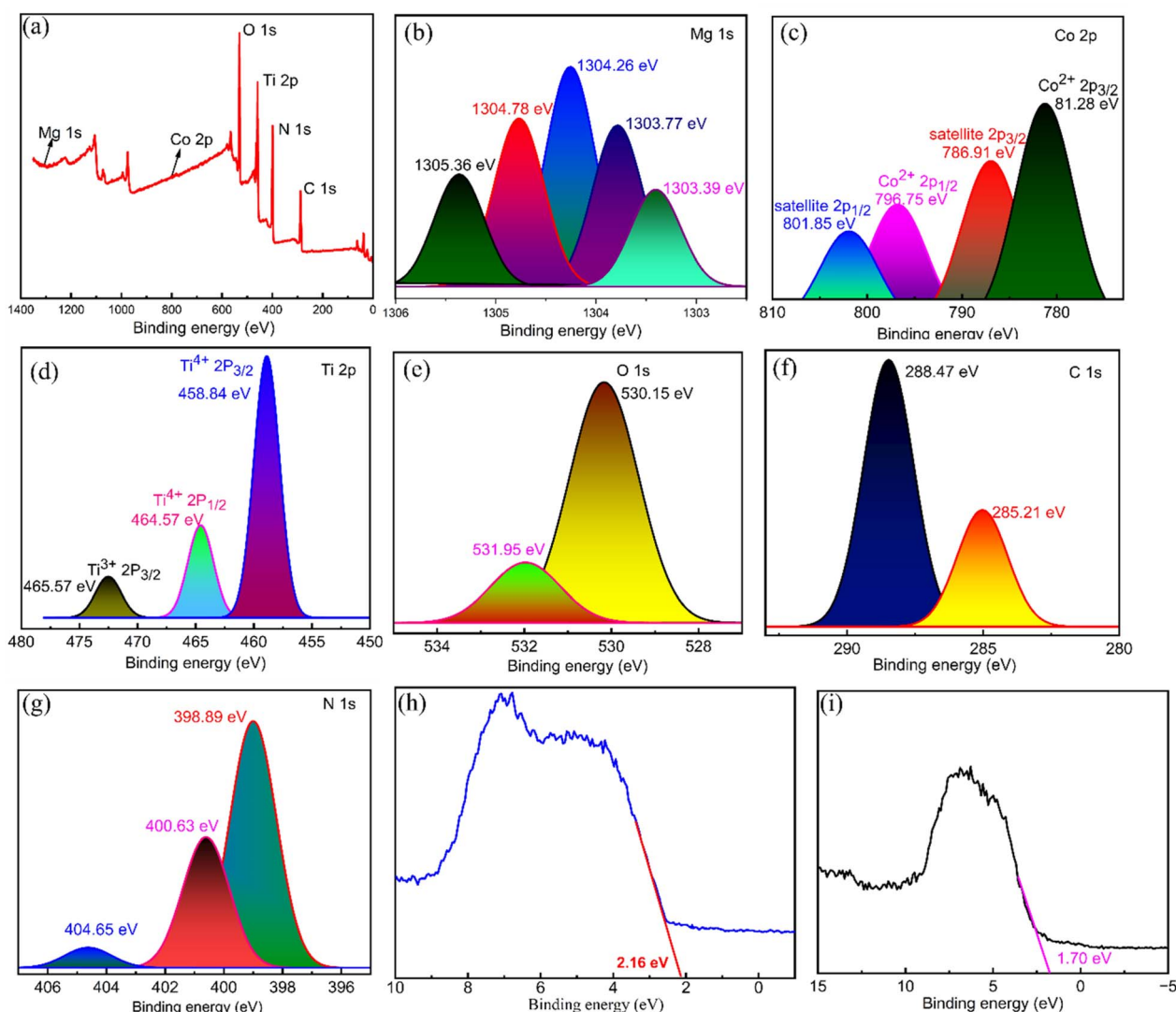


Fig. 3 XPS survey spectrum of $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (a), high-resolution spectra of Mg 1s (b), Co 2p (c), Ti 2p (d), O 1s (e), C 1s (f), and N 1s (g) and VBM of TiO_2 (h) and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (i).



781.28 eV (Co 2p_{3/2}) and 796.75 eV (Co 2p_{1/2}). Two satellite peaks were observed at the binding energies of 786.91 eV and 801.85, corresponding to Co 2p_{3/2} and Co 2p_{1/2}, respectively, further the confirming the presence of Co²⁺ in a high-spin configuration and indicating the presence of Co²⁺ in a Ti–O–Co or Co–O–N–C coordination environment. These results indicate that Co²⁺ ions were successfully incorporated into the TiO₂ lattice by substituting Ti⁴⁺ ions. As shown in Fig. 3d, the Ti 2p core-level peaks observed at binding energies of 458.84 eV (Ti 2p_{3/2}) and 464.57 eV (Ti 2p_{1/2}) confirm the existence of Ti–O bonds within the TiO₂ lattice. A third peak appearing at a binding energy of 465.57 eV, positioned above the main Ti 2p_{3/2} peak and close to the Ti 2p_{1/2} peak, is identified as a satellite peak. This feature likely arises from the influence of the Mg and Co dopants or from the interface interaction between Ti and g-C₃N₄ within the heterostructure composite. The O 1s core-level spectrum displays two distinct binding energies attributed to the presence of dopants and the formation of interface states in the heterostructure MgCo-TiO₂/g-C₃N₄ composite (Fig. 3e). The peak at 530.15 eV corresponds to lattice oxygen, likely associated with Ti–O–Ti, Ti–O–Mg, or Ti–O–Co bonds. The second peak at 531.98 eV is attributed to oxygen vacancies or defects, most likely resulting from doping or the formation of O–C or O–N bonds. The C 1s core-level spectrum shows two binding energy peaks (Fig. 3f), *i.e.*, the main peak at a binding energy of 288.47 eV, which corresponds to sp²-hybridized carbon (C=N–C), and at 285.21 eV, revealing the C–C or C=C bond conjugated aromatic structure of the g-C₃N₄ composite. These findings confirm that the g-C₃N₄ composite was successfully synthesized. As illustrated in Fig. 3g, the N 1s core-level spectrum reveals three distinct binding energy peaks, indicating the influence of the dopants in the MgCo-TiO₂/g-C₃N₄ composite. The first peak at 398.89 eV corresponds to electron-rich nitrogen from sp²-hybridized nitrogen (C=N–C) in the g-C₃N₄ structure. The second peak at 400.63 eV is likely due to electron donation from graphitic nitrogen to the π -conjugated system. The third peak observed at 404.65 eV is attributed to the formation of Mg–N, Ti–N or Co–N bonding interface interactions in the heterostructure environment. The fitted peak components, corresponding areas, FWHM values, and quantitative atomic percentages of each element are summarized in Table 3.

3.1.4. VB-XPS. The valence binding maximum (VBM) was determined by extrapolating the peak tangent line with the baseline for the undoped TiO₂ and MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites. The valence band maximum (VBM) of the undoped TiO₂ nanoparticles was located at 2.16 eV below

the zero potential energy level (Fig. 3h). Upon co-doping TiO₂ with magnesium and cobalt *via* the microwave-assisted sol gel method, and subsequently coating it onto g-C₃N₄ nanosheets, the valence band edge shifted to 1.70 eV (Fig. 3i), indicating a 0.46 eV upward movement of VB toward the Fermi level compared to undoped TiO₂. This enhanced visible-light absorption improves photon utilization and promotes the generation of more photo-carriers under visible light. The introduction of Mg²⁺/Co²⁺ dopant states and coupling with g-C₃N₄ creates mid-gap states and forms a heterojunction, providing efficient charge transfer pathways where electrons and holes are spatially separated or trapped in different sites. The conduction band (CB) positions of undoped TiO₂ and the MgCo-TiO₂/g-C₃N₄ heterostructure were estimated using the relation $E_g = E_{VB} - E_{CB}$, with the values of –0.90 eV and –0.71 eV, respectively. The corresponding schematic representation is shown below for clarity (Scheme 2). The undoped TiO₂ exhibits a more negative conduction band potential than the MgCo-TiO₂/g-C₃N₄ heterostructure; consequently, the photogenerated electrons transfer from TiO₂ to the MgCo-TiO₂/g-C₃N₄ composite.

