Direct Z-Scheme g-C₃N₅/Cu₃TiO₄ Heterojunction Enhanced Photocatalytic Performance of Chromene-3-Carbonitriles Synthesis under Visible Light Irradiation

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Abstract: In order to make the synthesis of pharmaceutically active carbonitriles efficient, environmentally friendly, and sustainable, the method is regularly examined. Here, we introduce a brand-new, very effective Cu₃TiO₄/g-C₃N₅ photocatalyst for the production of compounds containing chromene-3-carbonitriles. The direct Z-Scheme photo-generated charge transfer mechanism used by the Cu₃TiO₄/g-C₃N₅ photocatalyst results in a suppressed rate of electron-hole pair recombination and an increase in photocatalytic activity. Experiments showed that the current method has some advantages, such as using an environmentally friendly and sustainable photocatalyst, having a simple procedure, quick reaction times, a good product yield (82–94%), and being able to reuse the photocatalyst multiple times in a row without noticeably decreasing its photocatalytic performance.

Keywords: chromene-3-carbonitriles; Cu₃TiO₄; g-C₃N₅; photocatalyst; Nanomaterials; Z-Scheme heterojunction

1. Introduction

Multi-component reactions (MCRs) have garnered a lot of interest recently as a method for creating a variety of heterocyclic compounds with applicability in medicine, pharmaceuticals, and agrochemistry [1,2]. One-pot MCRs, which induce organic reactants to react together in a single step, have emerged as an alternative platform for organic chemists due to their simple operation, effective purification techniques, side products, and quick turnaround times [3,4]. In simple terms, a multi-component reaction is one in which three or more reactants mix in a single vessel to create a single output that effectively contains every atom of the starting elements (with the exception of condensation products, such as water molecules, hydrochloric acid, or methanol) [5–7].

A number of naturally occurring O-bearing heterocyclic organic moieties, which are widely present in edible fruits and vegetables, contain the chromone and related structural skeletons as their major structural motifs [8,9]. Numerous industries, like agrochemistry, medicine, as well as material sciences, use carbonitrile-based heterocycles and their derivatives as ligands and catalysts [10]. Carbonitrile compounds have a high level of therapeutic activity and can be employed as antibacterial [11,12], anti-tumor [13,14], anti-inflammatory, anti-cancer [15–17], and anti-convulsant drugs [18]. Compounds with a carbonitrile base are also employed to make electrical and optical materials as well as anion sensors [19,20]. Given the many different uses for chromenes, synthetic chemists have been exploring new and effective catalysts. In the traditional way of making carbonitrile-based chemicals, the product needed to be made at a high temperature and through a long process called “synthesis”.

As a result of growing environmental worry, a lot of work has been put into creating innovative procedures that reduce emissions in chemical synthesis. From the perspective
of green and sustainable chemistry [21–23], designing effective and affordable chemical processes utilising heterogeneous catalysts to create fine chemicals and pharmaceutical goods through MCRs has recently attracted a lot of attention from academics and businesses. The fundamental drawback of heterogeneous catalysts is, however, their decreased catalytic activity. The best way to deal with this issue is to minimize the size of the particles in the heterogeneous catalyst [24,25]. Metal oxide nanocatalysts combine the benefits of photo and heterogeneous catalysts. Although this type of material has many valuable advantages, including a high surface area, efficient particle distribution, a straightforward recovery procedure, effective light absorption property, good stability, and non-toxic behaviour, their propensity to agglomerate and oxidise is a drawback [26–28]. Immobilizing organic molecules on metal oxide nanoparticles is thought to be a workable way to address this drawback.

