


Cite this: *RSC Adv.*, 2023, 13, 35369

In situ synthesis of g-C₃N₄/Ti₃C₂T_x nano-heterostructures for enhanced photocatalytic H₂ generation *via* water splitting†

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Herein, we demonstrated the *in situ* synthesis of g-C₃N₄/Ti₃C₂T_x nano-heterostructures for hydrogen generation under UV visible light irradiation. The formation of the g-C₃N₄/Ti₃C₂T_x nano-heterostructures was confirmed *via* powder X-ray diffraction and supported by XPS. The FE-SEM images indicated the formation of layered structures of MXene and g-C₃N₄. HR-TEM images and SAED patterns confirmed the presence of g-C₃N₄ together with Ti₃C₂T_x nanosheets, *i.e.*, the formation of nano-heterostructures of g-C₃N₄/Ti₃C₂T_x. The absorption spectra clearly showed the distinct band gaps of g-C₃N₄ and Ti₃C₂T_x in the nano-heterostructure. The increase in PL intensity and broadening of the peak with an increase in g-C₃N₄ indicated the suppression of electron–hole recombination. Furthermore, the nano-heterostructure was used as a photocatalyst for H₂ generation from water and methylene blue dye degradation. The highest H₂ evolution (1912.25 μmol/0.1 g) with good apparent quantum yield (3.1%) and an efficient degradation of MB were obtained for gCT-0.75, which was much higher compared to that of the pristine materials. The gCT-0.75 nano-heterostructure possessed a high surface area and abundant vacancy defects, facilitating the separation of charge carriers, which was ultimately responsible for this high photocatalytic activity. Additionally, TRPL clearly showed a higher decay time, which supports the enhancement in the photocatalytic activity of the gCT-0.75 nano-heterostructure. The nano-heterostructure with the optimum concentration of g-C₃N₄ formed a hetero-junction with the linked catalytic system, which facilitated efficient charge carrier separation also responsible for the enhanced photocatalytic activity.

Received 27th October 2023
Accepted 15th November 2023

DOI: 10.1039/d3ra07321a

rsc.li/rsc-advances

1. Introduction

The excessive use of fossil fuels satisfies the energy demand in society but simultaneously generates significant pollution in the ecosystem, and also results in the depletion of fossil fuel reserves. Consequently, this excessive usage will totally deplete fossil fuel reservoirs in the near future. Thus, to keep the ecosystem pollution free together with the availability of an ample amount of useful energy, the search for alternative energy sources was initiated. To address the above-mentioned issues, research in the area of solar energy emerged and newer technologies have also been developed to harvest solar energy in useful form.¹ The most important way to harvest solar energy is the use of photovoltaic technology, which directly

converts solar energy into electricity. However, photovoltaic technology requires the development of highly efficient solar cells. Alternatively, a major way to harvest solar energy is the use of the photocatalysis technique where solar energy is also utilized to generate hydrogen *via* water splitting over semiconductor oxides or sulphides.^{2,3} Thus, to increase the efficiency of H₂ generation *via* photocatalytic water splitting, many researchers have focused their research on tuning the band gap of semiconductors for the maximum absorption of solar light and also techniques for the separation of photo-generated charge carriers.^{4–6} However, due to the weak visible-light absorption and quick charge recombination of a single semiconductor, it shows low photocatalytic efficiency. Therefore, the creation of heterojunctions, metal/cationic doping, and coupling co-catalysts have been proposed to increase the photocatalytic activity of semiconductors. In this case, numerous substances, including graphene, carbon nanotubes, graphitic carbon nitride, carbon quantum dots, and noble metals, have been utilised as co-catalysts to improve the photocatalytic efficiency.^{7,8} However, it is essential to identify effective and affordable catalytic systems to improve their photocatalytic efficiency for commercial applications.^{9,10}

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ra07321a>


Recently, many researchers have reported the properties of two-dimensional (2D) graphene, serving as inspiration for the development of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$)-based photocatalysts. Due to the unique physicochemical characteristics of its 2D structure, 2D $g\text{-C}_3\text{N}_4$ shows benefits compared to conventional bulk $g\text{-C}_3\text{N}_4$ such as a large surface area, a short charge diffusion route, and a large number of active sites.^{11–14} Single or few-layer $g\text{-C}_3\text{N}_4$ nanosheets with high photocatalytic performance have been fabricated using liquid or thermal exfoliation techniques. Wu *et al.* reported that graphene-like $g\text{-C}_3\text{N}_4$ nanosheets have a large specific area and quick charge transport capabilities, resulting a greater hydrogen evolution rate than bulk $g\text{-C}_3\text{N}_4$.¹⁵ However, after the photocatalytic process, it is challenging to recycle the tiny $g\text{-C}_3\text{N}_4$ nanosheets from the suspension. Further, during the photocatalytic process, 2D $g\text{-C}_3\text{N}_4$ nanosheets have a tendency to stack together, resulting in a reduction in their photocatalytic performance.^{16–19} This problem can be solved by creating composite catalytic systems with other materials, which can also form heterostructures, resulting in efficient charge transport ability.^{20–23} Dong *et al.* reported the assembly of 2D $g\text{-C}_3\text{N}_4$ into a 3D interconnected porous network, which harvested abundant photons owing to the multireflection inside the 3D-linked structure.²⁴

Recently, MXenes, a unique family of 2D layered transition metal carbides, carbonitrides and nitrides, have received attention for the development of coupled catalytic systems. The synthesis of Ti_3C_2 was first reported in 2011 by Gogotsi *et al.*,²⁵ and soon after, many researchers reported the synthesis and properties of layered materials such as Ti_3C_2 . For the synthesis of MXenes, the selective etching of the 'A' layers from the MAX phases ($\text{M}_{n+1}\text{X}_n\text{T}_x$) is frequently performed. The primary group of IIIA and IVA elements is represented by the letter 'A'.^{26,27} $\text{M}_{n+1}\text{X}_n\text{T}_x$ is the general formula for MXene, where M is a transition metal (Sc, Ti, Cr, Mo, Ta, Zr, Nb, Hf, V, and Nb) element, X denotes C and/or N, and T_x denotes surface terminations such as $-\text{F}$, $-\text{O}$, and $-\text{OH}$, and n is 1, 2, or 3.^{28,29} Due to the presence of hydroxy groups or terminal oxygen species on their surfaces, MXene materials show similar conductivity toward transition metal carbides.^{30–34} Furthermore, considering the conducting behaviour and layered structure of MXenes, they will be good co-catalysts for the development of coupled catalysts to separate photogenerated charge carriers efficiently.

In this regard, herein, we synthesized an MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) from the MAX (Ti_3AlC_2) phase and prepared nano-heterostructures of a $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composite with different proportions. These nano-heterostructures were characterised thoroughly and utilized for photocatalytic H_2 generation *via* water splitting. It is noteworthy that the nano-heterostructures demonstrated excellent H_2 evolution under UV visible light.

