Crystalline \( C_3N_4/CeO_2 \) composites as photocatalyst for hydrogen production in visible light

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Abstract. Crystalline carbon nitride (C-C\( _3N_4 \)) doped with cerium oxide (CeO\( _2 \)) was synthesized using ionothermal method to increase the photocatalytic activity for H\( _2 \) production. Graphitic carbon nitride (g-C\( _3N_4 \)) obtained from direct pyrolysis of urea at 550°C was subsequently annealed with a mixture of KCl and LiCl to obtain C-C\( _3N_4 \). CeO\( _2 \) was doped onto C-C\( _3N_4 \) and g-C\( _3N_4 \) via calcination at 550°C. XRD analysis showed the formation of high intensity C\( _3N_4 \) and CeO\( _2 \) peaks in C-C\( _3N_4/CeO_2 \), meanwhile g-C\( _3N_4/CeO_2 \) only showed CeO\( _2 \) peaks. FTIR analysis confirmed all the samples contained C\( _3N_4 \) polymeric structure. The specific surface area of gC\( _3N_4 \) was measured at 61 m\(^2\)/g. The surface area increased to 92 m\(^2\)/g when g-C\( _3N_4 \) transformed into C-C\( _3N_4 \), and further increased to 106 m\(^2\)/g on C-C\( _3N_4/CeO_2 \). The photocatalytic activity for H\( _2 \) gas production showed significant increase of H\( _2 \) rate on C-C\( _3N_4/CeO_2 \) compared to g-C\( _3N_4/CeO_2 \) and g-C\( _3N_4 \). The high crystallinity and high surface area were suggested to enhance photocatalytic activity of C-C\( _3N_4/CeO_2 \) in visible light presumably due to the increase of electron and hole lifetimes.

1. Introduction

The increasing demands for energy have ultimately intensified the usage of fossil fuel, resulting in serious environmental issues cause by production of greenhouse gas (GHG). The depletion of fossil fuel and the growing environmental issues from fossil fuel consumption, have risen a concern to explore other sustainable alternative sources of energy. Hydrogen (H\( _2 \)) have created some traction as a highly efficient clean energy carrier since the combustion of hydrogen produced only water as by-product [1]. H\( _2 \) has a higher energy content (120–142 MJ kg\(^{-1}\)) compared to fossil fuels [2]. However, around 90% of global hydrogen is attained by steam reforming of fossil fuel, which yet defeats the purpose of being a sustainable source of energy [3]. Subsequently the production of green H\( _2 \) by utilizing the abundant solar energy can resolve the environmental issues and the future energy source complications [4]. One approached frequently investigated for the green energy route is photocatalytic water splitting (reaction involved: 2H\( _2O \rightarrow 2H_2 + O_2 \)). There are several advantages from this method such as using the abundant solar energy and water to produce H\( _2 \) with the help of low-cost semiconductor photocatalyst.

The development of a low-cost, sustainable and highly effective photocatalyst in visible light (>420nm) for water-splitting reaction have been investigated for over 50 years [5]. Metal oxide is considered as one of the materials well studied as semiconductor photocatalyst. TiO\( _2 \) have been intensively investigated due to its ability to produce hydrogen from water, additionally it possesses attractive quality such as being inexpensive, abundantly available and stable [6]. However, similar to other metal oxide which generally occupies a large band gap (~3.2 eV), photogeneration of energy...
carriers only taking place in ultra-violet range, hence limits the ability to fully utilizing 96% of visible light region [7]. Generation of photocatalyst to fully utilize the abundant photon energy in visible light energy would increase the efficiency and viability of production of green hydrogen energy [8].

A metal-free graphitic carbon nitride photocatalyst consisting of tri-s-triazine repeating unit, have gained considerable recognition due to the capacity to harness photon in visible region for water splitting [9]. Interestingly, g-C_3N_4 has a high thermal stability (~600˚C), a flexible electronic structure, cost effective, non-toxic, abundantly available and a lower band gap of 2.7 eV which corresponded to the 460 nm visible light region [10], [11]. Comparison to metal base photocatalysts which are only adsorbed photon in the UV region, hence g-C_3N_4 is considered a promising contender to fully utilised sunlight energy for water splitting [12]–[14]. Despite the positive features of g-C_3N_4, the performance is hampered by small specific surface area (10-15 m²g⁻¹) and high photogenerated electron-hole recombination rate [10], [15], [16]. Improving the limiting factors of g-C_3N_4 have been studied substantially. Structural modification of g-C_3N_4 would affect the activity of photocatalyst by decreasing the band gap, increasing the specific surface area and eliminating defects on the surface of g-C_3N_4 [15].