Given the significance of metal oxide, nanoparticles (metal oxide NPs) have received a lot of attention and are widely employed in water splitting, catalysis, photocatalysis, energy, and environmental remediation [29–32]. Titanium dioxide (TiO$_2$) and copper oxide (CuO) nanoparticles have attracted a great deal of interest. It was discovered that CuO and TiO$_2$ NPs worked effectively as catalysts for the oxidation of organic molecules as well as CO and NO [33,34]. Additionally, in last decade, a lot of attention has been focused on the use of CuO and TiO$_2$ NPs for chemical reactions [35]. CuO NPs’ high levels of electron-hole pair recombination and TiO$_2$’s less obvious active nature are some of its disadvantages. We created the Cu$_3$TiO$_4$ NPs for the organic reaction based on the aforementioned investigative information. In the context of heterogeneous nanocatalysts, this class of catalysts seems to be one of the most promising approaches toward effective reactions under mild and ecologically nonthreatening circumstances.

Organic synthesis research in the area of photocatalysis, notably with regard to visible light, is appealing [36]. Heterogeneous photocatalysis has been given a significant role by carbon-based materials. Due to a variety of characteristics, including stability, narrow bandgap, 2D nanomaterial, excellent visible-light active absorption, low density, and low toxicity, graphitic-carbon nitride (g-C$_3$N$_4$) is an effective catalyst under visible light [37,38]. Additionally, its layered structure makes the anchor metal an appropriate substrate for its direct use as a heterogeneous photocatalyst. A variety of modified carbon nitrides, including nanosheets, nanorods, metal-doped and non-metal modified carbon nitrides are effective nanomaterials [39–41]. An intriguing method has been recently created to modify the polymeric structure of C$_3$N$_4$ in order to create novel carbon nitrides with a wider visible-light sensitive range. For instance, integrating an N-rich 3-amino-1,2,4-triazole unit into the s-heptazine motif led to the highly ordered C$_3$N$_5$, which can increase the C:N atom ratio from 3:4–3:5. The lower bandgap energy is a result of the extra N-atoms connected to the terminal NH$_2$ groups in the form of 1,2,4-triazole, which are different from the usual C$_3$N$_4$ in that they are bridged by a N-atom through sp$^2$ hybridization [42–44]. The construction of heterojunction photocatalysts based on C$_3$N$_4$ has received extensive research, due to its viability and efficiency for the spatial separation of photogenerated electron-hole pairs. Appropriate catalyst materials can generate heterojunctions, which can lower the activation energy needed for the reduction reaction. The secondary target is to encourage the division of photogenerated charge carriers while simultaneously providing more active locations for the photocatalytic activity. Meticulous design of a heterojunction is a promising method to increase photocatalytic activity, because of its rapid charge carrier separation caused by the integrated electric field [45–48]. A switch from photocatalysts based on C$_3$N$_5$ to those based on the organic transformation reaction is driving recent advancements for cleaner, more sustainable chemistry. The heterojunction is followed by carbon nitride-based catalysts like Type-II and Z-Scheme. A Z-scheme system has also been built with a pertinent shuttle mediator to obtain better light-harvesting potential with high charge separation performance and sturdy redox ability, furthermore to photocatalysts with conventional heterojunctions that can successfully separate photogenerated electron-hole pairs via band alignment [49,50]. Numerous studies on g-C$_3$N$_4$ linked to the Z-Scheme electron transfer
mechanism have been reported, including those on TiO$_2$/g-C$_3$N$_4$ [51], CuO/g-C$_3$N$_4$ [52], ZnO/g-C$_3$N$_4$ [53], WO$_3$/g-C$_3$N$_4$ [54], V$_2$O$_5$/C$_3$N$_4$ [55], MnO$_2$/C$_3$N$_4$ [56] and Bi$_2$O$_3$/g-C$_3$N$_4$ [57], among others. In recent years, g-C$_3$N$_5$-based heterojunction production has become increasingly significant in photocatalysis and other applications. There are currently very few studies on Z-Scheme mechanisms for g-C$_3$N$_5$-based heterojunctions, including Ag$_3$PO$_4$/C$_3$N$_5$ [58], FeOCl/g-C$_3$N$_5$ [59], Bi$_4$O$_2$I$_2$/g-C$_3$N$_5$ [60], LaCoO$_3$/g-C$_3$N$_5$ [61] and Bi$_2$WO$_6$/g-C$_3$N$_5$ [62,63]. Still, there is no report carried out on Cu$_3$TiO$_4$/g-C$_3$N$_5$ heterojunction fabrication and photocatalytic application.