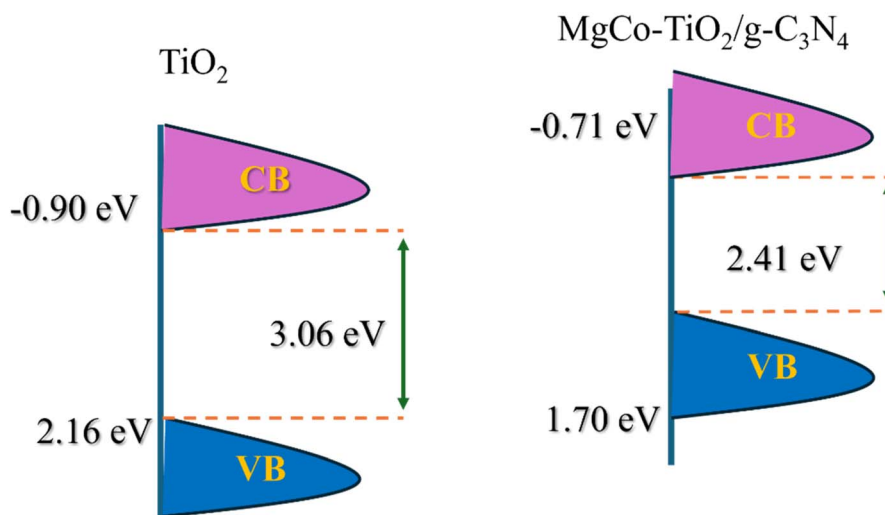
3.1.5. Photoluminescence (PL) spectral study. Photoluminescence (PL) analysis was performed to evaluate the electron–hole separation efficiency of the synthesized semiconductors and heterostructure composites. As shown in Fig. 7d, pure g-C₃N₄ exhibited strong PL emission, indicating the rapid recombination of electron–hole pairs. Coating the g-C₃N₄ nanosheets with undoped TiO₂ reduced the emission intensity, reflecting suppressed recombination due to the formation of a heterostructure and electron transfer from TiO₂ to g-C₃N₄, as TiO₂ possesses a higher conduction band. Mg and Co doping in TiO₂ introduced trap states, which further promoted charge transfer, minimized recombination, and enhanced the redox activity. Consequently, MgCo-TiO₂/g-C₃N₄ exhibited the lowest PL intensity, signifying the most effective recombination suppression and improved conductivity. Overall, the PL emission intensity decreased in the order of g-C₃N₄ > TiO₂/g-C₃N₄ > MgCo-TiO₂/g-C₃N₄, while the conductivity increased in the same sequence, confirming that MgCo-TiO₂/g-C₃N₄ is a highly promising electrocatalyst for facilitating electron transfer between the electrode and electrolyte.

3.1.6. Surface area and pore distribution study (BET) analysis. The surface area and pore distribution of the synthesized materials were characterized using nitrogen gas adsorption–desorption at 77 K based on the Brunauer–Emmett–Teller (BET) surface area analysis method. The N₂ adsorption–

Table 3 XPS fitted peak components, corresponding areas, FWHM values, and quantitative atomic percentages

Name of element	Peak BE (eV)	FWHM (eV)	Area (P) CPS (eV)	Atomic (%)
Ti 2p	459	3.15	1 562 284.71	12.07
O 1s	530.87	2.94	1 318 786.63	24.17
N 1s	399.44	3.33	1 127 019.2	32.2
C 1s	288.18	4.35	695 985.5	30.93
Co 2p	781.71	3.32	85 454.96	0.31
Mg 1s	1303.78	2.32	29 930.69	0.32





Scheme 2 Schematic for the VB and CB shifting during the coupling of MgCo-TiO₂ and g-C₃N₄.

desorption isotherms of all the synthesized materials, as shown in Fig. 4a, exhibit hysteresis loops characteristic of the H3 type, with the loops appearing at higher relative pressures (P/P_0) ranging from 0.4 to 1.0 except for g-C₃N₄, which shows a shift between 0.7 and 1.0. Additionally, the presence of two capillary condensation steps indicates type IV isotherms, according to the IUPAC classification. When undoped TiO₂ and Mg-Co co-doped TiO₂ (synthesized *via* the microwave-assisted method) were coated onto the surface of g-C₃N₄, the specific surface area of the resulting heterostructure composites increased compared to that of pure g-C₃N₄. The obtained BET specific surface area of TiO₂, g-C₃N₄, MgCo-TiO₂, TiO₂/g-C₃N₄ and MgCo-TiO₂/g-C₃N₄ was observed to be 83.46 m² g⁻¹, 15.47 m² g⁻¹, 116.06 m² g⁻¹, 59.63 m² g⁻¹ and 81.61 m² g⁻¹, respectively (Table 4). g-C₃N₄ has a narrow band gap, is visible light active and has more electron-rich species than TiO₂ but it has low porosity and limited surface area. For instance, in a reported

study,³⁸ TiO₂ was combined with g-C₃N₄, leading to an increase in the heterostructure surface area from 29.4 m² g⁻¹ to 36.2 m² g⁻¹. Similarly, in another reported study,⁴⁰ copper and chromium-doped g-C₃N₄ achieved a surface area of 15.7 m² g⁻¹. Furthermore, when the surface of g-C₃N₄ was modified with

Table 4 Specific surface area and total pore volume and average pore diameter of the particles

Catalyst	S_{BET} (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore width (nm)
TiO ₂	83.46	0.17	3.15
g-C ₃ N ₄	15.47	0.09	3.83
MgCo-TiO ₂	116.06	0.12	3.43
TiO ₂ /g-C ₃ N ₄	59.63	0.08	3.41
MgCo-TiO ₂ /g-C ₃ N ₄	81.61	0.07	3.82

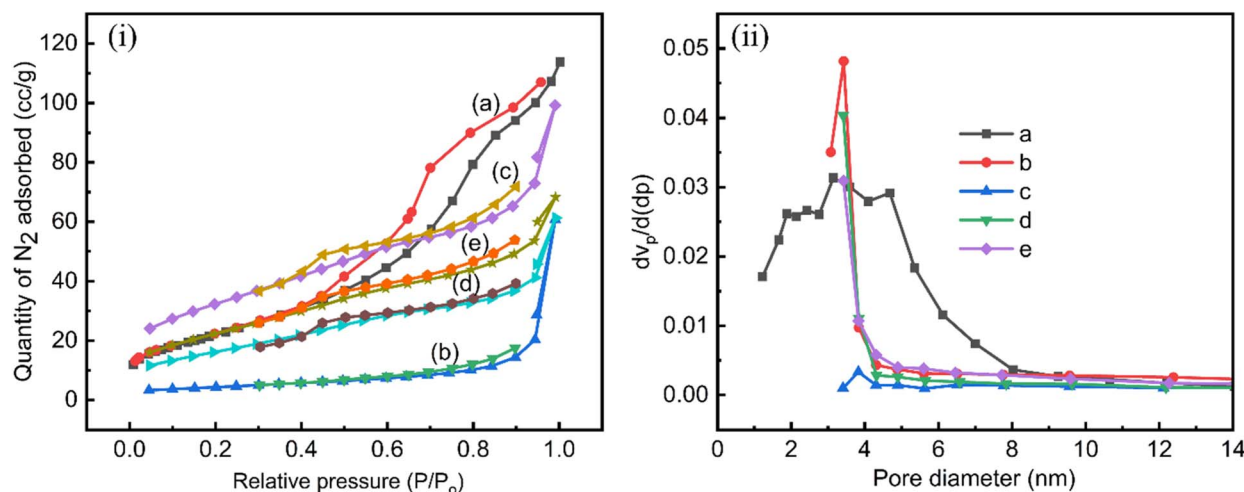


Fig. 4 N₂ adsorption-desorption isotherms (i) and BJH pore size distribution of (ii) TiO₂ (a), g-C₃N₄ (b), MgCo-TiO₂ (c), TiO₂/g-C₃N₄ (d) and MgCo-TiO₂/g-C₃N₄ (e).

green-synthesized TiO_2 , its BET surface area increased from $10.41 \text{ m}^2 \text{ g}^{-1}$ to $32.52 \text{ m}^2 \text{ g}^{-1}$, which enhanced the photocatalytic performance in a reported study.⁴¹