Urea is nitrogen-rich precursor commonly used to synthesis g-C_3N_4 due to the availability, inexpensive price and ability to produce large surface area. Several methods have been studied for the synthesis of g-C_3N_4 such as chemical vapour deposition [19], sol-gel method [20], hydrothermal method [21] and microwave method [22]. Thermal condensation or direct pyrolysis of nitrogen-rich precursors is one of the main method due to its simplicity and low-cost production[4], [23]. However, direct pyrolysis of urea only produced ~6% of g-C_3N_4 [17], [18]. Apart from that, bulk g-C_3N_4 synthesized from direct pyrolysis of nitrogen-containing precursors results in low crystallinity, as the consequences of incomplete deamination during thermal condensation of intermediates. Incomplete deamination increased the formation of terminal defects such as -CNH₂ and -C₂NH which acted as a recombination centres [24]. Subsequently instead of producing g-C_3N_4, they are producing melem monomers which are connected by hydrogen bond to form the tri-s-triazine-based melon structure [25]. These hydrogen bonds lead to low conductivity caused by the blocking electron conductivity of the plane [4].

To improve the thermal condensation and the crystallinity of the g-C_3N_4, ionic salts (KCl and LiCl) were used in the synthesis process referred as ionothermal method [24]. The molten salts combination was considered as suitable solvent to facilitate thermal condensation at high temperatures [26]. By improving the structure of the crystalline g-C_3N_4, the photocatalytic activity for H₂ generation in the visible light region has increased compared to the bulk g-C_3N_4 [26]. Rapid photogenerated electron-hole recombination is one of the limitations of g-C_3N_4. In order to gain optimum efficiency of photocatalyst g-C_3N_4, the electron-hole recombination needs to be deferred as long as possible for complete oxidation/reduction reaction to takes place. The alteration by doping of metal is one method to delay the electron hole recombination [27]. Metal acts as electron-hole trapping sites which effective facilitates the electron-hole separation for maximum photocatalytic activity[28], [29]. Some commonly used noble metal are Ag, Pt, Rh, Au and Pd, although this addition is beneficial to increasing the activity of photocatalyst, the material production cost would significantly increase [27].

Apart from that, the fast recombination of electron-hole can also be delayed by doping with transitional metal and metal oxide base semiconductor. These nanocomposites will create a heterojunction structure which act as a separation for the electron and hole of the photocatalyst [6]. Two common heterojunctions investigated are traditional type-II heterojunctions and Z-scheme heterojunctions. Doping cerium oxide (CeO₂) with g-C_3N_4 was predicted to improve the limitations of the photocatalyst. CeO₂ has gained popularity due their abundance, inexpensive, inert, non-toxic, high stability in absorption of photon energy, and excellent transfer of charged electron promoting electron-hole separation which would enhance photocatalytic activity [30]–[33]. The g-C_3N_4/CeO₂ composite would form a heterojunction structure supporting the separation for photogenerated electron-hole. In a heterojunction situation the photoexcited electron would move from valence band to the conduction band of g-C_3N_4, to the conduction band of CeO₂, this creates a delay of the electronhole recombination which improve the photocatalytic activity [34].
Currently there is no definitive technique of synthesizing the ideal $g$-$C_3N_4$ base photocatalytic, which resulted in various methodologies and outcomes. There is still a need to determine the right combination of semiconductor material to synthesis the best of $g$-$C_3N_4$ photocatalyst. For our research, we have focused on two main objectives. First, we aimed to improve the crystallinity of $g$-$C_3N_4$ by applying ionothermal method using the molten salts (KCl and LiCl). Secondly, we aimed to create a heterojunction structure for $g$-$C_3N_4$ by doping with metal oxide CeO$_2$. We expected the semiconductor composite to have an improved photocatalytic activity for hydrogen production in visible light region.