Light-emitting diodes (LEDs) are the best type of light source for photocatalytic applications. BLUE LEDs have benefits over other light sources in terms of efficiency, the qualities of power, compatibility, longevity, and environmental friendliness. Due to their unique characteristics, BLUE LEDs offer an improvement over traditional lighting sources and allow for more innovative scope when designing different photochemical reactions [64].

In this research, we have developed a novel and very effective Cu$_3$TiO$_4$/g-C$_3$N$_5$ photocatalyst for the construction of chromene-3-carbonitrile molecules under BLUE LED light. The direct Z-scheme charge separation mechanism employed by the Cu$_3$TiO$_4$/g-C$_3$N$_5$ hetero-junction photocatalyst reduces the rate of electron-hole ($e^−$/$h^+$) pair recombination of Cu$_3$TiO$_4$ and increases its photocatalytic activity. The as-prepared g-C$_3$N$_5$/Cu$_3$TiO$_4$ nanocomposites showed better photocatalytic activity and stability when compared to pure Cu$_3$TiO$_4$ and pure C$_3$N$_5$. The spatial separation of photoinduced charge carriers could be attributed to the improved photocatalytic performance. The characteristics of the obtained catalysts have been studied with the help of XRD, UV-Vis DRS, FT-IR, FE-SEM, TEM, Zetapotential, and XPS. The applications for the catalyst have also been demonstrated and characterized. This work will be opening up a new path in the field of photocatalysts and MCRs and can further be developed for a wide range of applications other than the proposed one.

2. Results and Discussion

2.1. Characterization of Prepared Nanomaterials

The synthesized nanocomposite nanomaterial crystalline phase structure was investigated using the X-ray diffraction technique. In Figure 1, the pristine g-C$_3$N$_5$ sheets peak at 13.1$^\circ$ was related to (100), and another strong peak at 27.2$^\circ$ was related to (002) for graphitic g-C$_3$N$_5$ sheets (JCPDS card-87-1526) [65]. Peaks for Cu$_3$TiO$_4$ nanoparticles were found at 2theta = 26.4, 34.2, 38.6, 51.5, 59.1, 63.2, and 70.3$^\circ$ in relation to planes (004) (101) (102) (104) (006) (110) (107), which corresponds well to JCPDS card no. 83-1285 [66]. Both are well-reflected in all CN5CT nanocomposites. Figure 1 shows the p-XRD patterns obtained for g-C$_3$N$_5$/Cu$_3$TiO$_4$ with varying wt. % Cu$_3$TiO$_4$. The XRD patterns of the 5% CN5CT composite showed no discernible change, while less Cu$_3$TiO$_4$ has been deducted because of the low loading percentage. The intensity of Cu$_3$TiO$_4$ nanoparticles peaks increased as the Cu$_3$TiO$_4$ nanoparticles ratio was increased to 10%, 20%, and 30%. Finally, Cu$_3$TiO$_4$ nanoparticles were supported on g-C$_3$N$_5$ nanosheets. As confirmed, they have shown good crystalline nature.
In BET analysis the surface area of the designed nanocomposites was examined, and depicted in Figure 2a. The surface area of Cu3TiO4 nanoparticles, g-C3N5 and g-C3N4 values are 10, 15, and 14 m²/g respectively. Then 10% CN5CT nanocomposite has 19 m²/g after supporting Cu3TiO4 nanoparticles, which thereby increased the surface area. The Cu3TiO4/g-C3N4 has less surface area compared to 10% CN5CT, as shown in Figure 2a. From BET analysis, 10%CN5CT exhibited more surface and active sites compared to others. In FT-IR spectroscopy (Figure 2b), g-C3N5 sheets showed peaks at 808, 1234, 1405, and 2160 cm⁻¹, respectively. The signal at 808 cm⁻¹ corresponds to the existence of triazine units in g-C3N5 nanosheets. NH2 and NH peaks were obtained at 3500 cm⁻¹. The g-C3N5 nanosheet FT-IR report is consistent with previous literature. [67,68]. The FT-IR spectrum of Cu3TiO4 exhibited a range between 400–700 cm⁻¹ bands, which is owing to Ti-O-Ti and Cu-O stretching vibration [69]. After that, Cu3TiO4 nanoparticles supported the slight shift that happened in 5%, 10%, 20%, and 30% CN5CT nanocomposite.