2. Experimental

2.1 Materials

Titanium aluminium carbide powder MAX (Ti_3AlC_2) (99.8%) was supplied commercially by Aritech Chemazone Private Limited. Hydrofluoric acid (HF, 48% AR/ACS) and melamine

were provided by Loba Chemicals Ltd. PVDF filter paper was procured from Microgram Ltd. All chemicals were utilized as received without further purification.

2.2 Synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$

MXene was synthesised from MAX (Ti_3AlC_2) *via* HF etching approach.^{35,36} For this purpose, 20 mL of 48% aqueous HF solution was transferred to a 100 mL Teflon beaker. Subsequently, 1 g of Ti_3AlC_2 powder was slowly added to the beaker (up to 30 min) and stirred for 24 h at room temperature. The resulting solution was centrifuged at 3500 rpm to yield a $\text{Ti}_3\text{C}_2\text{T}_x$ slurry. This slurry was washed several times with deionized (DI) water, and then filtered with a 0.22 μm pore size polyvinylidene difluoride (PVDF) filter paper. Subsequently, the resulting powder ($\text{Ti}_3\text{C}_2\text{T}_x$) was dried in a vacuum oven at 80 $^\circ\text{C}$ for 24 h. The dried powder was obtained and identified as MXene ($\text{Ti}_3\text{C}_2\text{T}_x$).

2.3 Synthesis of $g\text{-C}_3\text{N}_4$

For the synthesis of $g\text{-C}_3\text{N}_4$, melamine was kept in a crucible with a lid and heated at 550 $^\circ\text{C}$ for 4 h in a muffle furnace at the heating rate of 5 $^\circ\text{C min}^{-1}$. After natural cooling, the obtained material was finely ground using an agate mortar and pestle. For 1 g melamine, 0.3 g $g\text{-C}_3\text{N}_4$ was obtained, *i.e.*, almost 30% yield. Accordingly for the synthesis of $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$, we employed an excess amount of melamine so to get the desired wt% composite material.

2.4 Synthesis of $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites

For the synthesis of $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites, different amounts of melamine (100, 75, 50, 25, and 5 wt%) were mixed with 0.5 g of $\text{Ti}_3\text{C}_2\text{T}_x$ using a mortar and pestle, and then heated at 550 $^\circ\text{C}$ for 4 h in a muffle furnace at a heating rate of 5 $^\circ\text{C min}^{-1}$ under an N_2 atmosphere. The in situ-formed composites were denoted as gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 for $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ with ratios of 1 : 1, 0.75 : 1, 0.5 : 1, 0.25 : 1 and 0.05 : 1, respectively. This process is schematically shown in Fig. 1.

2.5 Characterization

The prepared $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ composites were analysed using various techniques. X-ray diffraction was conducted using

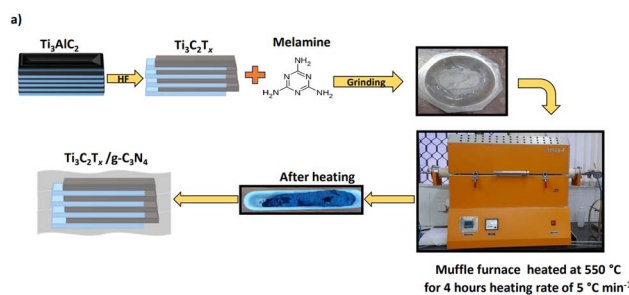


Fig. 1 Schematic process for the synthesis of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) from MAX (Ti_3AlC_2) phase and $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nano-heterostructure.



a Bruker D-8 Advance equipped with an Ni-filtered Cu target, having Cu-K α radiation with a wavelength of 1.5418 Å, in the 2θ range of 5–80° at a scan rate of 1° min^{−1}. Field emission scanning electron microscopy (FE-SEM, HITACHI 4800) was used to examine the surface morphology. Field-emission TEM (FE-TEM) and selected area electron diffraction (SAED) were also recorded using a JEOL JEM-2200 FS at an operating voltage of 200 kV. To analyse the chemical states of the atoms and the composition of the surface elements, X-ray photoelectron spectroscopy (XPS) measurement was performed using an ESCALAB 250 (Thermo Electron, Al K α) spectrometer. A Shimadzu UV-Vis-NIR spectrophotometer (Model UV-3600) was used to record at the room temperature diffuse reflectance UV-visible spectra in the wavelength range of 200 to 800 nm. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301pc spectrofluorophotometer. Further, time-resolved photoluminescence (TRPL) experiments were performed using a photoluminescence Horiba model spectrometer with an xenon arc lamp. Fourier transform infrared (FTIR) spectroscopy was recorded in transmittance mode using a Shimadzu FTIR spectrometer in the range of 500–4000 cm^{−1}. The specific Brunauer–Emmett–Teller (BET) surface areas of the samples were determined using (Quanta chrome NOVA touch LX1) N₂ adsorption isotherms at liquid N₂ temperature. Prior to the BET analysis, the samples were degassed under vacuum for two hours at 150 °C.

2.6 Photocatalytic activity measurement

2.6.1 Photocatalytic H₂ generation. To check the photocatalytic activity of the prepared nanostructures for H₂ generation *via* water splitting, we used a 100 mL cylindrical quartz vessel and 400 W mercury vapor lamp. To measure the photocatalytic activity, 25 mL of distilled water was added to a quartz reactor containing 20 mg of prepared catalyst having 1 wt% preloaded Pt as a co-catalyst. To this mixture, 5 mL of methanol was added as a sacrificial reagent. To remove the dissolved gases, UHP grade N₂ was bubbled for 10 min in the reaction mixture, which was later sealed with a septum. The sealed quartz reactor with septum was stirred under a 400 W mercury vapour lamp. After a certain duration, 500 µL of the generated gas was removed from the reactor using a gas-tight syringe, and the amount of H₂ gas was measured using a gas chromatograph (Shimadzu: Model GC 2014) equipped with a 5 Å molecular sieve column. The standard fitted curve was used to calculate the amount of hydrogen gas produced. The same experimental procedure was also used to conduct catalyst recycling investigations.

2.7 Photocatalytic MB dye degradation

We utilised our previously described technique for the photocatalytic dye degradation studies.^{83,84} In a 150 mL conical flask, 50 mg of the prepared catalyst (Ti₃C₂T_x) was dispersed in 100 mL of 10 ppm methylene blue (MB) solution (10 ppm MB, pH = 7) and stirred for 15 min at room temperature in the dark to achieve adsorption–desorption equilibrium. Next, the conical flask containing catalyst and MB solution was stirred under

a 400 W mercury vapour lamp kept vertically in a quartz condenser having a water circulation arrangement to minimize the heating effect. The whole reaction set-up was fixed in a closed wooden box. Aliquots of the aqueous solution were removed from the flask at predetermined intervals, centrifuged, and the UV-visible absorption spectra of the clear solutions recorded using a double-beam UV-visible spectrophotometer. The decrease in absorbance at the wavelength of 664 nm was employed to determine the extent of MB degradation as a function of time. To calculate the % of MB degradation, the maximum absorbance value at the wavelength of 664 nm was employed. The % MB degradation was quantified using eqn (1), as follows

$$\% \text{ MB degrades} = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

where C_0 is the initial concentration of MB and C_t is the concentration of MB after irradiation time ' t '.