These reported works show the significant impact of the surface modification of $\text{g-C}_3\text{N}_4$ on its photocatalytic and adsorption capacity. In this work, surface modification of $\text{g-C}_3\text{N}_4$ with undoped TiO_2 and Mg-Co doped TiO_2 increased the heterostructure surface areas to $59.63 \text{ m}^2 \text{ g}^{-1}$ and $81.61 \text{ m}^2 \text{ g}^{-1}$, respectively, which are significantly higher than previously reported values. This improvement is attributed to the microwave-assisted method and the dopants, which generated smaller TiO_2 crystallites, increased particle numbers, and inhibited excessive crystal growth. Furthermore, the pore volume and pore diameter of TiO_2 , $\text{g-C}_3\text{N}_4$, MgCo-TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ were determined using the Barrett-Joyner-Halenda (BJH) method, as shown in Fig. 4b. The pore volume and pore average diameter of TiO_2 , $\text{g-C}_3\text{N}_4$, MgCo-TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ are $0.17 \text{ cm}^3 \text{ g}^{-1}$, $0.09 \text{ cm}^3 \text{ g}^{-1}$, $0.12 \text{ cm}^3 \text{ g}^{-1}$, $0.08 \text{ cm}^3 \text{ g}^{-1}$ and $0.07 \text{ cm}^3 \text{ g}^{-1}$ and 3.15 nm , 3.83 nm , 3.43 nm , 3.41 nm and 3.82 nm , respectively.

3.1.7. Surface and morphology study. The TEM analysis (Fig. 5a) revealed that the MgCo-TiO_2 nanoparticles have a predominantly spherical morphology with slight aggregation. As shown in Fig. 5b and c, these nanoparticles are uniformly coated onto the agglomerated $\text{g-C}_3\text{N}_4$ sheets, where the black spherical structures correspond to MgCo-TiO_2 and the gray nanosheet background represents $\text{g-C}_3\text{N}_4$.⁴² The HRTEM image (Fig. 5d) displayed a clear lattice fringe with a d -spacing of 0.35 nm , corresponding to the (101) plane of anatase TiO_2 , as measured using the ImageJ software. Although Mg and Co

doping did not alter the crystal structure or phase of TiO_2 , it improved the nanoparticle dispersion and reduced the band gap. In contrast, the MgCo-TiO_2 coated $\text{g-C}_3\text{N}_4$ sheets (Fig. 5e) appeared with a disordered interface region, which made the fringes indistinct, indicating the formation of a heterostructure. The SAED pattern of $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (Fig. 5f) showed well-defined rings corresponding to the tetragonal anatase phase of TiO_2 , while $\text{g-C}_3\text{N}_4$ exhibited no distinct rings due to its amorphous or semi-crystalline nature. Overall, these results confirm the successful coating of the MgCo-TiO_2 nanoparticles onto layered $\text{g-C}_3\text{N}_4$, forming heterostructure nanocomposites.

3.1.8. FESEM. As shown in Fig. 6, the surface morphologies of the $\text{g-C}_3\text{N}_4$, $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ synthesized nanomaterials were examined using SEM analysis. The $\text{g-C}_3\text{N}_4$ polymer (Fig. 6a) exhibited a layered nanosheet structure resembling loosely stacked graphite-like layers with agglomerated sheets. The MgCo-TiO_2 nanoparticles (Fig. 6b) displayed a nearly spherical morphology with slight aggregation. The heterostructure composites (Fig. 6c) showed a coupled structure, where spherical MgCo-TiO_2 nanoparticles were uniformly coated onto the $\text{g-C}_3\text{N}_4$ nanosheets, confirming their successful interfacial contact. EDX analysis and elemental mapping (Fig. 6d–i) verified the presence of C, N, O, Mg, Ti, and Co, with a uniform distribution across the composite. The combined elemental map (Fig. 6j) further demonstrated that Ti, Mg, and Co signals were concentrated on the outer surface, while the C and N signals overlapped with them, confirming the successful coating of Mg-Co-doped TiO_2 onto $\text{g-C}_3\text{N}_4$ and the formation of heterostructure nanocomposites.

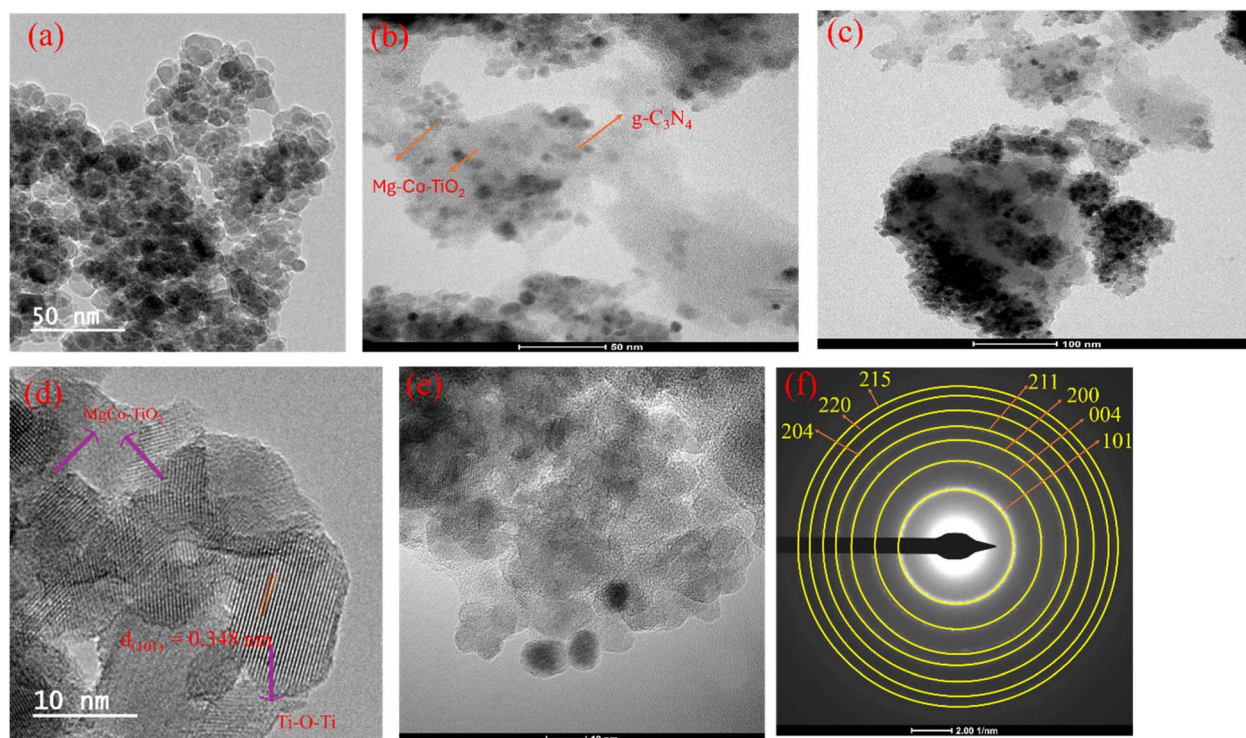


Fig. 5 TEM images of TiO_2 (a) and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (b and c), HRTEM images of TiO_2 (d) and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (e) and SAED pattern of $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (f).