Figure 1. XRD images of prepared CN, CT and various percentages CNCT nanocomposites.

Figure 2. (a) BET isotherm and (b) FT-IR spectra.
In XPS, the chemical state of the prepared 10% CN5CT was exposed in Figure S1. Figure S1a shows the survey spectrum of the synthesized 10% CN5CT nanocomposite and all the signals confirmed the presence of C, N, Cu, Ti, and O. For C 1s, in Figure S1b, the three strong peaks at ~287, 285.8 and 283 eV show the presence of C 1s in nanocomposite, which corresponds to N-C-N, C-N and C-C bonds [70]. Then N 1s displayed two peaks at 399 and 397 eV, providing evidence for the presence of N 1s species (Figure S1c) with different environments of N-C and C-N-C bonds [71]. Cu 2p exposed two major peaks at 953 and 933 eV (Figure S1d) combined with two satellite lines, confirming the presence of Cu 2p species in the CN5CT composite [72]. The two peaks (Figure S1e) at 462 and 456 eV confirm the presence of Ti 2p species in CN5CT nanocomposite [72]. Finally, for O 1s species, two strong peaks (Figure S1f) at 529 and 531 eV confirmed the existence of oxygen-metal and oxygen-hydrogen bonds in the composite.

The typical morphology of the g-C3N5 and g-C3N5/Cu3TiO4 nanocomposite is shown in Figure 3a,b, indicating that the prepared g-C3N5 has a sheet-like morphology. As seen in Figure 3a, exfoliation caused the evolution of 3-amino-1,2,4-triazole into a typical layered structure, showing the formation of a loosely packed 2D g-C3N5 structure. In Figure 3b, 10%CN5CT nanocomposite, and Cu3TiO4 nanoparticles are marked. The 10% CN5CT nanocomposites showed a strong connection between g-C3N5 and Cu3TiO4, indicating that there would be a physical adsorption. It also implied that g-C3N5 might prevent the aggregation of Cu3TiO4 NPs as compared to Figure 3b. The effectiveness of the electron-hole separation can be increased by closing interfacial contacts between g-C3N4 and Cu3TiO4 nanoparticles by excellent dispersion. According to the elemental mapping in Figure 3c–f, the elements C, N, Ti, Cu, and O were evenly distributed throughout the 2D layered and 3D nanoparticle structures.