3 Results and discussion

3.1 XRD analysis

The crystal structure and phase of the synthesized nano-heterostructures were examined by XRD (Fig. 2). The XRD patterns of MAX (Ti₃AlC₂) show prominent peaks, similar to the previous report.³⁷ After the chemical exfoliation of MAX with HF, a decrease in the intensity of the peak at the 2θ of 38.8° was observed, indicating the complete removal of Al from MAX and formation of MXene (shown as Ti₃C₂T_x).^{38–40} Further, the (002) and (004) planes corresponding to the peaks at $2\theta = 8.7^\circ$ and 18.1° of Ti₃C₂T_x shifted to a lower angle due to the increase in the interlayer spacing of Ti₃C₂T_x, indicating that Ti₃AlC₂ was successfully converted into Ti₃C₂T_x.⁴¹

The XRD pattern of the g-C₃N₄ nanosheets shows two typical diffraction peaks at 12.2° and 27.8°, corresponding to the (100) plane with in-plane structural packing motif and (002) plane of interplanar stacking with conjugated aromatic segments, respectively.⁴² Furthermore, the formation of composites

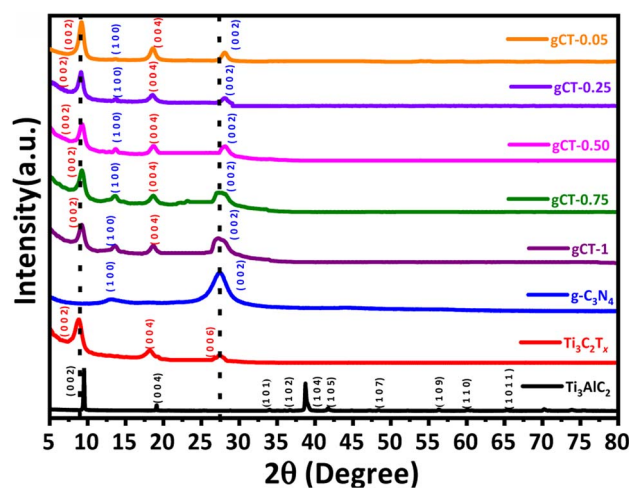


Fig. 2 XRD patterns of Ti₃AlC₂, Ti₃C₂T_x, g-C₃N₄, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 nano-heterostructures.



between MXene and $g\text{-C}_3\text{N}_4$ was confirmed by XRD. It was observed that the peak intensity of $g\text{-C}_3\text{N}_4$ decreased with a decrease in the concentration of $g\text{-C}_3\text{N}_4$. The broad peak at 27.5° validates the presence of $g\text{-C}_3\text{N}_4$ together with $\text{Ti}_3\text{C}_2\text{T}_x$ (28.2°), confirming the formation of nano-heterostructures of $g\text{-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ with different weight ratios.

3.2 Morphological studies

Field-emission scanning electron microscopy was used to examine the surface morphology of $\text{Ti}_3\text{C}_2\text{T}_x$, $g\text{-C}_3\text{N}_4$ and its composite gCT-0.75 (Fig. 3). After the selective removal of Al from MAX (Ti_3AlC_2) by etching with HF, the formation of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) was observed, having a perfect accordion-like morphology. It showed layers with a thickness of around 90–140 nm (Fig. 3a and b),^{43,44} which were stacked periodically. In contrast, we observed wavy layers in the image of the pristine $g\text{-C}_3\text{N}_4$ (Fig. 3c and d), which were quite difficult to quantify.^{45,46} Further, the presence of $g\text{-C}_3\text{N}_4$ together with $\text{Ti}_3\text{C}_2\text{T}_x$ was observed with a uniform distribution in the nano-heterostructure, gCT-0.75 (Fig. 3e and f). This validates the *in situ* formation of a nano-heterostructure between $g\text{-C}_3\text{N}_4$ and $\text{Ti}_3\text{C}_2\text{T}_x$ with a weight ratio 0.75 : 1 (gCT-0.75). The FESEM images of gCT-1 (Fig. 3g and h), gCT-0.50 (Fig. 3i and j), gCT-0.25 (Fig. 3k and l) and gCT-0.05 (Fig. 3m and n) are shown in the ESI (Fig. S1†), also confirming the formation of heterostructures between $g\text{-C}_3\text{N}_4$ and $\text{Ti}_3\text{C}_2\text{T}_x$.

3.3 FE-TEM

Fig. 4 shows the field-emission and high resolution transmission electron microscopy images of gCT-0.75. The FE-TEM images (Fig. 4a–d) of the gCT-0.75 nano-heterostructure

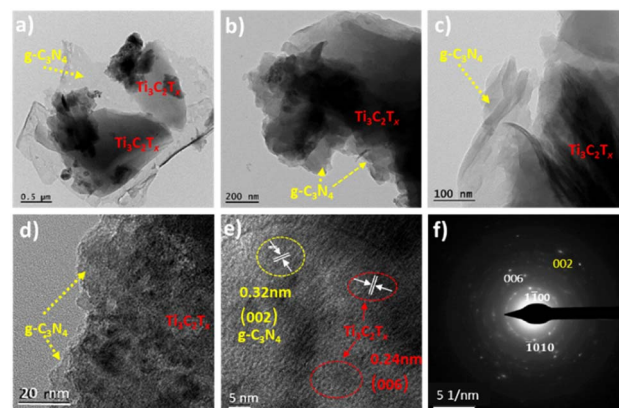


Fig. 4 FE-TEM (a–c) and HRTEM (d and e) images and selected area electron diffraction pattern (SAED) (f) of gCT-0.75.

depicts the formation of a 2D layered morphology of nano-sheets, confirming the formation of a nano-heterojunction between $g\text{-C}_3\text{N}_4$ and $\text{Ti}_3\text{C}_2\text{T}_x$.^{47–49} The HRTEM images indicate that the interplanar spacing in the gCT-0.75 sample is around 0.24 nm and 0.32 nm, corresponding to the (006) and (002) planes of $\text{Ti}_3\text{C}_2\text{T}_x$ and $g\text{-C}_3\text{N}_4$, respectively (Fig. 4e).^{50–52} This image authenticates the formation of a nanocomposite between $g\text{-C}_3\text{N}_4$ and MXene. The SAED (Fig. 4f) pattern also confirms the existence $\text{Ti}_3\text{C}_2\text{T}_x$ together with $g\text{-C}_3\text{N}_4$ and supports the XRD results. Overall, the HRTEM images indicate the presence of $g\text{-C}_3\text{N}_4$ and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