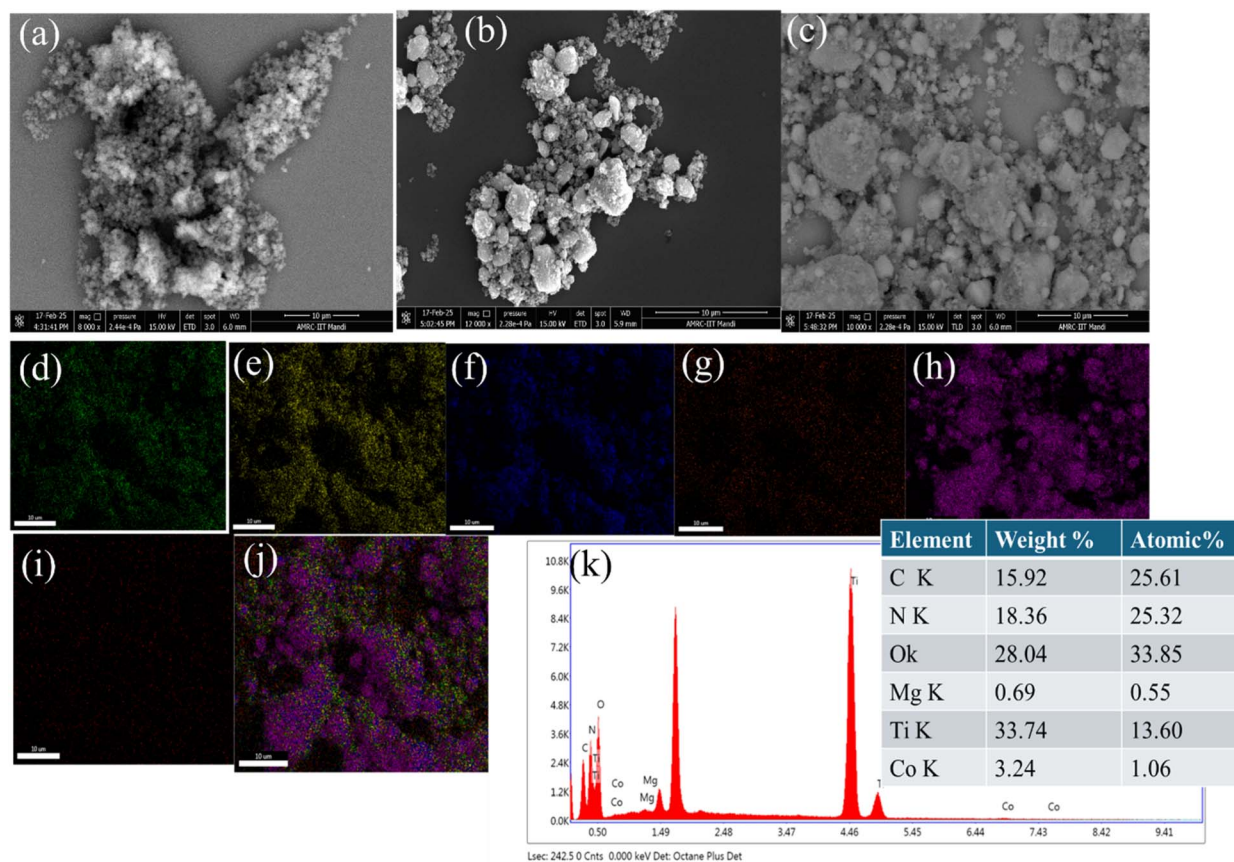


Fig. 6 FESEM images of g-C₃N₄ (a), MgCo-TiO₂ (b) and MgCo-TiO₂/g-C₃N₄ (c), elemental distribution mapping of C (d), N (e), O (f), Mg (g), Ti (h), and Co (i), combined elemental mapping in MgCo-TiO₂/g-C₃N₄ (j) and EDX spectrum of MgCo-TiO₂/g-C₃N₄ (k).

3.1.9. FT-IR characterization. The functional groups and chemical bonding characteristics of g-C₃N₄, TiO₂, and the MgCo-TiO₂/g-C₃N₄ heterostructures were investigated using Fourier transform infrared spectroscopy (FT-IR) (Fig. 1d). In the spectrum of pure TiO₂, the pronounced absorption band at 506 cm⁻¹ corresponds to the Ti-O-Ti stretching vibration of the TiO₂ lattice. In the case of pristine g-C₃N₄, the characteristic absorption band at 1641 cm⁻¹ is attributed to C=N stretching vibrations, while the peaks at 1411 cm⁻¹ and 1355 cm⁻¹ are associated with the aromatic C-N stretching modes.^{43,44} Additionally, the band observed at 804 cm⁻¹ is assigned to the s-triazine ring breathing mode, a structural feature of g-C₃N₄. Upon the incorporation of TiO₂ and MgCo-TiO₂ onto the surface of g-C₃N₄, the intensity of this band decreased and became broader, suggesting successful surface coating and the formation of metal-nitrogen (M-N; M = Ti, Mg, and Co) interactions between the doped TiO₂ and g-C₃N₄. Furthermore, the broad absorption band in the range of 3060–3540 cm⁻¹ corresponds to the N-H stretching vibrations of amine groups and O-H stretching from surface-adsorbed hydroxyl species, confirming the presence of hydrogen-bonded surface functionalities.

3.2. Electrochemical characterization of MgCo-TiO₂/g-C₃N₄

The electrochemical properties of the samples were evaluated using various techniques including electrochemical impedance

spectroscopy (EIS), cyclic voltammetry (CV), and chronocoulometry. Each catalyst, g-C₃N₄, TiO₂, TiO₂/g-C₃N₄ and MgCo-TiO₂/g-C₃N₄, was compared and investigated using the known redox behavior of 2 mM K₃[Fe(CN)₆] electrolyte solution with 0.1 M KCl as the supporting electrolyte. As shown in Fig. 7a, the cyclic voltammetry characterization of all the synthesized materials g-C₃N₄, TiO₂, TiO₂/g-C₃N₄, and MgCo-TiO₂/g-C₃N₄ exhibited well-defined and reversible redox peaks. The oxidation and reduction currents corresponding to the Fe²⁺/Fe³⁺ redox couple in the electrolyte increased progressively in the following order: bare GCE < g-C₃N₄/GCE < TiO₂/GCE < TiO₂/g-C₃N₄/GCE < MgCo-TiO₂/g-C₃N₄/GCE. The obtained anodic current response for each electrode GCE, g-C₃N₄/GCE, TiO₂/GCE, TiO₂/g-C₃N₄/GCE, and MgCo-TiO₂/g-C₃N₄/GCE is 5.56, 8.21, 9.79, 12.05 and 14.25 μA, respectively. The active surface area of the electrodes was calculated using the Randles-Sevcik equation, as follows:

$$I_p = 269\,000AD^{1/2}n^{3/2}\gamma^{1/2}C$$

where I_p is the peak current, A is the electrochemical active surface area, D is the diffusion coefficient, which is 6.7×10^{-6} cm² s⁻¹, n is number of electrons, which is 1, C is the concentration of electrolyte, *i.e.*, 2×10^{-6} mol cm⁻³ for the given electrolyte, and γ is the scan rate, *i.e.*, 0.05 V s⁻¹. The obtained electrochemical active surface area for GCE, g-C₃N₄/GCE, TiO₂/GCE, TiO₂/g-C₃N₄/GCE, MgCo-TiO₂/g-C₃N₄/GCE is 0.018 cm², 0.026 cm², 0.031 cm², 0.039