Figure 3. FE-SEM images of (a) g-C3N5 (b) 10% CN5CT nanocomposite and (c–g) elemental mapping of 10% CN5CT.
The perfect morphology and structural nature of the g-C$_3$N$_5$ and 10% CN5CT were recorded by using TEM (Figure 4a,b). The agglomerated sheet-like structure of g-C$_3$N$_5$ was confirmed by a TEM image at 50 nm (Figure 4a). The surface of the g-C$_3$N$_5$ was smooth and had high porosity, which was confirmed by the sheet-like structure of the g-C$_3$N$_5$. The 3-AT was thermal disintegration, copolymerization, and elimination of CO$_2$ and NH$_3$, which may result in the development of g-C$_3$N$_5$ nanosheets, which have a smaller and thinner nanosheet like structure than g-C$_3$N$_4$. Both g-C$_3$N$_4$ and g-C$_3$N$_5$ are similar in appearance. The EDS of g-C$_3$N$_5$ provides information about the given sample, g-C$_3$N$_5$, which has a higher quantity of nitrogen atoms compared to carbon atoms (Figure 4c). On introducing Cu$_3$TiO$_4$ into g-C$_3$N$_5$ nanosheets, no changes were observed on the surface of g-C$_3$N$_5$. The Cu$_3$TiO$_4$ NPs are uniformly distributed on the g-C$_3$N$_5$ surface and form an effective heterojunction (Figure 4b). In Figure 4d, EDS analysis of 10%CN5CT confirms the elements with weight percentage viz., N (52.4%), C (35.1%), O (8.7%), Ti (2%), and Cu (1.8%). Figure 4e depicts the SEAD pattern of the 10%CN5CT, demonstrating that the prepared composite has a good crystalline nature and corresponding planes of (111), (103), (102), and (106) in XRD. The average particle size of Cu$_3$TiO$_4$ (~26 nm) in 10%CN5CT was calculated and given in Figure 4f. From the TEM image, the surface area of the compound increased with the decrease in Cu$_3$TiO$_4$ particle size. The photocatalyst 10% CN5CT was found to coexist on the surface of g-C$_3$N$_5$ sheets. The Cu$_3$TiO$_4$ (dark-coloured) nanoparticles are uniformly scattered on the g-C$_3$N$_5$ matrix to produce an efficient heterojunction structure, with the average particle size of Cu$_3$TiO$_4$ being found to be around 50 nm. The large surface area enhances the photocatalytic activity. Due to their excellent surface area, both g-C$_3$N$_5$ and Cu$_3$TiO$_4$ have close contact with each other. Due to this nature, the 10%CN5CT nanocomposite has better photocatalytic activity.

The charge separation and transfer of the electron-hole pair were analysed by using photoluminescence (PL) emission spectroscopy. Figure 5a shows the PL results for the prepared CN, CT, and CN5CT at various loading percentages. The g-C$_3$N$_5$ nanosheets emission peak was observed at around ~470 nm with high intensity, which confirmed the high recombination rate. On the other hand, the introduction of Cu$_3$TiO$_4$ nanoparticles on the surface of g-C$_3$N$_5$ nanosheets reduced the intensity of the peak, which confirmed the suppression of recombination rate of the CN5CT nanocomposite. Notably, when compared to other CN5CT nanocomposite, the 10% CN5CT nanocomposite has a lower emission peak. The PL investigation is strong evidence that 10%CN5CT has less electron-hole pair recombination than 5%, 20%, and 30% of CN5CT.

The thermal stability of the prepared nanocomposite was carried out by using thermogravimetric analysis (TGA). Here, in Figure 5b, is depicted the high stability of Cu$_3$TiO$_4$ nanoparticles, because no characteristic decomposition occurred in the Cu$_3$TiO$_4$ nanoparticles and up to 98% of Cu$_3$TiO$_4$ nanoparticles were getting residue at 800 °C, showing the high stability nature of nanoparticles. At 530 °C, g-C$_3$N$_5$ nanosheets began decomposing, and all of the carbon and nitrogen in g-C$_3$N$_5$ was easily eliminated above 700 °C (1% residue at 800 °C). In 10% CN5CT nanocomposite, g-C$_3$N$_5$ nanosheets got decomposed at 530 °C but the residue obtained was 12%, which shows the presence of Cu$_3$TiO$_4$ nanoparticles in g-C$_3$N$_5$ nanosheets at a 10% ratio was confirmed. The 10%CN5CT nanocomposite has improved the thermal stability compared to g-C$_3$N$_5$. 
In this study, we concentrated on the synthesis of different carbonitriles using a g-C₃N₅/Cu₃TiO₄ nanocomposite. The catalyst exhibited better efficiency for the synthesis of carbonitriles in the presence of light. Ethanol has been used as solvent, which results in good yields (Table 1, entry 5, 7, 8).