2. Methodology

2.1. Materials

Urea fertilizer (CO(NH$_2$)$_2$) was used as carbon and nitrogen-rich precursors. Potassium Chloride (KCl) and Lithium Chloride (LiCl) were used as the ionic solvent for preparation of crystalized carbon nitride. Cerium Oxide (CeO$_2$) was used for the doping of carbon nitride. Triethanolamine (TEAO) was used as a sacrificial agent in the H$_2$ production experiment. All chemicals were used without any purification. Distilled water was used in all experiment.

2.2. Preparation of photocatalyst

2.2.1. Preparation of bulk $g$-$C_3N_4$ ($g$-$C_3N_4$). In a typical procedure, 25 grams of urea fertilizer (CO(NH$_2$)$_2$) in a covered alumina crucible was heated to 550°C held for 3 hours with a ramping rate of 1°C/min in a muffle furnace. The powder product was collected and ground in a mortar. The obtained sample is referred as Graphitic Carbon Nitride ($g$-$C_3N_4$) and produced 6% yield.

2.2.2. Preparation of crystalized $C_3N_4$ ($C$-$C_3N_4$). 1 gram of $g$-$C_3N_4$ were grounded with 3.3 grams of KCl and 2.7 grams LiCl in a glass dish. 25 ml of distilled water was added to the powder mixture and magnetically stirred for 1 hours. The sample was poured into an alumina crucible and heated to 120°C for 2 hours in oven. Then, the mixture was heated with a covered alumina to 550°C for 3 hours at ramping rate of 1°C/min under an air atmosphere in a muffle furnace. The product was washed 3 times with boiling water and using centrifuge at 40 000 rpm for 10 minutes to collect the sediments. The product was dried at 60°C overnight. The sample obtained was referred as Crystallized Carbon Nitride ($C$-$C_3N_4$).

2.2.3. Preparation of graphitic $C_3N_4$ doped with CeO$_2$ (g-$C_3N_4$/CeO$_2$). 1 gram of $g$-$C_3N_4$ and 1 gram of CeO$_2$ were mixed and dissolved in 25 ml H$_2$O. The sample heated at 65 °C on the hot plate to evaporate water and stirred for 3 hours. The sample collected was ground with mortar and transferred to a covered alumina crucible. The mixture was heated with a covered alumina to 550°C for 3 hours at ramping rate of 1°C/min under an air atmosphere in a muffle furnace. The sample collected was ground using mortar, this sample was denoted as Graphitic Carbon Nitride Doped Cerium Oxide (g-$C_3N_4$/CeO$_2$).

2.2.4. Preparation of crystalized $C_3N_4$ doped with CeO$_2$ (C-$C_3N_4$/CeO$_2$). 1 gram of g-$C_3N_4$ and 100 mg of CeO$_2$ samples were ground with 3.3 grams of KCl and 2.7 grams LiCl in a glass dish. 25 ml of distilled water was added to the powder mixture and mixture was magnetically stirred for 1 hours. The sample was moved into an alumina crucible and heated to 120°C for 2 hours in oven. Then, the mixture was heated with a covered alumina to 550°C for 3 hours at ramping rate of 1°C/min under an air atmosphere in a muffle furnace. The product was washed 3 times with boiling water and using centrifuge at 40 000 rpm for 10 minutes to collect the sediments. The product was dried overnight at 60°C overnight. The sample obtained was referred as Crystallized Carbon Nitride Doped Cerium Oxide (C-$C_3N_4$/CeO$_2$).
2.3. **Characterization**

The crystal structural properties of the powder photocatalyst was analyzed via X-ray diffraction (XRD) on a Shimadzu XRD-7000 at a scanning rate of 20/min in the 2θ range from 10θ to 80θ. The detailed morphology and structure were investigated by high-resolution transmission electron microscopy (HRTEM) using Tecnai G2 F20 STWIN. Fourier transform infrared (FTIR) spectra were obtained using Agilent Cary 630 FTIR Spectrometer from 600 – 4000 cm⁻¹. The diffuse reflection spectra (DRS) of the samples were recorded on a UV–vis spectrophotometer using Agilent Cary 4000/5000/6000i Series UVVis-NIR. The wavelength recorded was in the range of 200 to 800 nm. The Brunauer-Emmett-Teller (BET) specific surface areas and Barret-Joyner-Halenda (BJH) pore structures were obtained via measurements from the volumetric N₂ absorption and desorption isotherms at liquid nitrogen temperatures using Micromeritics ASAP2020. The samples were degassed under vacuum at 300°C for 2 hours at the ramp of 10°C/min before measurements.