3.4 XPS

The chemical composition and oxidation state of the $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-0.75 and $g\text{-C}_3\text{N}_4$ samples were determined using XPS. As shown in Fig. 5 and the ESI (Fig. S2†), Ti, C, O, F and N elements were detected in the XPS survey spectra of the $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-0.75 (Fig. S2a†) and $g\text{-C}_3\text{N}_4$ (Fig. S2c†) samples. The Ti, C, O, F and N elements were further investigated by XPS (Fig. 5 and S2†). The Ti 2P spectrum (Fig. 5a) was fitted with four doublets of $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ with an area ratio of 2 : 1 and doublet separation of 5.8 eV. The $\text{Ti } 2p_{3/2}$ spectrum exhibits primary deconvoluted peaks centred at 454.6, 455.4, 456.3, 459.1, 461.5 and 464.9 eV, corresponding to Ti-C , Ti^{2+} , Ti^{3+} , Ti-O , C-Ti-T_x and $\text{TiO}_2\text{-xF}_x$, respectively, which indicate the presence of $\text{Ti}_3\text{C}_2\text{T}_x$ in the $g\text{-C}_3\text{N}_4$ -0.75 sample, in agreement with the previous report.⁵³ The C 1s spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 5b) exhibited five distinct peaks at 281.6, 284.4, 285.0, 286.1 and 288.4 eV, which are assigned to the C-Ti , C-Ti-T_x , C-C , $\text{CH}_x\text{-COO}$ and C-F/COO bonds, respectively.⁵⁴ These peaks can be ascribed to the adventitious carbon (284.6 eV). In addition, the C 1s spectrum of gCT-0.75 (Fig. 5b) exhibited four distinct peaks at 281.0, 284.5, 286.8 and 287.8 eV, corresponding to C-Ti , C-C , C-N=C and N-C=N , which clearly indicate the presence of $g\text{-C}_3\text{N}_4$ in the gCT-0.75 sample.^{41,55} The N 1s spectrum of gCT-0.75 (Fig. S2b†) exhibited three distinct peaks at 397.9, 398.8 and 400.2 eV, corresponding to the C-N=C , N-(C)_3 and C-N-H bonds, respectively.⁵⁶ The O 1s spectrum (Fig. 5c) exhibited four peaks at 529.9, 530.7, 531.8 and 533.2 eV, which are assigned to TiO_2 , Ti-O_x , Ti-OH and Ti-

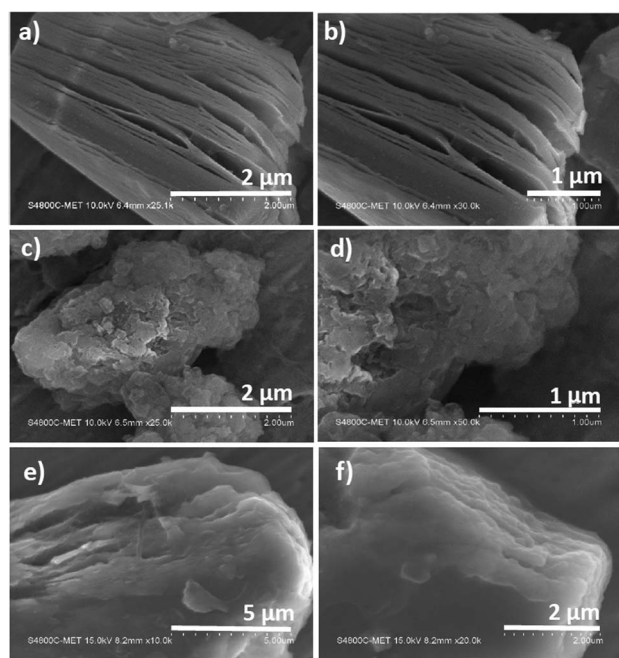


Fig. 3 FE-SEM of $\text{Ti}_3\text{C}_2\text{T}_x$ (a and b), $g\text{-C}_3\text{N}_4$ (c and d) and gCT-0.75 (e and f).



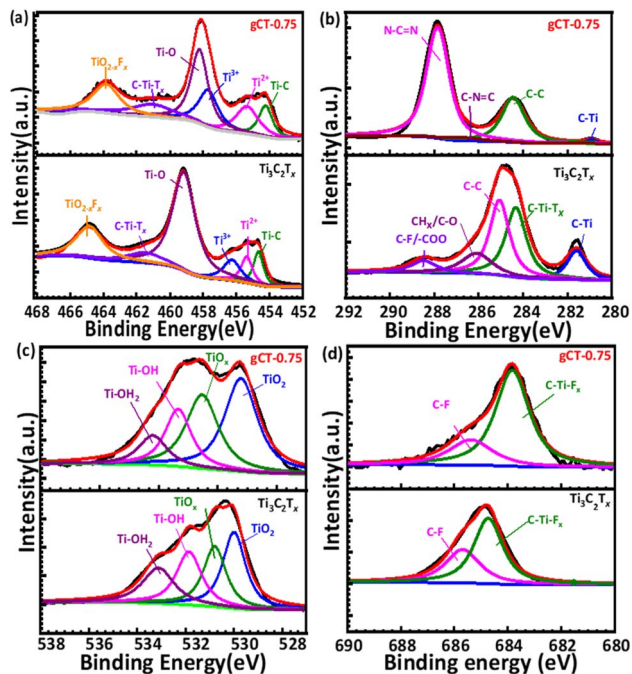


Fig. 5 XPS peak deconvolution of Ti 2p (a) C 1s (b) O 1s (c) and F 1s (d) for $\text{Ti}_3\text{C}_2\text{T}_x$ and gCT-0.75.

H_2O , respectively.⁵⁷ The peak at 531.4 eV shows the presence of -OH groups on the surface (formation of Ti-OH bond) of the gCT-0.75 sample. In the F 1s spectrum (Fig. 5d), the dominant peak located at 685.7 eV corresponds to the C-F species, while the peak at the lower binding energy of 684.7 eV corresponds to C-Ti-T_x from $\text{Ti}_3\text{C}_2\text{T}_x$.⁵⁸ The C 1s spectra of the g- C_3N_4 sample shown Fig. S2d† exhibit three carbon species at 284.2, 286.8 and 287.8 eV, which are assigned to the adsorbed carbon species (C-C) on the g- C_3N_4 surface, sp^2 -hybridized carbon in the triazine rings (C-N=C) and N-containing aromatic ring (N-C=N), respectively. The carbon in N-C=N is considered as the major carbon species in the g- C_3N_4 nanosheets.⁵⁶ Three peaks were observed in the N 1s spectrum (Fig. S2e†), and the peaks located at binding energies of 398.2, 399.1, and 400.5 eV can be assigned to the sp^2 -hybridized nitrogen involved in the triazine rings (C-N=C), tertiary nitrogen N-(C)₃ groups, and free amino groups (C-N-H), respectively^{41,58} (XPS, ESI Table S1†). Overall, the presence of peaks at 286.1 eV and 286.8 eV corresponds to $\text{CH}_x/\text{C-O}$ and C-N=C, respectively. Also, the increase in the intensity of the peak at 287.8 eV corresponding to N-C=N indicates the formation of the g- $\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nano-heterostructure (gCT-0.75).