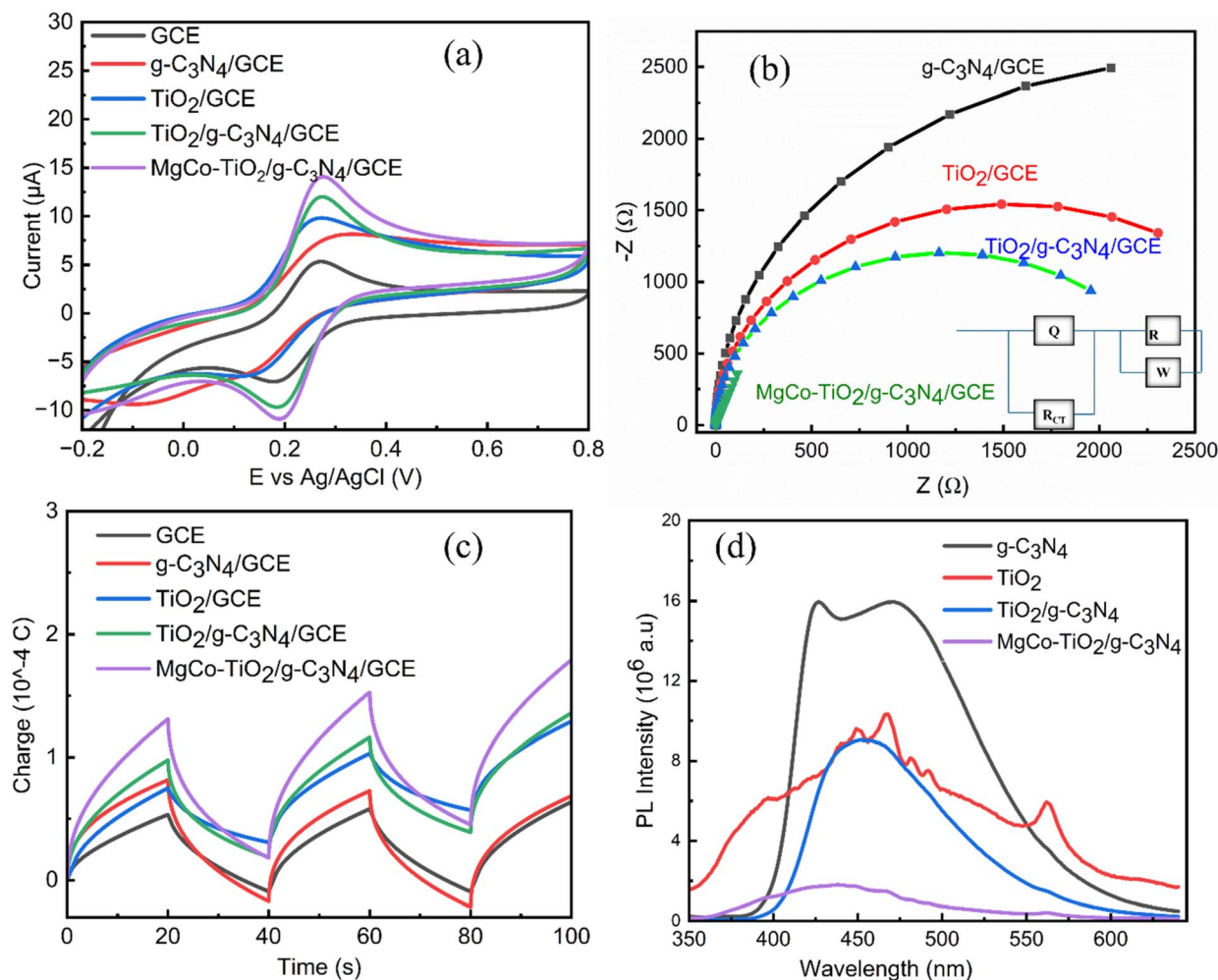


Fig. 7 CV curves (a), EIS Nyquist plots (b), chronocoulometric curves (c) and PL spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, MgCo-TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ (d).

cm^2 and 0.046 cm^2 , respectively. These results indicate that the electrochemical conductivity improves with $\text{g-C}_3\text{N}_4$ surface modification, particularly with TiO_2 and Mg-Co co-doped TiO_2 . This enhancement is attributed to the increased surface area of $\text{g-C}_3\text{N}_4$, which promotes greater ion adsorption, and the presence of defect-trap dopants, suppressing electron-hole recombination.

As shown in Fig. 7b, the electrochemical conductivity performance of all the synthesized catalysts was evaluated and compared using EIS. The Nyquist plots of the prepared catalysts display two characteristic regions, a semicircular arc in the high-frequency range, corresponding to charge-transfer processes, and a straight line at lower frequencies, associated with ion diffusion. The charge-transfer resistance (R_{ct}) for each catalyst-coated glassy carbon electrode was estimated from the intercept of the semicircle with the real (Z') axis. Among the tested materials, $\text{g-C}_3\text{N}_4$, TiO_2 , $\text{TiO}_2/\text{g-C}_3\text{N}_4$, and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ heterostructure exhibited the smallest semicircle diameter, reflecting a substantial decrease in R_{ct} from 1123Ω ($\text{g-C}_3\text{N}_4$) to 129.38Ω . This significant reduction in resistance confirms that the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ heterostructure possesses the most efficient charge transfer and superior electrochemical conductivity among the evaluated catalysts.

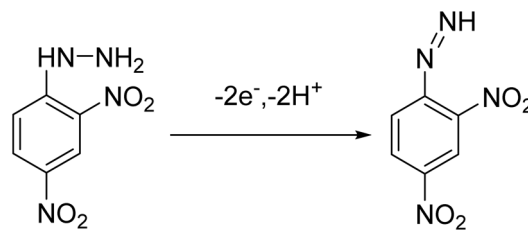
The quantity of ions absorbed by the catalyst on the electrode surface was evaluated through potential step experiments using the chronocoulometric technique (Fig. 7c). The charge associated with the electrolyte for each catalyst-coated electrode was determined from its charge *versus* time plots.⁴⁵ During the first 60 s of the anodic step, the charge (q) associated with $\text{Fe}^{2+}/\text{Fe}^{3+}$ adsorption was measured for each catalyst-modified electrode. The q value for GCE, $\text{g-C}_3\text{N}_4/\text{GCE}$, TiO_2/GCE , $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ was $0.58 \times 10^{-4} \text{ C}$, $0.725 \times 10^{-4} \text{ C}$, $1.035 \times 10^{-4} \text{ C}$, $1.155 \times 10^{-4} \text{ C}$ and $1.53 \times 10^{-4} \text{ C}$, respectively. Among them, the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ catalyst exhibited the highest charge, reflecting its greater ion uptake due to its higher porosity and surface area. Therefore, the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ catalyst-coated GCE is suitable for electrochemical sensor applications due to its improved electrocatalytic performance.

3.3. Electrochemical detection of 2,4-DNPH using $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$

2,4-Dinitrophenylhydrazine (2,4-DNPH) contains a hydrazine ($-\text{NH}-\text{NH}_2$) functional group, which is electrochemically active due to its electron-rich nature. However, the presence of



strongly electron-withdrawing nitro groups at the 2 and 4 positions of its aromatic ring affects the oxidation process, causing the $-NH-NH_2$ group to undergo electrochemical oxidation at a relatively higher positive potential. As shown in Fig. 8a, the electrochemical oxidation of 2,4-DNPH was studied using cyclic voltammetry at a concentration of $0.4\ \mu\text{M}$ in a solution with pH 3. The oxidation peak was observed at a potential of 1.02 V using a glassy carbon electrode as the working electrode. At this higher potential, the $-NH-NH_2$ group oxidized to aryl diazene ($\text{Ar}-\text{N}=\text{NH}$) at the nitrogen center (Scheme 3),⁴⁶ rather than the reduction of the nitro groups, which typically takes place at lower negative potentials. To evaluate and compare the electroanalytical responses toward 2,4-DNPH detection, different modified electrodes were used, including bare GCE, $\text{g-C}_3\text{N}_4/\text{GCE}$, $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$. The corresponding oxidation current response values obtained were 14.29, 15.19, 18.26, and 25.47 μA , respectively. Graphitic carbon nitride contains electron-rich nitrogen groups, which can chemically interact with the functional groups of 2,4-DNPH, offering potential for electrochemical interactions. However, due to the inherently low surface area and poor electrical conductivity of $\text{g-C}_3\text{N}_4$, its electroanalytical response was not significantly enhanced. Thus, to improve this, TiO_2 nanoparticles were coated onto the surface of $\text{g-C}_3\text{N}_4$, forming a $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterostructure catalyst. This modification improved the electrochemical communication between the electrolyte solution and the glassy carbon electrode by increasing both the surface area and conductivity. Nevertheless, the wide bandgap of TiO_2 leads to electron-hole recombination, which limits the further enhancement of the analytical response. Thus, to overcome this limitation and achieve a better electrochemical performance, a two metal-doping approach was employed, where Mg and Co were co-doped into TiO_2 , and subsequently coated onto $\text{g-C}_3\text{N}_4$. As shown in the bar graph in Fig. 8b, $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ exhibited the highest electroanalytical response toward 2,4-DNPH, which is attributed to the synergistic effects of the



Scheme 3 Electrochemical oxidation of 2,4-dinitrophenylhydrazine to 2,4-dinitrophenyl diazene.

heterostructure nanocomposite. Therefore, $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ was selected for further optimization and applied in the electrochemical sensing of 2,4-DNPH.