2.4. **Photocatalytic activity**

Photocatalytic activities of the photocatalysts were determined for H₂ generation under visible-light. Typically, 20 mg of catalyst powder was dispersed in a 25 ml of aqueous solution containing 10 vol.% triethanolamine (TEOA) in a 64 ml cylindrical quartz vial and covered using a rubber septum. Prior to the irradiation, the reaction suspension was magnetically stirred for 10 minutes to ensure equal dispersion of photocatalyst and purged using N₂ for 5 minutes to remove residual air in the reaction tube. The photocatalytic test was implemented under irradiation of Osram Powerstar light with UV filter providing visible light irradiation. At 30 minutes intervals, 0.5 ml of the gas suspension was collected by gas syringe and analyzed via a gas chromatography, Shimadzu GC-2014 with a thermal conductive detector (TCD).

3. **Result and Discussion**

3.1. **Physiochemical Properties**

3.1.1. **XRD analysis.** The X-ray diffraction analysis in figure 1 shows all the carbon nitride samples and CeO/C₃N₄ composites. g-C₃N₄ appears to have two different peaks at 13.4˚ and 27.7˚ indicating successful synthesis of carbon nitride by thermal polymerization of urea (JCPDS 87–1526) [35]. The minor diffraction peak at 2θ = 13.4˚ was indexed to (100) plane of tri-s-triazine unit in-planar structural packing motif [36], [37]. The dominant diffraction peak at 2θ = 27.7˚ is the characteristic interlayer staking of aromatic ring system repeating units of that correspond to (002) plane. This corresponds with the d-space of 3.22 Å with an interlayer spacing distance of 0.323 nm [38], [39]. In previous research the dominate peak of g-C₃N₄ was ascribed as 27.4˚, the slight shift from 27.4˚ to 27.7˚ indicates the sample has a shorter interlayer spacing distance hence the aromatic ring stacks are denser due to higher polymerization [8], [18].
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Figure 1. XRD pattern of g-C₃N₄, C-C₃N₄, g-C₃N₄/ CeO₂ and C-C₃N₄/ CeO₂. The asterisk (*) denotes the peak that represents CeO₂ peaks.

When g-C₃N₄ was treated with molten salts, the resulting peaks showed the main peak shift to 26.8° and 28.0°, while the minor peak shifted to 12.2° which corresponded to the intercalation of K⁺ ion in the plane. The use of molten salts decreased the overall peak intensity of C-C₃N₄. However, the appearances of different crystalline planes suggested the formation of other crystalline structure. New peaks were visible at 21.0°, 24.7° and 32.5°. The main diffraction peak at 2θ = 26.8° is considered to be in a nematic-discotic phase, similarly it is the interlayer staking that corresponds to (002) plane [26]. The peak shifted have resulted in the enlargement of the interlayer stacking distance of the C₃N₄ nanosheet at 0.336 nm [40]. Interestingly another peak ascribed to the (002) plane appears in C-C₃N₄, the diffraction peak shifted to a higher angle at 2θ = 28.0° have led to the decreased of interlayer distance to 0.317 nm, presenting a denser and tighter packing layer of C₃N₄ nanosheet [41]. The coexisting of both peaks represents a slight undulation of the layer of C₃N₄ nanosheet hence producing two interlayer stacking distance, which suggest a mixture of both crystalline and amorphous structure in C-C₃N₄. The minor diffraction peak at 2θ = 12.2° corresponding to the (100) plane, represent the interplanar structural packing motif. The shift to a lower angle may indicate smaller tri-s-triazine units hence increasing the interplanar distance to 0.73 nm.