3.5 FTIR

Fig. S3† shows the FTIR spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, g- C_3N_4 , gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05. MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) does not show any peaks corresponding to C-C or C-Ti bonds.⁵⁹ Further, g- C_3N_4 shows a vibration peak at 810 cm^{-1} , corresponding to the symmetric stretching of the triazine unit, and peaks in the range of 1200 cm^{-1} to 1650 cm^{-1} , which are ascribed to heterocyclic C-N and C=N, respectively.^{60,61} The g-

$\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nano-heterostructure shows a peak at 810 cm^{-1} with a slight shift in the range of $790\text{--}810\text{ cm}^{-1}$, which indicates the formation of a nano-heterostructure between g- C_3N_4 and $\text{Ti}_3\text{C}_2\text{T}_x$.

3.6 Optical characterization

3.6.1 UV-visible analysis. The UV-Visible diffuse reflectance spectra (UV-vis DRS) of the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and nano-heterostructure are shown in Fig. 6a. $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits an absorbance with a wide surface plasmon resonance (SPR) peak extending from 450 to 700 nm and centred at 670 nm. This SPR peak centred at 670 nm corresponds to $\text{Ti}_3\text{C}_2\text{T}_x$. The pristine g- C_3N_4 has an absorption band at about 460 nm. All the composites of g- $\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ showed an extended absorption compared to the pure g- C_3N_4 nanosheets. The absorbance of the g- $\text{C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nano-heterostructure gradually increased between 360 and 720 nm as the content of g- C_3N_4 decreased.^{41,62} All the prepared nano-heterostructures exhibited a greater absorbance compared to the pristine g- C_3N_4 . This enhanced absorbance will help to capture a greater number of photons, resulting in the formation of more electron-hole pairs. Further, the formed heterojunction will also facilitate effective charge separation, resulting in a higher photocatalytic performance.^{63–65} The optical band gap energies of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$, g- C_3N_4 , gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 were calculated using the Tauc plot, as shown in Fig. 6b, and the band gap values are listed in Table 1. The Tauc plot made it evident that two separate band gap values for gCT-1 and gCT-0.75 were formed, indicating the formation of a nano-heterostructure between g- C_3N_4 and $\text{Ti}_3\text{C}_2\text{T}_x$.

3.6.2 Photoluminescence (PL) spectroscopy. Photoluminescence spectra were recorded by dispersing 1 mg of prepared composite in 10 mL of DI water and sonicating it for

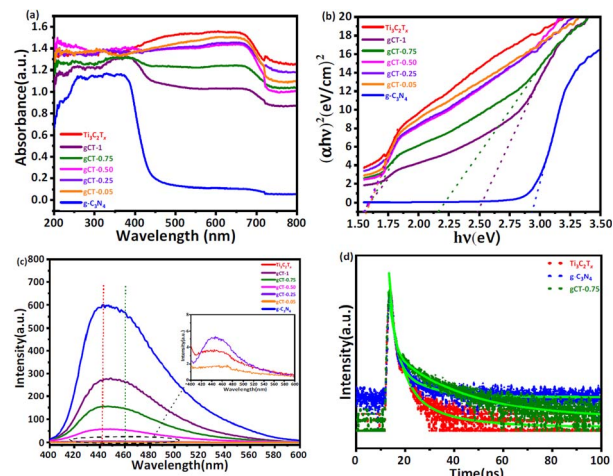


Fig. 6 (a) Diffuse reflectance UV-visible absorbance spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, g- C_3N_4 , gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05. (b) Tauc plots of $\text{Ti}_3\text{C}_2\text{T}_x$, g- C_3N_4 , gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05. (c) Photoluminescence spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, g- C_3N_4 , gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05. (d) Time-resolved photoluminescence spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-0.75 and g- C_3N_4 .



Table 1 The band gap, specific surface area, pore volume (BJH), and average pore radius of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 , and gCT-0.05 catalyst

S. No	Catalyst name	Band gap (eV)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume BJH ($\text{cm}^3 \text{g}^{-1}$)	Average pore radius (nm)
1	$\text{Ti}_3\text{C}_2\text{T}_x$	1.57	9.1	0.0346	1.69
2	$\text{g-C}_3\text{N}_4$	2.93	55.7	0.3028	10.69
3	gCT-1	1.54, 2.45	10.4	0.0403	7.07
4	gCT-0.75	1.56, 2.16	16.7	0.0635	7.75
5	gCT-0.50	1.56	8.8	0.0198	6.43
6	gCT-0.25	1.55	5.7	0.0179	4.81
7	gCT-0.05	1.58	3.8	0.0185	2.13

15 min. The pristine $\text{g-C}_3\text{N}_4$ showed the highest emission peak centred at 442 nm, corresponding to the band edge emission.^{66,67} As the concentration of $\text{g-C}_3\text{N}_4$ increased, the PL intensity centred at 442 nm also increased. Fig. 6c depicts the PL spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 , and gCT-0.05 , showing a decline in intensity with a decrease in the amount of $\text{g-C}_3\text{N}_4$. The higher PL intensity of $\text{g-C}_3\text{N}_4$ indicates the formation of a large number of charge carriers, which further reduced the recombination rate by the addition of MXene. The broadening of the emission peaks may be due to the radiative emission of the electrons in $\text{Ti}_3\text{C}_2\text{T}_x$.^{68,69} The $\text{Ti}_3\text{C}_2\text{T}_x$ energy level is -0.635 V lower than that of the conduction band level of $\text{g-C}_3\text{N}_4$ (-1.165 V), which can facilitate the easy transfer of photogenerated electrons from the conduction band of $\text{g-C}_3\text{N}_4$ to $\text{Ti}_3\text{C}_2\text{T}_x$. This resulted in a red shift in the emission peak ($\sim 460 \text{ nm}$), and subsequently broadening of the emission peak of the prepared nano-heterostructure.^{70,71} This is beneficial to separate photoelectrons and holes, creating electron transfer channels.