The charge separation and transfer of the electron-hole pair were analysed by using photoluminescence (PL) emission spectroscopy. Figure 5a shows the PL results for the g-C₃N₅, 5% CN5CT, 30% CN5CT, 20% CN5CT, 10% CN5CT nanocomposites. The PL investigation is strong evidence that 10% CN5CT has less electron-hole recombination than 5%, 20%, and 30% of CN5CT. Notably, when compared to other CN5CT nanocomposites, the 10% CN5CT nanocomposite has a lower emission peak. The PL investigation is strong evidence that 10% CN5CT has less electron-hole recombination than 5%, 20%, and 30% of CN5CT. Notably, when compared to other CN5CT nanocomposites, the 10% CN5CT nanocomposite has a lower emission peak.

The thermal stability of the prepared nanocomposite was carried out by using thermogravimetric analysis (TGA). Here, in Figure 5b, is depicted the high stability of Cu₃TiO₄, g-C₃N₅, and 10% CN5CT nanocomposite. The residue at 800 °C). In 10% CN5CT nanocomposite, g-C₃N₅ nanosheets got decomposed at 530 °C but the residue obtained was 12%, which shows the presence of Cu₃TiO₄ nanoparticles. In 20% CN5CT nanocomposite, g-C₃N₅, Cu₂OAc, and CuOAc nanoparticles got decomposed at 530 °C and the residue obtained was 13%, which shows the presence of Cu₃TiO₄ nanoparticles. In 10% CN5CT nanocomposite, the g-C₃N₅ nanosheets got decomposed at ~800 °C but the residue obtained was 12%, which shows the presence of Cu₃TiO₄ nanoparticles.

The thermal stability of the prepared nanocomposite was carried out by using thermogravimetric analysis (TGA). Here, in Figure 5b, is depicted the high stability of Cu₃TiO₄, g-C₃N₅, and 10% CN5CT nanocomposite. The residue at 800 °C). In 10% CN5CT nanocomposite, g-C₃N₅ nanosheets got decomposed at 530 °C but the residue obtained was 12%, which shows the presence of Cu₃TiO₄ nanoparticles. In 20% CN5CT nanocomposite, g-C₃N₅, Cu₂OAc, and CuOAc nanoparticles got decomposed at 530 °C and the residue obtained was 13%, which shows the presence of Cu₃TiO₄ nanoparticles. In 10% CN5CT nanocomposite, the g-C₃N₅ nanosheets got decomposed at ~800 °C but the residue obtained was 12%, which shows the presence of Cu₃TiO₄ nanoparticles.
2.2. Photocatalytic Activity of g-C\textsubscript{3}N\textsubscript{5}/Cu\textsubscript{3}TiO\textsubscript{4} Nanocomposite

In this study, we concentrated on the synthesis of different carbonitriles using a g-C\textsubscript{3}N\textsubscript{5}/Cu\textsubscript{3}TiO\textsubscript{4} (CN5CT) photocatalyst. The catalyst exhibited better efficiency for the synthesis of carbonitriles in the presence of light. Ethanol has been used as solvent, which generated a yield of 94% (Table 1, entry 6). The reaction was carried out in the presence of BLUE LED visible light using a photocatalyst employing diketone, malononitrile, and aldehyde (Scheme 1). Based on the characterization results, we investigated the CN5CT nanocomposite, which has a strong light absorption capacity and thereby increases the life time of electrons in the conduction band. The high electron-hole recombination rate improves the activity of the catalyst in the production of 1.4a. In this case, 20 mg of the catalyst was combined with the reactants and exposed to Blue LED light. Simultaneously, radicals formed on the catalyst surface, resulting in the formation of activated complexes. These are highly active species that are rapidly degraded to create products on the catalyst surface. In Table 1, the reaction conditions were adjusted to determine the optimal conditions for carbonitrile synthesis. Here, the solvent, catalyst, condition, and time were varied to determine the optimization condition. (Table 1 entries 1 and 3), produced yields (62% and 33%) that were significantly lower than the CN5CT nanocomposite. CN5CT nanocomposite and ethanol solvent worked better in all situations in the presence of light for 3 min. In all situations, the CN5CT nanocomposite and ethanol solvent worked better in all situations in the presence of light for 3 min. The increase in catalyst percentage also did not affect the product yield and for 5%, 20% and 30%, CN5CT nanocomposites give good yields (Table 1, entry 5, 7, 8).