When CeO₂ was added into g-C₃N₄, the peaks corresponded to g-C₃N₄ observed at 13.4° and 27.4° was not visible due to low intensity compared to CeO₂ peaks in g-C₃N₄/ CeO₂. The peak associated with CeO₂ with the respective crystal planes were observed at 28.4° (111), 33.1°(200), 47.4°(220), 56.3°(311), 59.1°(222), 69.8°(400), 75.6°(331), 79.0°(420) (JCPDS 34-0394) [34]. The XRD of g-C₃N₄/ CeO₂ indicate the present of higher number of amorphous g-C₃N₄ structure in catalyst when obtained via direct calcination. Without the addition of molten salts, there is an increased possibility of thermal decomposition of g-C₃N₄. Decomposition of g-C₃N₄ led to formation of defects which act as a recombination site and reduced specific surface area hence detrimental towards photocatalytic activity of g-C₃N₄/ CeO₂ [8]. When C-C₃N₄/ CeO composite was prepared using molten salt method, the peaks corresponded to C-C₃N₄ were still visible at 12.2°, 21.0°, 24.4°, 26.8° and 32.24°. Significantly low intensity of peak corresponding to CeO₂ was also observed at 28.7°, 47.2° and 56.2° indexed to (111), (220) and (311), respectively.
3.1.2. Transmission electron microscope (TEM) analysis. The synthesis of C-C₃N₄/CeO₂ using ionothermal method by utilizing molten salts (KCl and LiCl) was expected to enhance the polymerization process hence increasing its crystallinity. From the XRD result, multiple crystalline peaks were revealed in C-C₃N₄/CeO₂, therefore further investigation in order to understand the morphological structure was performed using transmission electron microscope.

![Figure 2. TEM images of C-C₃N₄-CeO₂](image)

(a) C₃N₄ nanorods can be observed (b-d) 5-50 nm sized agglomerated cluster of CeO₂ nanoparticles was observed on C₃N₄ (e) the interlayer stacking distance ranges from 0.333-0.329 nm were attributed to the (002) plane of C₃N₄, the interlayer distance of 0.275 nm was assigned to the (200) plane of CeO₂ (f) lattice spacing of 0.324 nm were assigned to the (111) plane and lattice spacing of 0.199 nm were assigned to the (220) plane of 2θ = 47.5°, both representing CeO₂ structure. (CeO₂ structure was shown in green (*) and C₃N₄ was shown in yellow)

At the lower magnification on figure 2 (a)-(d) it is observed that C-C₃N₄/CeO₂ consisted of large nanorods of C-C₃N₄ and agglomerated CeO₂ on C-C₃N₄. The CeO₂ is not evenly distributed on the C-C₃N₄ surface and show sign of agglomeration. The metal oxide was not dispersed homogeneously on the surface of C-C₃N₄, suggesting although the heterojunction structure is established, the efficiency may be slightly reduced. This may affect the photocatalytic activity of C-C₃N₄/CeO₂.

On further investigation at a higher magnification in figure 2 (e), two distinct structures attributed to C₃N₄ were perceived. The 2D layers of conjugated sheet of tri-s-triazine specifies the interlayer stacking distance of 0.329 nm – 0.333 nm, and corresponds to the (002) plane of 2θ = 26.6° denoted as C₃N₄ structure [42]. Apart from that, the amorphous structure of C₃N₄ was also observed which displayed as a corrugated structure [30]. It was suggested that the formation of amorphous structure responsible to the reduction of XRD peak intensity for (100) and (002) planes of C₃N₄. Structures identified as CeO₂ were observed in figure 2 (e-f). CeO₂ displayed a varied interlayer spacing which corresponds with their XRD peaks. The interlayer spacing of 0.275 nm was attributed to the (200) plane of 2θ = 31.3°, while interlayer spacing of 0.324 nm were assigned to the (111) plane of 2θ = 28.6° and interlayer spacing of 0.199 nm were assigned to the (220) plane of 2θ = 47.5° which representing CeO₂. The amorphous
structure of C₃N₄ and the agglomeration of CeO₂, displayed a disorganized structure of C-C₃N₄/CeO₂, which led to the lower intensity of crystalline peak at (002) plane in XRD analysis.

There is an abundance of porous structure of C-C₃N₄ due to the higher polymerization thus increase the surface area and the available active sites for photoreaction to occur [43] [44]. The layered structure provide pore channels that promotes the mobility for photogenerated charges and provide abundant photoreaction sites for the production of electron hole pairs [26]. The exfoliation of layered C-C₃N₄ sheet is considered beneficial as it increase the specific surface area and reduces the transport distant for charged electrons, this can be achieved by enhancing the polymerization [18]. The HRTEM analysis showed a varied structure for C-C₃N₄ and CeO₂, which was supported by the XRD analysis. The addition of molten salts in the calcination process have given rise to new crystalline peaks, which can be interpreted as the present of multiple different structure C-C₃N₄ and CeO₂.