3.6.3 TRPL study. The lifetime of the charge carriers was also determined by time-resolved PL spectroscopy, as shown in Fig. 6d, and the biexponential model function was employed (eqn (2) and (3)), as follows

$$R(t) = A_1 \exp\{-t/\tau_1\} + A_2 \exp\{-t/\tau_2\} \quad (2)$$

$$(\tau_{\text{ave}}) = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (3)$$

where A_1 and A_2 are the PL amplitudes and τ_1 and τ_2 are the decay times for the faster and slower components, respectively. The fast component (τ_1) corresponds to the direct generation of free electrons and holes, whereas the slow component (τ_2) results from the indirect formation of self-trapped excitations.^{72–74} The kinetic parameters are presented in Table S2, ESI.† The time constants for $\text{Ti}_3\text{C}_2\text{T}_x$ were evaluated to be $\tau_1 = 0.6801 \text{ ns}$ and $\tau_2 = 3.9214 \text{ ns}$, representing the electron trapping and formation time of electron-hole pairs. The time constants for $\text{g-C}_3\text{N}_4$ was evaluated to be $\tau_1 = 0.7682 \text{ ns}$ and $\tau_2 = 4.0123 \text{ ns}$, respectively. Comparatively, gCT-0.75 showed longer time constants with $\tau_1 = 0.9723 \text{ ns}$ and $\tau_2 = 4.5923 \text{ ns}$, respectively. The average lifetime (τ_{ave}) of the entire fluorescence decay process was computed using eqn (3). According to the calculations, the average lifetime (τ_{ave}) of $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-0.75 and $\text{g-C}_3\text{N}_4$ is 1.8290, 2.7656 and 1.9390 ns, respectively. It was

found that the τ_{ave} of gCT-0.75 was almost 1.5-times that of $\text{Ti}_3\text{C}_2\text{T}_x$. The longer decay time shows the trapping of electrons, *i.e.*, enhanced electron-hole separation.

3.7 Surface area analysis (using BET equation)

The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}), pore size distribution, pore volume distribution and average pore radius of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$ and their nano-heterostructure

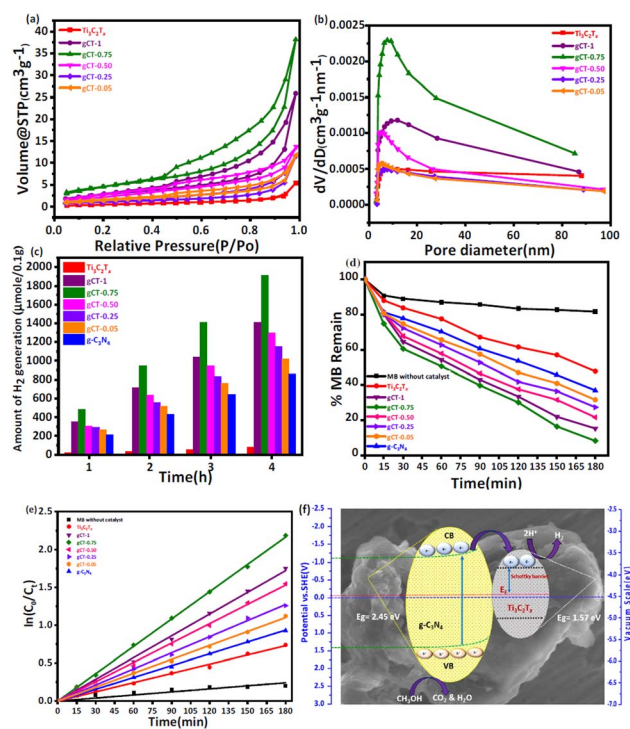


Fig. 7 (a) BET surface area using N_2 adsorption–desorption isotherms of $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 , and gCT-0.05 . (b) Pore size distributions calculated from N_2 desorption isotherms for $\text{Ti}_3\text{C}_2\text{T}_x$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 and gCT-0.05 . (c) Photocatalytic H_2 generation by $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 and gCT-0.05 as a function of time. (d) Amount of MB remaining with irradiation time using $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 and gCT-0.05 catalyst prepared at different temperatures. (e) Plots of $\ln(C_0/C_t)$ versus irradiation time for photocatalytic MB degradation using prepared $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1 , gCT-0.75 , gCT-0.50 , gCT-0.25 and gCT-0.05 catalysts. (f) Proposed mechanism of photocatalytic hydrogen evolution by $\text{Ti}_3\text{C}_2\text{T}_x/\text{g-C}_3\text{N}_4$.



are listed in Table 1. The specific surface area of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{g-C}_3\text{N}_4$ powder was measured to be $9.1 \text{ m}^2 \text{ g}^{-1}$ and $55.7 \text{ m}^2 \text{ g}^{-1}$, respectively. The measured specific surface areas of the synthesised nano-heterostructures gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 were 10.4, 16.7, 8.8, 5.7 and $3.8 \text{ m}^2 \text{ g}^{-1}$, respectively.⁷⁵ The specific surface area (SSA) was estimated using BET equation for the gCT-0.75 composite and found to be $16.7 \text{ m}^2 \text{ g}^{-1}$, which is a factor of 1.84-greater than that of the as-synthesised $\text{Ti}_3\text{C}_2\text{T}_x$ ($9.1 \text{ m}^2 \text{ g}^{-1}$). The increase in specific surface area (SSA) can be explained by the formation of a nano-heterostructure between $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{g-C}_3\text{N}_4$ nanosheets, enlarging the interlayer spacing between the MXene multilayers after increasing the content of $\text{g-C}_3\text{N}_4$ in the composite.⁷⁶ All the prepared nano-heterostructures, as shown in Fig. 7a, showed a clear hysteresis loop between the adsorption and desorption branches at relative pressures in the range of 0.4–1.0, indicating the existence of mesopores. At a relative pressure near to 1.0, the practically vertical tails indicated the existence of macropores. According to this, $\text{Ti}_3\text{C}_2\text{T}_x$ mostly consists of macropores, while the gCT-0.75 sample typically has mesopores and macropores. The BJH ($\text{cm}^3 \text{ g}^{-1}$) pore volume and average pore radius (nm) of the prepared nano-heterostructures, i.e., gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05, are shown in Table 1. The pore size distributions calculated from the nitrogen desorption branches for all the samples are depicted in Fig. 7b. The results show the presence of more mesopores in gCT-0.75 than $\text{Ti}_3\text{C}_2\text{T}_x$ (almost 4.5-times more), as well as a very close pore size distribution with a peak centred at ca. 7.5 nm. This indicates the presence of more active sites and surface area available for photocatalytic reactions.

3.8 Photocatalytic activity

Under a 400 W mercury vapour lamp, the photocatalytic performance of the prepared $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ nanostructures was evaluated by monitoring H_2 generation *via* water splitting and methylene blue (MB) dye degradation.