3.3.1. Effect of pH. The solution pH significantly influences the electrochemical oxidation of the hydrazine functional group in 2,4-DNPH due to protonation and deprotonation processes. The electrochemical sensing performance of $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ was evaluated using CV in a the same $0.4\ \mu\text{M}$ 2,4-DNPH concentration over a range of pH values. As illustrated in Fig. 9a, the oxidation peak potential shifts to less positive values with an increase in pH. This behavior can be attributed to the reduced availability of H^+ ions, which are essential for protonating the $-NH-NH_2$ group during the oxidation process of 2,4-DNPH at the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ surface. Fig. 9b further demonstrates a linear correlation between the peak potential and pH, which can be expressed as follows:

$$E_p (\text{V}) = -0.0295 \text{ pH} + 1.12$$

The slope of $0.0295\ \text{V pH}^{-1}$ is approximately half of the theoretical Nernstian value ($0.059\ \text{V pH}^{-1}$), indicating a proton-to-electron ratio of 1:2. During the oxidation process, two hydrogen atoms are removed (corresponding to the release of two protons, $2H^+$) to form $\text{Ar}-\text{N}=\text{NH}$. However, the observed half-Nernstian slope of $0.0295\ \text{V pH}^{-1}$ indicates that only one proton is directly involved in the potential-determining step.

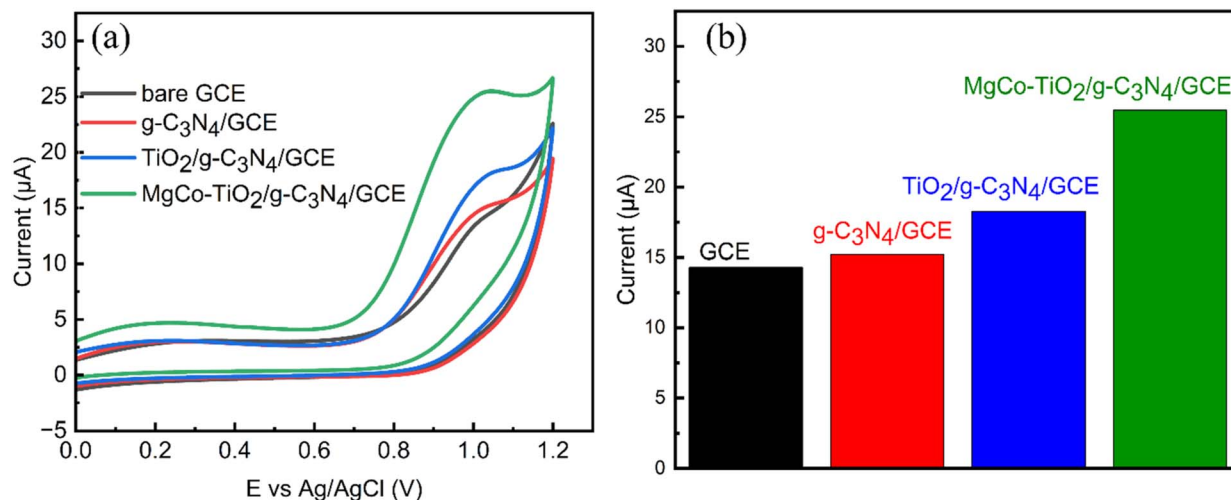


Fig. 8 CV curves (a), and bar diagram for GCE, $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ and $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ (b).

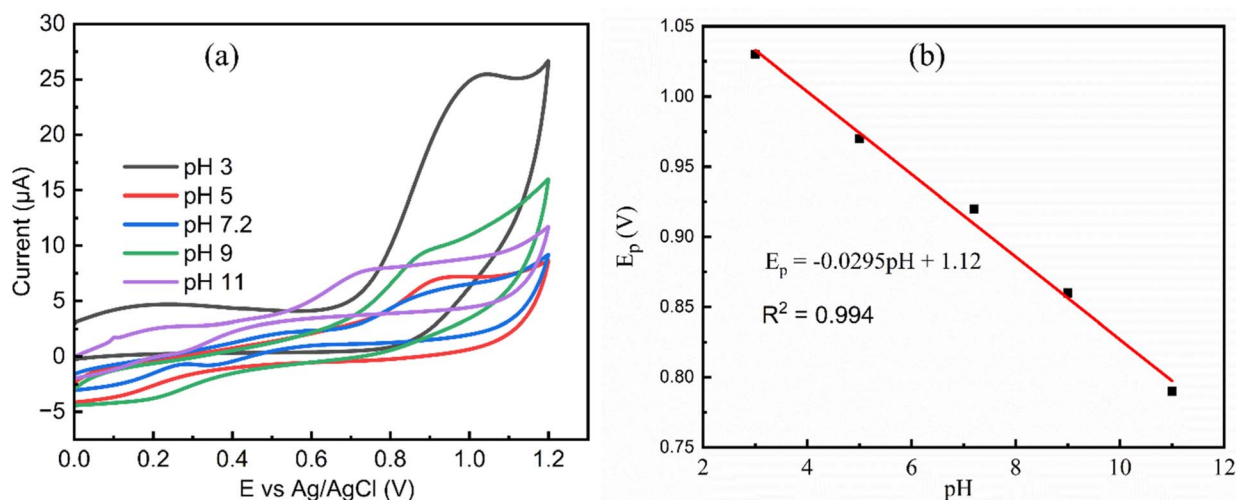


Fig. 9 CV curves of MgCo-TiO₂/g-C₃N₄/GCE under a constant concentration of 0.4 μM 2,4-DNPH over a range of pH values (a) and linear relationship between its potential peak and pH at a scan rate of 30 mV s⁻¹ (b).

The second proton is likely released through a subsequent, rapid radical rearrangement step that facilitates the stabilization of the intermediate species. This behavior is a characteristic feature of the electrochemical oxidation of 2,4-DNPH, where the hydrazine nitrogen serves as the electron-active center. The MgCo-TiO₂/g-C₃N₄ heterostructure catalyst-modified GCE exhibits an oxidation current over a wide pH range, including neutral pH, which is particularly advantageous for the electrochemical detection of hazardous organic compounds in real environmental samples, given that most of these samples typically have a neutral pH.¹⁴ However, to enhance the sensitivity and achieve a sharper oxidation peak current with a highest intensity at lower concentrations of 2,4-DNPH, pH 3 was selected as the optimal working condition in this study.

3.3.2. Effect of scan rate. The scan rate plays a crucial role in determining the electrochemical behavior during electrochemical sensing. Most organic compounds display sharp and well-defined peaks at lower scan rates, whereas at higher scan rates, their peaks tend to become broader when analyzed using the cyclic voltammetry technique. As illustrated in Fig. 10a, the effect of scan rate was investigated for the MgCo-TiO₂/g-C₃N₄-modified electrode as an electrochemical sensor for 0.4 μM 2,4-DNPH solution, at a potential in the range of 0 to 1.2 V at various scan rates (20, 30, 40, 50, 60, 70, 80, and 90 mV s⁻¹). As shown in Fig. 10b, with an increase in the scan rate, the anodic peak current increased linearly, indicating enhanced conductivity by the catalyst and diffusion-controlled behavior. A clear and defined peak was observed at 30 mV s⁻¹ and this lower scan rate is recommended for the electrochemical detection of organic

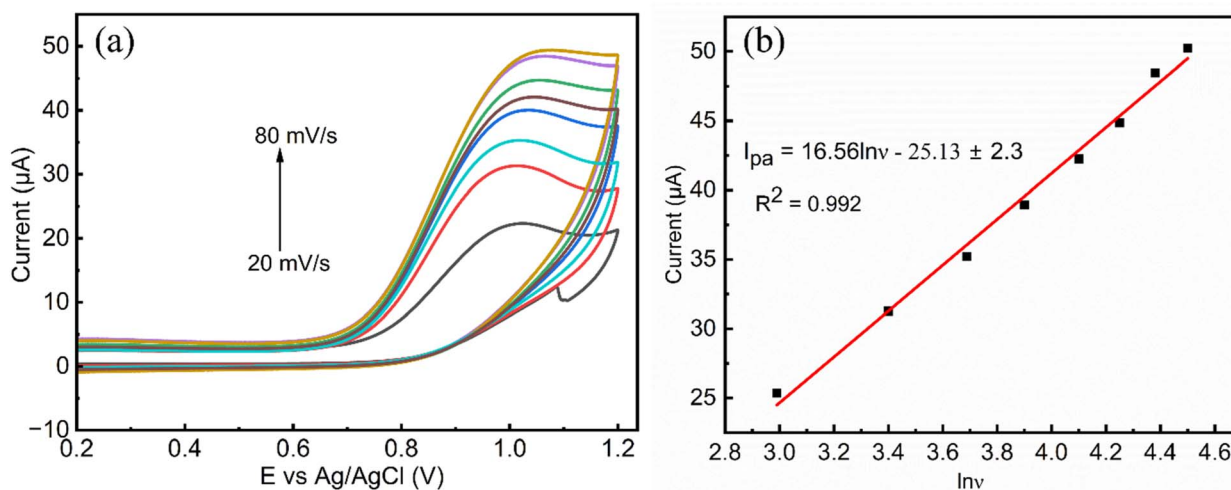


Fig. 10 (a) MgCo-TiO₂/g-C₃N₄/GCE CV curves at different scan rates (20, 30, 40, 50, 60, 70, 80, and 90 mV s⁻¹) with 0.4 μM 2,4-DNPH solution in 0.1 M PBS (pH 3) and (b) plot of linear regression redox peak current vs. square root of the scan rate.