3.1.3. BET isotherm plot. The nitrogen adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore-size distributions curve of all catalyst are shown in figure 3. According to the adsorptiondesorption isotherms BDHT classification, all samples exhibit type III isotherm. The samples exhibit type H3 hysteresis loop according to IUPAC classification which is associated with slit-shaped pores present in the aggregated of sheet-like particles, complying to the morphology of C₃N₄ [38]. Different precursors such as melamine, dicyanamide and urea would produce different morphology features of C₃N₄, it was concluded that urea produce the larger specific surface area due to the light and fluffy texture of C₃N₄ [43]. Based on previous results calcination temperature of 550°C is considered ideal, providing a enlarge specific surface area by exfoliation without decomposing the samples [8]. Hence increasing the photocatalytic activity due to higher number of available active sites for photoreaction to occur.

![Figure 3](image_url)

**Figure 3.** (a) Nitrogen adsorption-desorption isotherms for graphitic and crystalline carbon nitride composites, (b) and corresponding Barret-Joyner-Halenda (BJH) poresize distributions curve of samples.

The specific surface area of g-C₃N₄ was measured at 61.3 m²/g. When CeO₂ was added via direct calcination, the surface area of g-C₃N₄/CeO₂ was significantly reduced to 35.9 m²/g. It is interesting to see that the surface area of C-C₃N₄ and C-C₃N₄/CeO₂ were enhanced to 92.1 m²/g and 106.4 m²/g when molten salt method was applied in the calcination process. The increase in surface area indicates that the C-C₃N₄ produced when using molten salt method increased the stability of carbon nitride thus contributed to the increase in specific surface area. However, for g-C₃N₄/CeO₂ obtained from direct calcination without the ionic liquid solvent, we suggest that the C₃N₄ has decomposed which may resulted in a larger ratio of CeO₂ in the catalyst, hence resulted in a smaller specific surface area of 35.9 m²/g.
Table 1. A summary for the surface area, pore volume and pore size for the photocatalyst retrieved from the nitrogen adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore-size distributions.

| Photocatalyst         | Surface Area | Pore Volume | Pore Size |
|-----------------------|--------------|-------------|-----------|
| g-C₃N₄               | 61.3 m²/g    | 0.3723 cm³/g| 24.3 nm   |
| C-C₃N₄              | 92.1 m²/g    | 0.3268 cm³/g| 14.2 nm   |
| g-C₃N₄/CeO₂         | 35.9 m²/g    | 0.1936 cm³/g| 21.6 nm   |
| C-C₃N₄/CeO₂         | 106.4 m²/g   | 0.4462 cm³/g| 16.8 nm   |

The BJH pore-size distribution curve, shows all samples are composed of small mesopores (~2.6 nm) which are associated to the porosity formed in between the nanoparticles [38]. A larger area of hysteresis loop and a shift to a lower relative pressure of C-C₃N₄/CeO₂ was observed from the adsorption curve in figure 3(b), suggesting the formation of bigger mesopores in the catalyst [18]. Apart from that, the C-C₃N₄/CeO₂ also formed larger mesopores (~15 nm - 23 nm) which are attributed to the pores formed between packed C₃N₄ layers. Summary from table 1 shows CC₃N₄/CeO₂ have the largest pore volume of 0.4462 cm³/g and pore-size average of 16.8 nm, indicating a higher porosity of this sample.

It is reasonable to conclude that the molten salt method has enhanced the C-C₃N₄/CeO₂ photocatalytic activity by increasing the porosity and specific surface area of the composite. A larger specific surface area is considered favourable to photocatalytic activity due to the higher number of active sites; this acts as site for the separation of photogenerated electron and holes, hence improving the photocatalytic reaction rate.