3.8.1 Photocatalytic H_2 generation. The photocatalytic performance of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$ and their nano-heterostructures gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 was measured using photocatalytic hydrogen production from water under UV-visible light irradiation.^{59,77} As shown in Fig. 7c, the $\text{Ti}_3\text{C}_2\text{T}_x$ sample exhibited the lowest H_2 generation of around $74.90 \mu\text{mol}/0.1 \text{ g}$ of H_2 upon 4 h of irradiation. However, the prepared nano-heterostructures with different $\text{g-C}_3\text{N}_4$ to $\text{Ti}_3\text{C}_2\text{T}_x$ ratios showed enhanced photocatalytic H_2 generation. The cumulative amounts of H_2 evolved in 4 h were 1410.21, 1912.25, 1296.23, 1150.32 and $1021.23 \mu\text{mol}/0.1 \text{ g}$ for gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05, respectively (ESI, Tables S3 and S4†). The pristine $\text{g-C}_3\text{N}_4$ nanosheets showed H_2 generation of around $860.98 \mu\text{mol}/0.1 \text{ g}$ in 4 h. Among them, gCT-0.75 exhibited the highest hydrogen evolution ($1912.25 \mu\text{mol}/0.1 \text{ g}$), which was almost 25.5-times higher than that of $\text{Ti}_3\text{C}_2\text{T}_x$ ($74.90 \mu\text{mol}/0.1 \text{ g}$). This higher photocatalytic H_2 generation by gCT-0.75 is due to the formation of a nano-heterostructure between $\text{g-C}_3\text{N}_4$ and $\text{Ti}_3\text{C}_2\text{T}_x$.⁷⁸ This formation of a nano-heterostructure led to the effective separation of

photogenerated charge carriers due to existence of the coupled catalytic system. Yuliang *et al.* reported the H_2 generation of around $88 \mu\text{mol h}^{-1} \text{ gcat}^{-1}$ using $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$.⁷⁶ In the present case, gCT-0.75 showed the highest H_2 generation of $1912.25 \mu\text{mol}/0.1 \text{ g}$ among the prepared compositions. Further, the apparent quantum yield (AQY) was also calculated and found to be 0.2%, 1.4%, 2.3%, 3.1%, 2.1%, 1.9% and 1.7% for $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25 and gCT-0.05, respectively⁷⁹ (ESI, Table S5†). In the PL study, the PL intensity decreased with a decrease in the content of $\text{g-C}_3\text{N}_4$ in the case of gCT-0.75. This clearly shows the enhancement in electron-hole separation, which is responsible for its higher photocatalytic activity. Further, the higher decay time observed in the TRPL of gCT-0.75 exhibits higher charge carrier separation, which also supports its higher photocatalytic H_2 evolution. Additionally, gCT-0.75 has a larger specific surface area (SSA), which provides a greater surface area and active sites for photocatalytic H_2 generation. The optimum concentration of $\text{g-C}_3\text{N}_4$ facilitated fast electrons transport to the surface, which ultimately suppressed the charge carrier recombination. The optimised nano-heterostructures also facilitated higher electron hole separation due to self-trapping at the interface.

3.8.2 Dye degradation. The amount of MB dye degraded with time using the prepared catalysts is depicted in Fig. 7d. Upon 3 h of irradiation, the amount of MB degradation without the use of catalyst was found to be around 18.4%. The prepared $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25 and gCT-0.05 showed 52.3%, 63.1%, 84.7%, 91.7%, 78.3%, 72.6% and 67.4% MB degradation within 3 h of irradiation, respectively. In the case of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$ and their composite, the UV-visible absorbance spectra of MB dye with irradiation time are shown in ESI, Fig. S4.† Among, the prepared catalysts, gCT-0.75 showed the highest photocatalytic activity towards MB degradation. This is because $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{g-C}_3\text{N}_4$ formed a heterojunction, which facilitated the easy separation of photo-generated electron-hole pairs, making them available for further degradation reaction. Consequently, when $\text{Ti}_3\text{C}_2\text{T}_x$ and the $\text{g-C}_3\text{N}_4$ nanosheets form a nanostructure, a linked catalytic system was created, resulting in increased photoactivity compared to the pristine material (ESI, Tables S6 and S7,† respectively). The rate constant for the photocatalytic MB degradation process was computed for the purpose of comparing the photocatalytic activity by plotting the graph of $\ln(C_0/C_t)$ against irradiation time, as shown in Fig. 7e. The apparent rate constant is shown by the slope of the graph of $\ln(C_0/C_t)$ vs. irradiation time, where C_0 represents the starting concentration of MB and C_t the concentration at time 't' (In Table 2), respectively. The observed rate constant values for the prepared $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{g-C}_3\text{N}_4$, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25 and gCT-0.05 catalysts are $4.06 \times 10^{-3} \text{ min}^{-1}$, $5.2 \times 10^{-3} \text{ min}^{-1}$, $9.58 \times 10^{-3} \text{ min}^{-1}$, $12.05 \times 10^{-3} \text{ min}^{-1}$, $8.52 \times 10^{-3} \text{ min}^{-1}$, $7.08 \times 10^{-3} \text{ min}^{-1}$ and $6.12 \times 10^{-3} \text{ min}^{-1}$, respectively. In contrast, the MB degradation without catalyst showed a rate constant value of $1.35 \times 10^{-3} \text{ min}^{-1}$. This clearly shows that the gCT-0.75 nano-heterostructure has the highest overall photocatalytic activity among the nano-heterostructures and pristine materials. The reason for the enhancement in

Table 2 The MB degradation rate and H₂ generation using Ti₃C₂T_x, g-C₃N₄, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25, and gCT-0.05 catalysts

S. no.	Catalyst	Rate constant (min ⁻¹) with standard fitting error	H ₂ generation μmol/0.1 g
1	Ti ₃ C ₂ T _x	$4.06 \times 10^{-3} \pm 0.00010709$	74.90
2	g-C ₃ N ₄	$5.2 \times 10^{-3} \pm 0.00017425$	860.98
3	gCT-1	$9.58 \times 10^{-3} \pm 0.00012244$	1410.21
4	gCT-0.75	$12.05 \times 10^{-3} \pm 0.00006253$	1912.25
5	gCT-0.50	$8.52 \times 10^{-3} \pm 0.00000981$	1296.23
6	gCT-0.25	$7.08 \times 10^{-3} \pm 0.00000798$	1150.32
7	gCT-0.05	$6.12 \times 10^{-3} \pm 0.00000730$	1021.23
8	Without catalyst	$1.35 \times 10^{-3} \pm 0.00012001$	—

photocatalytic activity was also briefed in the previous photocatalytic H₂ generation section. In summary, all the nano-heterostructures showed an enhancement in photocatalytic activity with an optimum concentration of g-C₃N₄.

We also performed *I-V* photoconductivity measurements (ESI, Fig. S5†) on all the Ti₃C₂T_x, g-C₃N₄, gCT-1, gCT-0.75, gCT-0.50, gCT-0.25 and gCT-0.05 nano-heterostructures. The highest photoconductivity was obtained for gCT-0.75, which also supports the highest photocatalytic ability of this nano-heterostructure.