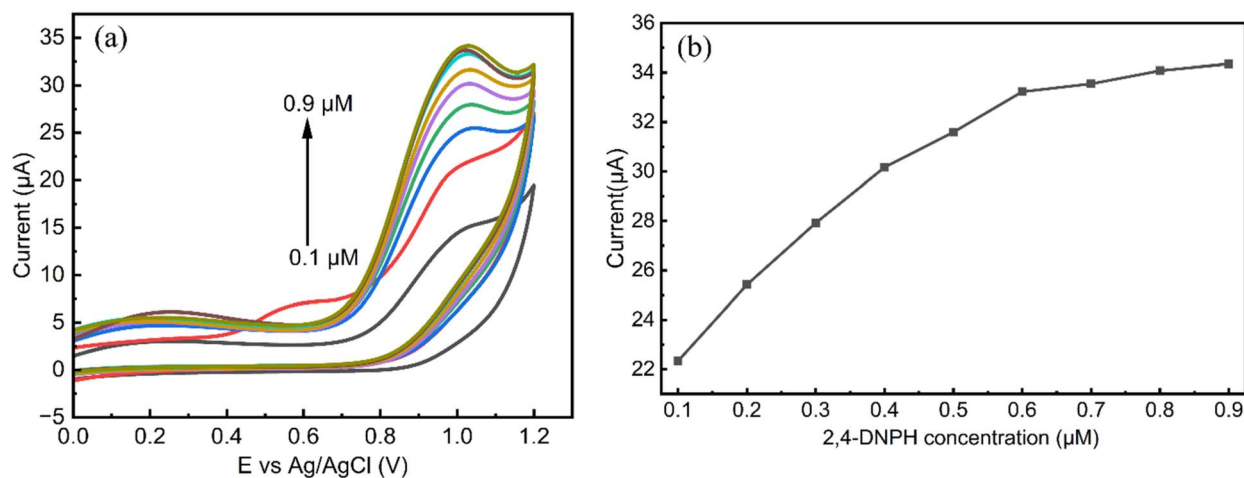


Fig. 11 CV curves for different 2,4-DNPH concentrations in 0.1 M PBS and pH 3 at a scan rate of 30 mV s^{-1} (a) and linear calibration of oxidation peak current vs. 2,4-DNPH concentration (b).

compounds, and therefore selected as the optimal scan rate for the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ sensor for 2,4-DNPH detection.

3.3.3. Effect of 2,4-DNPH concentration. The influence of 2,4-DNPH concentration on the electrochemical performance of the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ catalyst-modified GCE was examined using cyclic voltammetry at different concentrations (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and $0.9 \mu\text{M}$) in a pH 3 solution, within the potential range of 0 to 1.2 V at a scan rate of 30 mV s^{-1} , as presented in Fig. 11a. As the concentration of 2,4-DNPH increased, the oxidation peak current showed a linear increase from 0.1 to $0.6 \mu\text{M}$ (Fig. 11b), indicating that the $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4$ catalyst possesses high porosity and more active sites, which enhance the electrocatalytic interaction between 2,4-DNPH and the GCE surface. However, at concentrations of $0.7 \mu\text{M}$ to $0.9 \mu\text{M}$, the oxidation peak current plateaued, suggesting that the effective working range of the developed sensor for 2,4-

DNPH detection using the cyclic voltammetry technique is between 0.1 and $0.6 \mu\text{M}$.

3.3.4. Electrochemical detection of 2,4-DNPH using LSV. $\text{MgCo-TiO}_2/\text{g-C}_3\text{N}_4/\text{GCE}$ was employed as an electrochemical sensor for the detection of 2,4-DNPH using the linear sweep voltammetry (LSV) technique, which is more sensitive compared to CV, under the optimized conditions with varying analyte concentrations. As shown in Fig. 12a, the oxidative current of 2,4-DNPH increases linearly with an increase in concentration from 0.1 to $0.9 \mu\text{M}$, which can be attributed to the high surface area and abundant reactive sites of the catalyst on the GCE surface. Consequently, the electroanalytical current response also increased with an increase in the analyte concentration. The calibration plot of LSV current *versus* 2,4-DNPH concentration (Fig. 12b) demonstrates a strong linear relationship in the range of 0.1 to $0.9 \mu\text{M}$, represented by the

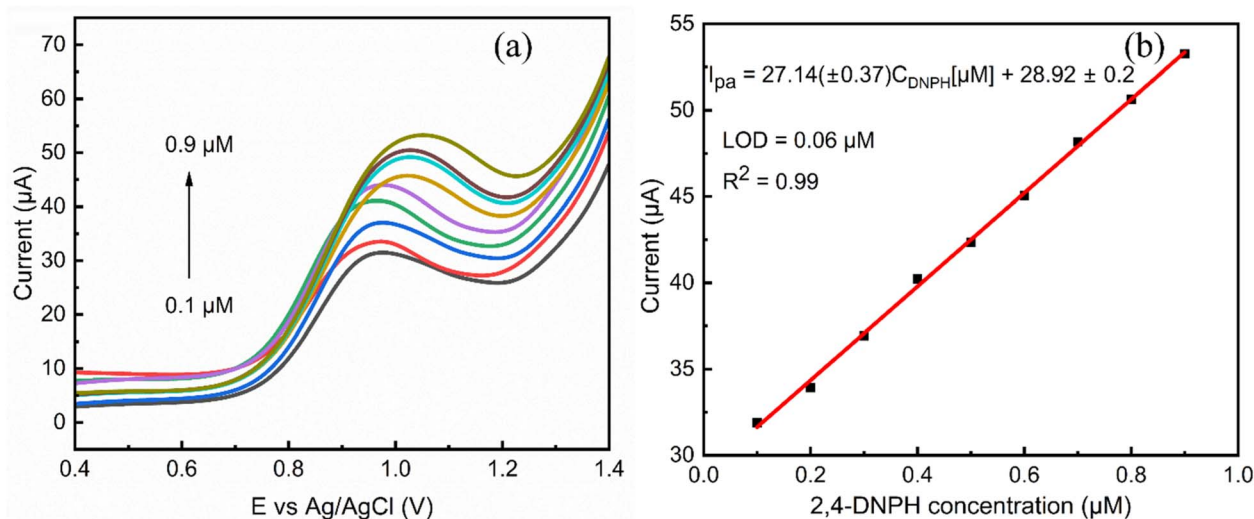


Fig. 12 (a) LSV voltammogram for different 2,4-DNPH concentrations (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and $0.9 \mu\text{M}$) in 0.1 M PBS at pH 3 with a corrected current base line and (b) linear calibration of oxidation peak current vs. 2,4-DNPH concentration.