3.1.4. Fourier-transform infrared spectroscopy (FTIR). The functionality of the photocatalysts were measured using FT-IR spectra from 650 - 4500 cm⁻¹, as shown in figure 4. The analysis provided information on the structure of C₃N₄ based on the adsorption bands appeared at three regions i.e. 800900 cm⁻¹, 1200-1650 cm⁻¹, 3000-3400 cm⁻¹ [37], [45], [46]. All the photocatalysts showed a prominent peak at 800-812 cm⁻¹ which indicated a typical breathing mode of tri-s-triazine [47]–[50]. The addition of CeO₂ on g-C₃N₄ and C-C₃N₄ revealed minor difference towards the position of the band. The adsorption band at 887-889 cm⁻¹ observed in g-C₃N₄ and g-C₃N₄/CeO₂ was corresponded to the deformation mode of heptazine deformation [51], [52].
The absorption bands appeared at 1200-1650 cm\(^{-1}\) assigned to the typical characteristic of aromatic C-N heterocyclic \cite{37}, \cite{45}, \cite{46}, \cite{49}, \cite{50}. The peaks at 1203-1357 cm\(^{-1}\) are attributed to the aromatic C-N stretching vibration. It is assigned to the stretching vibration of connected units of CN \cite{22}. The peaks at 1400–1632 cm\(^{-1}\) are attributed to the stretching vibration of heptazine-derived repeating unit \cite{46} which originated from the C=N stretching \cite{22}. With the addition of CeO\(_2\), the peaks gained increase intensity compared to bulk g-C\(_3\)N\(_4\). The small band observed at 2128 cm\(^{-1}\) was due to the dissociated CN network, forming both C≡N and N=C=N bonds, formed by broken aromatic unit of C\(_3\)N\(_4\) \cite{49}.

The broad adsorption band at 3000-3250 cm\(^{-1}\) is attributed to the stretching vibration of N-H (primary and secondary amine), which indicates that uncondensed amino functional group is present in the sample \cite{22}, \cite{37}, \cite{49}, \cite{52}. A highly intense peak attributes to higher number of -NH/-NH\(_2\) groups were observed on g-C\(_3\)N\(_4\) and CeO\(_2\)/g-C\(_3\)N\(_4\), which indicates a larger number of particles are present as smaller polymer contained fewer heptazine units \cite{53}. The increase of amine terminals in these smaller segment are concluded as defects, which acts as the recombination sites in the photocatalytic reaction \cite{53}. The N-H stretching bands were disappeared on C-C\(_3\)N\(_4\) and CeO\(_2\)/C-C\(_3\)N\(_4\), which implied crystallisation in the presence of ionic salt removed defects. The broad peak 3250-3313 cm\(^{-1}\) is attributed to the vibration of intermolecular O-H hydrogen bonds or hydroxyl groups from the absorption of water in CN \cite{22}, \cite{49}–\cite{51}.

As seen from the figure 2, g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/CeO\(_2\) undergoes direct calcination without molten salts resulted in a higher number of defects. Defects such heptazine deformation, dissociated CN network and higher number of -NH/-NH\(_2\) groups, which ultimately would decrease the photocatalytic performance of the two samples. Generally the peaks observed by the catalysts were similar to other reported literatures on the CN synthesis from urea \cite{17}, \cite{50}, \cite{54}. All these characteristic FTIR peaks suggest that the overall structure of g-C\(_3\)N\(_4\) maintained the original form even after CeO\(_2\) doping. As stated previously in XRD analysis, g-C\(_3\)N\(_4\)/CeO\(_2\) have a lack of carbon nitride peaks, however from the FTIR result, it is certain that carbon nitride is still present in the photocatalyst.

3.1.5. UV-vis (optical absorption studies). Photocatalytic reaction depends on the ability of catalyst to harvest photon from the light. The photon energy absorbed by the photocatalysts would then excite the electrons on the valance band to the conduction band, generating holes and ultimately create a chain

![Figure 4. FTIR spectra for graphitic (g-C\(_3\)N\(_4\), g-C\(_3\)N\(_4\)/CeO\(_2\)) and crystalline carbon nitride (C-C\(_3\)N\(_4\) and C-C\(_3\)N\(_4\)/CeO\(_2\)) composites.](image-url)
redox reaction. Factors influencing the photocatalytic activity generally depends on catalyst ability to harvest light energy and reduced the recombination rate of the electron and hole in the valance band. Structural modification of photocatalyst carbon nitride is one of the methods used to improve the optical absorption. UV-visible diffused reflectance spectra reveal the optical property and the band energy of the samples synthesized by direct calcination and ionothermal calcination. The light absorbance graph was constructed using the Kubelka Munk calculation.