Table 1. Optimization for the synthesis of Carbonitriles in BLUE LED visible light.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Time (minutes)</th>
<th>Yield (^a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CuO</td>
<td>EtOH</td>
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<td>60</td>
<td>62</td>
</tr>
<tr>
<td>2.</td>
<td>CuOAc</td>
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<td>Light</td>
<td>60</td>
<td>66</td>
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<tr>
<td>3.</td>
<td>TiO\textsubscript{2}</td>
<td>EtOH</td>
<td>Light</td>
<td>60</td>
<td>33</td>
</tr>
<tr>
<td>4.</td>
<td>Cu\textsubscript{3}TiO\textsubscript{4}</td>
<td>EtOH</td>
<td>Light</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>5.</td>
<td>5% CN5CT</td>
<td>EtOH</td>
<td>Light</td>
<td>3</td>
<td>67</td>
</tr>
<tr>
<td>6.</td>
<td>10% CN5CT</td>
<td>EtOH</td>
<td>Light</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>7.</td>
<td>20% CN5CT</td>
<td>EtOH</td>
<td>Light</td>
<td>3</td>
<td>81</td>
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<td>8.</td>
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<td>89</td>
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<tr>
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<td>H\textsubscript{2}O</td>
<td>Light</td>
<td>10</td>
<td>61</td>
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<tr>
<td>10.</td>
<td>10% CN5CT</td>
<td>THF</td>
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<td>95</td>
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<td>Without Catalyst</td>
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<td>Trace</td>
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<tr>
<td>14.</td>
<td>10% CN5CT</td>
<td>Solvent free</td>
<td>Heat</td>
<td>10</td>
<td>78</td>
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Diketone (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), ethanol, photocatalyst (20 mg). \(^a\) Yields—Isolated yields.

Scheme 1. Synthesis of hexahydroquinoline-2-carbonitrile using CN5CT nanocomposite in Blue LED light.
The optimal condition from Table 1 was utilized to synthesize different carbonitrile derivatives, which is shown in Table 2. The physicochemical properties and evidence (FT-IR, $^1$H, $^{13}$C NMR, and GC-MS) of the synthesized carbonitrile derivatives 1.4a-g are shown in Supporting Information Figures S2–S29. Light excites the electrons on the catalyst surface, causing them to move into the excited conduction band. The radicals ($^\bullet$O$_2^-$ and $^\bullet$OH) then react with the reactants to generate intermediates, which are then broken down to form the desired products on the catalyst surface. The catalyst, CN5CT nanocomposite, showed exceptional activity in the preparation of compound 1.4a. The recovered catalyst also performed admirably in the subsequent runs, with better yields.

Table 2. Scope of different substrate.