Table 5 Comparison of the electrocatalytic and photocatalytic performance of different catalysts for the detection of 2,4-DNPH

Electrocatalytic performance comparison					
S. no.	Sensor	Technique	Linear range (μM)	LOD (μM)	Ref.
1	Zn-MOF sensor	Fluorescent	0.1 to 500	0.01	13
2	Cu(II) at GCE	EIS	—	0.04	46
3	P-/pABA-MnO ₂	LSV	0.5 to 90	0.08	2
4	(P ₈ W ₄₈ /PDDA) ₇	Amperometry	1 to 700	0.012	14
5	MgCo-TiO ₂ /g-C ₃ N ₄ /GCE	LSV	0.1 to 0.9	0.06	This work

equation $I_{\text{pa}} = 27.14(\pm 0.37)C_{\text{DNPH}} [\mu\text{M}] + 28.92 \pm 0.2$, with a correlation coefficient (R^2) of 0.99. The sensitivity was determined from the slope of the calibration plot, normalized by the electrochemically active surface area (ECSA) of the modified electrode (sensitivity = slope/ECSA). The ECSA was evaluated from the cyclic voltammetry data using the Randles–Ševčík equation (0.046 cm^2), yielding an impressive sensitivity of $589.13 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$, and highlighting the excellent electrochemical performance of the electrode. The LOD was calculated using the formula $\text{LOD} = 3\sigma/m$, where σ represents the standard deviation of the blank solution of 9 measurements and m represents the slope of the calibration curve. The calculated detection limit was $0.06 \mu\text{M}$. The limit of detection and linear range for 2,4-DNPH detection in this work is compared with that reported in previous studies in Table 5.

3.3.5. Interference study of MgCo-TiO₂/g-C₃N₄ catalyst. The selectivity of the developed MgCo-TiO₂/g-C₃N₄-modified GCE sensor was evaluated using Na⁺ and Pb²⁺ ions as potential interferents, given that the nitrogen sites in g-C₃N₄ can interact with protons and metal cations. In this study, a solution containing $0.4 \mu\text{M}$ 2,4-DNPH, $0.4 \mu\text{M}$ NaNO₃, and $0.4 \mu\text{M}$ Pb(NO₃)₂ was prepared, and its response was measured using LSV under the optimized conditions. As shown in Fig. S2a, the presence of Na⁺ and Pb²⁺ ions resulted in only an 8% decrease in the maximum oxidation current of 2,4-DNPH. Additionally, because nitrogen in g-C₃N₄ can also interact with hydroxyl groups, the interference effect of 4-nitrophenol was examined by adding an equal concentration of 4-nitrophenol to the $0.4 \mu\text{M}$ 2,4-DNPH solution. The LSV results (Fig. S2b) showed that the maximum current of 2,4-DNPH decreased by only 3.08% in the presence of 4-nitrophenol. Furthermore, the interference from nitrobenzene was studied in $0.4 \mu\text{M}$ 2,4-DNPH and $0.4 \mu\text{M}$ nitrobenzene solution. After the addition of nitrobenzene, the maximum LSV current response of DNPH decreased by 4.96% due to the electron-withdrawing nitro group (Fig. S3). These findings

demonstrate that the MgCo-TiO₂/g-C₃N₄/GCE sensor exhibits excellent selectivity for the detection of 2,4-DNPH.

3.3.6. Reproducibility, repeatability and long-term stability study of MgCo-TiO₂/g-C₃N₄ catalyst. After modifying the GCE surface with the MgCo-TiO₂/g-C₃N₄ catalyst, the repeatability and long-term stability of the electrode were assessed using a 2,4-DNPH solution in an acidic medium *via* the LSV technique. The repeatability of the MgCo-TiO₂/g-C₃N₄/GCE sensor for detecting $0.4 \mu\text{M}$ 2,4-DNPH was evaluated under the optimized conditions by performing four consecutive measurements with the same electrode (Fig. S4a). The relative standard deviation (RSD) for these four assays was 1.38%, indicating the high precision and repeatability of the developed sensor toward 2,4-DNPH detection. The reproducibility of the MgCo-TiO₂/g-C₃N₄/GCE sensor for detecting 2,4-DNPH using the LSV technique was evaluated by measuring the responses of three independently fabricated MgCo-TiO₂/g-C₃N₄/GCE sensors under the same conditions. The calculated RSD% was found to be 3.57%.

The long-term stability of the fabricated MgCo-TiO₂/g-C₃N₄/GCE sensors for the electrochemical detection of 2,4-DNPH was evaluated using the LSV technique (Fig. S4b). Measurements were taken on the first day and again after storing the electrodes in air at room temperature for five weeks. The results showed a 2.37% decrease in the initial oxidation current, indicating that the catalyst coating remained firmly attached to the GCE surface, likely due to the strong carbon–carbon bonding between the GCE and g-C₃N₄ in the catalyst.

3.3.7. Real sample studies. The practical applicability of the developed electrochemical sensor toward 2,4-DNPH detection was evaluated using organic laboratory effluents collected from the Department of Chemistry, Andhra University, India. The wastewater samples were initially centrifuged at 2000 rpm, and the resulting supernatant was filtered through Whatman filter paper prior to analysis. Because the saturated aqueous DNPH suspension was measured to be a weak acid ($\text{pH} \approx 5.83$),

Table 6 Determination of 2,4-DNPH in wastewater effluent and recovery test for MgCo-TiO₂/g-C₃N₄/GCE sensor

Native 2,4-DNPH (μM)	Replicates (n)	Added (μM)	Obtained by sensor (μM)	RSD (%)	Recovery (%)
0.17	3	0	0.15	2.25	—
	3	0.3	0.45	2.48	95.74
	3	0.4	0.56	3.35	98.24
	3	0.5	0.68	2.57	101.49



it exhibits nearly neutral charge, and is poorly soluble in water, and thus the electrochemical measurements were performed in 0.2 M aqueous HCl solution (pH 3) to ensure adequate solubility and charge mobility. The filtered samples were analyzed in triplicate ($n = 3$), and the native 2,4-DNPH concentration in the matrix was quantified to be 0.17 μM using spectrophotometric analysis. The developed electrochemical sensor detected 0.15 μM concentration in the real sample. The recovery studies were performed *via* the standard addition method by spiking the real samples with 0.3, 0.4, and 0.5 μM 2,4-DNPH standards. The calculated recovery percentages ($R\%$) ranged from 95.74% to 101.49%, confirming the high accuracy and reliability of the proposed sensor for real sample analysis (Table 6).

4. Conclusion

In this work, we successfully enhanced the conductivity, specific surface area, and surface properties of g-C₃N₄ nanosheets through surface modification with TiO₂ nanoparticles to form TiO₂/g-C₃N₄ heterostructure nanocomposites. However, the large band gap of TiO₂ (3.2 eV) promotes rapid electron-hole recombination, thereby reducing the conductivity of the heterostructure. Thus, to overcome this limitation, TiO₂ nanoparticles were doped with Mg and Co prior to coupling with g-C₃N₄. Co-doping reduced their band gap to 2.58 eV, decreased their crystalline particle size to 6.28 nm, and introduced new electronic states, where Co contributed transitional d-orbital states, while Mg generated oxygen vacancy states. The integration of these improved TiO₂ nanoparticles with g-C₃N₄ nanosheets produced MgCo-TiO₂/g-C₃N₄ heterostructure nanocomposites with enhanced conductivity and enlarged surface area (81.61 m² g⁻¹). When coated on a GCE, the MgCo-TiO₂/g-C₃N₄ catalyst exhibited an excellent performance for the electrochemical sensing of 2,4-DNPH, demonstrating high selectivity, sensitivity, stability, reproducibility, and a low detection limit of 0.06 μM . Furthermore, the developed sensing platform holds great promise for monitoring other hazardous organic pollutants in environmental systems.

Author contributions

Samuel Chufamo Jikamo (first author): conceived and designed the study, conducted the primary research, analyzed the data, and prepared the main manuscript. He was primarily responsible for drafting, structuring, and organizing the content of the manuscript. Prof. T. Sivarao (corresponding author): critically revised and edited the manuscript for intellectual content, grammar, structure, and clarity. Prof. P. Shyamala (co-author): conducted a thorough review of the manuscript and offered constructive feedback, which greatly improved its coherence over several rounds of revision. Singupilla Sai Supriya (co-author): thorough meticulous review and constructive input. Sandhya Rani Nayak (co-author): thoroughly reviewed the manuscript and provided insightful minor revisions. Nageswararao Kadiyala (co-author): reviewing and refining the manuscript in terms of technical formatting and content alignment with visual elements. Winni Teja Dokka (co-author):

reviewed the manuscript. M. Ravichandra: instrumental characterization. M. V Kishore: reviewed the manuscript.

Conflicts of interest

The authors declare no competing interests.

Data availability

All data generated or analyzed during this study are included in the manuscript.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra07106b>.

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