![Figure 5](image)

**Figure 5.** The optical property was measured using UV-vis spectroscopy and constructed using Kubelka Munk calculation. (a) The absorbance and (b) the band gap of g-C$_3$N$_4$ and gC$_3$N$_4$/CeO$_2$, (c) the absorbance and (d) the band gap of C-C$_3$N$_4$ and C-C$_3$N$_4$/CeO$_2$.

From figure 5, all of the samples have an absorption edging towards the visible light region with absorbance between 395 nm to 418 nm. Following direct calcination of g-C$_3$N$_4$ and g-C$_3$N$_4$/CeO$_2$, the absorbance was red-shifted slightly to 416 nm and 418 nm with band gap energies were determined at 2.94 eV and 2.97 eV. When the samples produced with molten salt addition during the calcination, C-C$_3$N$_4$ and C-C$_3$N$_4$/CeO$_2$ exhibited a lower absorbance wavelength at 395 nm with band gap energy of 3.12 eV.

Theoretically the band gap energy from all the samples are adequate for endothermic reaction for water splitting [55]. However as seen in figure 5, the DRS curve contained several loops due to the defects arising from the polymerization of the samples [40]. This is supported by the FTIR of direct calcined samples containing more defects compared to the crystalline samples. The loop is attributed to multiple reflection of incident light within photocatalyst, subsequently varied the absorbance in the photocatalyst. This would result in inefficient transfer of electron which led to high recombination rate of photocatalyst resulting in low photocatalytic activities.

### 3.2. Photocatalytic activity

Triethanolamine (10 vol%) was used as the sacrificial agent in water splitting reaction. The hydrogen evolution reaction (HER) was performed under visible region with a UV filter to provide only photon energy in visible light region. Figure 6 shows the HER values of the samples g-C$_3$N$_4$ and C-C$_3$N$_4$/CeO$_2$ in 180 minutes. The C-C$_3$N$_4$ and g-C$_3$N$_4$/CeO$_2$ are not displayed in the graph due to only a trace of H$_2$ produced from both samples.
The hydrogen generated seen in figure 6 for g-C₃N₄ after 180 minutes is 170.84 µmol g⁻¹, whereas C-C₃N₄/CeO₂ generates a higher HER value of 268.47 µmol g⁻¹. Interestingly the outcome from the optical analysis predicted that g-C₃N₄ would performed better due to a smaller band gap energy of 2.94 eV compared to 3.12 eV for C-C₃N₄/CeO₂. However, the activity of C-C₃N₄/CeO₂ is higher compared to g-C₃N₄. There are several influences that play a role in this. g-C₃N₄ was presumed to have higher number of defects as revealed in FTIR analysis compared to C-C₃N₄/CeO₂. An excess number of defects may contribute to the lower HER of g-C₃N₄, as defects often acts as a recombination site for electron. The doping of metal oxide CeO₂ may contribute to the higher HER value by creating a heterojunction structure, delaying the recombination of electro-hole in C-C₃N₄/CeO₂, hence prolonging the redox reaction in the valance and conduction band. Lastly, the specific surface area of C-C₃N₄/CeO₂ was much larger at 105.4 m²/g with higher porosity density hence enhancing the number of available active sites for the photogenerated reaction to occur.

Nevertheless, the photocatalytic activity for both catalyst is still considered low. It was suspected that several factors may contribute to this predicament. As seen in the UV-vis DRS, there are several loops where absorbance varies in all the photocatalyst. These loops caused by defects during polymerization of catalyst attributed to inefficient transfer of photogenerated charge carriers which eventually led to fast recombination of electron and hence factoring the low photocatalytic activities. The absorbance in UV-vis DRS was measured at 395 nm – 418 nm, which is considered not favourable under visible light with a wavelength of 420 nm above. This may contribute to the low HER value of all samples as the photon energy available in the visible region is not efficiently harvested for the excitation of electron during hydrogen production.

4. Conclusion
In summary, a highly active C-C₃N₄/CeO₂ composite was synthesized by heating g-C₃N₄ and CeO₂ with molten salt mixtures at 550°C for 3 hours. The C-C₃N₄/CeO₂ resulted in high crystalline structure and large specific surface area when compared with the g-C₃N₄. The photocatalytic activity of C-C₃N₄/CeO₂ was significantly higher than g-C₃N₄, g-C₃N₄/CeO₂ and C-C₃N₄. The high H₂ production was due to a higher number of active sites as a result of a larger specific surface area.

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