3.8.3 Reaction mechanism. Among the prepared g-C₃N₄/Ti₃C₂T_x catalysts, gCT-0.75 showed the highest photocatalytic H₂ generation and MB dye degradation. A schematic of the band gap of the catalyst is shown in Fig. 7f. g-C₃N₄ showed a band gap of 2.93 eV and its conduction band (−1.165 V) level is higher than the H₂ evolution potential (1.765 V).⁸¹ The Fermi level (−0.53 V) of Ti₃C₂T_x just below the CB of g-C₃N₄ creates an easy path for the transfer of photogenerated CB electrons to the Ti₃C₂T_x level. This easy transfer minimizes the electron-hole recombination reaction, resulting in higher photocatalytic activity towards H₂ generation and MB degradation. Specifically, upon exposure to light, the electrons in the valence band (VB) of g-C₃N₄ can be excited to the conduction band (CB), generating photo-induced electrons and holes. Further, the migration rate of the photoinduced electrons may be significantly increased due to higher electronic conductivity of Ti₃C₂T_x (hopping of the electrons from the CB of g-C₃N₄ to the CB of Ti₃C₂T_x), and also the intimate contact between the Ti₃C₂T_x and g-C₃N₄ nano-heterostructure.^{41,80} Moreover, the contact between Ti₃C₂T_x and g-C₃N₄ results in the formation of a hetero-junction (at the interface).

3.8.4 Recyclability of the hydrogen generation behaviour. Ti₃C₂T_x functions as an electron acceptor and promotes the transfer of electrons from g-C₃N₄ to Ti₃C₂T_x.⁸² Consequently, the photogenerated electrons collected on Ti₃C₂T_x can reduce H⁺ to produce H₂ on its surface; meanwhile, methanol is oxidised into CO₂ and H₂O *via* the holes in the VB of g-C₃N₄. Hence, the nano-heterostructure of Ti₃C₂T_x and g-C₃N₄ can efficiently separate and transport the photo-induced electrons and holes, significantly improving the performance of the photocatalytic system.^{85,86} This enhanced activity was observed for gCT-0.75, given that this was the optimal combination of g-C₃N₄ and Ti₃C₂T_x for the formation of the coupled catalyst system among the prepared compositions, as discussed in the

previous section.⁷⁶ Furthermore, the stability and reusability of the catalyst were assessed using a recycling study of the most active sample for 3 cycles, *i.e.*, for gCT-0.75. For the hydrogen generation process, the identical catalyst was recycled three times (Fig. 8a). It was observed that the catalytic activity of gCT-0.75 did not exhibit any significant loss after the second and third cycles. After the third cycle, the amount of H₂ generated was approximately 7610.25 μmol of H₂ per 0.1 g of recycled catalyst (*i.e.*, 1912.25 μmol h⁻¹ 0.1 g⁻¹), indicating the high stability of the catalyst towards hydrogen generation.^{41,59} We did not find any structural changes in the recycled sample *via* examination by XRD (Fig. 8b), clearly indicating the good stability of the catalyst.

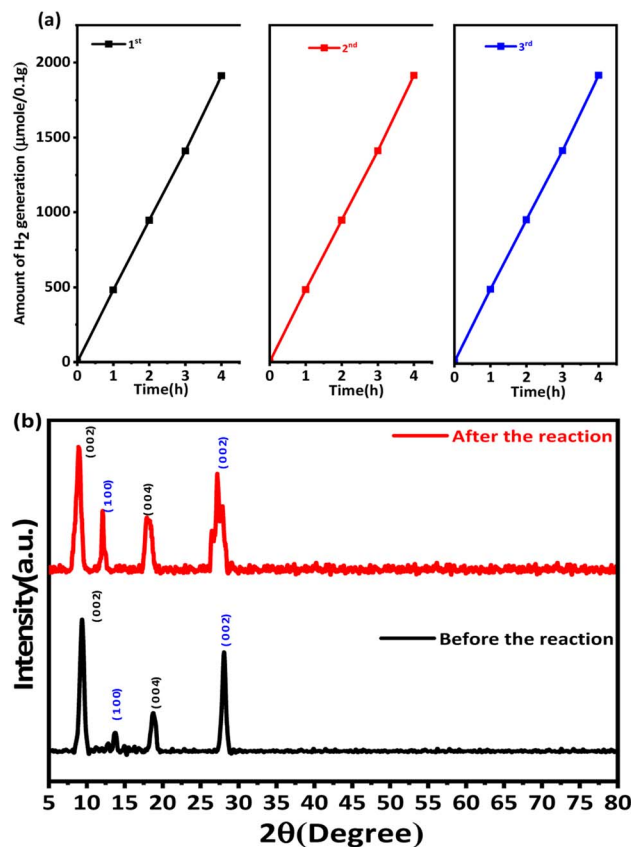


Fig. 8 (a) Recyclability of the hydrogen generation behaviour of gCT-0.75. (b) XRD patterns of gCT-0.75 before and after the photocatalytic reaction.



4. Conclusion

In summary, we demonstrated the process for the *in situ* synthesis of g-C₃N₄/Ti₃C₂T_x nanosheets, *i.e.*, nano-heterojunction. The formation of g-C₃N₄ nanolayers on the surface of MXene was confirmed by FE-SEM and HR-TEM. In comparison to the pristine Ti₃C₂T_x (74.90 μmol/0.1 g), the optimised gCT-0.75 showed a higher photocatalytic hydrogen evolution rate, which was almost 25-times higher (1912.25 μmol/0.1 g). The effective charge separation at the interface between Ti₃C₂T_x and g-C₃N₄ is the main reason for the enhanced photocatalytic performance compared to the pristine MXene. Overall, the gCT-0.75 nano-heterostructure exhibited improved photocatalytic activity due to the enhanced average lifetime of photogenerated electron-hole pairs, creation of an appropriate nano-heterostructure between Ti₃C₂T_x and g-C₃N₄, optimal surface, and suitable energy band modification. This technique shows potential for the *in situ* fabrication of other metal oxide/sulfide hetero-structure photocatalytic systems.

Author contributions

ABT performed the experimental work, material characterisation, photocatalytic performance measurements and wrote the initial draft of the manuscript. SSA given the research scheme and assisted in designing the experiment, analysed the results and modified the manuscript. GGU assisted in photo-conductivity measurements. SKK revised the manuscript and analysed the XPS data. BBK supervised the whole research work and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors are grateful to Dr Rahul Salunkhe, Assistant Professor, IIT Jammu and Dr Vinayak Kamble, Scientist, IISER, Trivandrum for XPS and TEM analysis respectively. One of the author SKK is thankful to INSA for senior scientist fellowship.

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