<table>
<thead>
<tr>
<th>Name</th>
<th>R</th>
<th>Time</th>
<th>TON a</th>
<th>TOF b</th>
<th>Yield b</th>
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<td>-Ph</td>
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<td>865</td>
<td>3.52</td>
<td>85</td>
<td>[73]</td>
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<tr>
<td>1.4b</td>
<td>4-(OCH$_3$)-Ph</td>
<td>5</td>
<td>832</td>
<td>3.26</td>
<td>82</td>
<td>[73]</td>
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<tr>
<td>1.4c</td>
<td>2-NO$_2$-Ph</td>
<td>3</td>
<td>876</td>
<td>3.78</td>
<td>88</td>
<td>[73]</td>
</tr>
<tr>
<td>1.4d</td>
<td>4-OH-Ph</td>
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<td>831</td>
<td>3.22</td>
<td>81</td>
<td>[73]</td>
</tr>
<tr>
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<td>4-F-Ph</td>
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<td>2-Cl-Ph</td>
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<td>4.63</td>
<td>94</td>
<td>[73]</td>
</tr>
<tr>
<td>1.4g</td>
<td>2-Nap</td>
<td>3</td>
<td>902</td>
<td>4.12</td>
<td>92</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Diketone (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), ethanol, photocatalyst (20 mg). a TON—Turn Over Number. TOF—Turn Over Frequency. b Yields—Isolated yields. c—reference.

In Table 2, we studied how several heterocycles were synthesized. We successfully prepared several substituted aldehydes such as electron donating, electron withdrawing, and halogenated aldehydes here. When donating substitutions were compared to others, they produced moderate yields (Table 2, compound 1.4b). In the proposed procedure, naphthaldehyde and benzaldehyde substitutions produced the highest yields of all. The multi-component technique made good yields and cut down on the amount of time needed to make 1.4a.

The reaction was carried out using CN5CT and irradiated for 3 min in an open environment at RT with a BLUE LED light. Remarkably, 94% of the targeted product (1.4a) was achieved. Nevertheless, when ambient O$_2$ was removed from the reaction mixture, the conversion was minimal and only a trace amount of product could be found if the reaction was completed in darkness or without photocatalysts. As a result, CN5CT photocatalyst, atmospheric oxygen, and BLUE LED visible light are all required for this transition.

2.3. Proposed Mechanism of 1.4a Synthesis

Based on the findings, a plausible mechanism was illustrated in Scheme 2. The more stable triplet state CN5CT* of the photoredox catalyst is then activated by the absorption of visible light and performs a single electron transfer (SET). This single electron transfer from 1.1 and 1.3 to the excited state of the CN5CT photocatalyst then lost a hydrogen atom and generated malononitrile radical (1.1a) and 1,3 cyclohexanedione radical (1.3a). The Knoevenagel condensation process between aldehyde (1.2) and activated malononitrile (1.1a) resulted in the synthesis of alkene intermediate (1.2a) [74]. Then, the intermediates 1.2b and 1.3a react in situ via Michael addition to give an adduct 1.3b, followed by intramolecular cyclisation of 1.3c, giving the desired product 1.4.

2.4. Transport Process of Photo-Excited Charge Carriers

The prepared samples’ light absorption in the 200–800 nm region was examined in order to obtain an appearance in the optical harvest property. The absorption edge of g-C$_3$N$_5$ is located at approximately 680 nm, as shown in Figure 6a. In contrast, the 10% CN5CT nanocomposite clearly showed a shift, which may have been caused by the intense interface interaction between Cu$_3$TiO$_4$ and g-C$_3$N$_5$. As a result, the representative
10 weight percentage (10%) CN5CT nanocomposite photocatalyst exhibits a greater capacity to capture visible light than 2D g-C3N5.


Figure 6. (a) UV-Vis DRS spectra and (b) bandgap plot.

As seen in Figure 6b, the band-gap values were also calculated from the intercept of tangents to plots of \((A\nu)^{1/2}\) versus photon energy. The optical band gap of g-C3N5,
Cu$_3$TiO$_4$ and 10% CN5CT was calculated and found to be 2.02, 2.15, and 2.04 eV respectively. In comparison to pure g-C$_3$N$_5$ and Cu$_3$TiO$_4$, the 10% CN5CT nanocomposite exhibits a narrower band gap. According to the findings, the photocatalyst for the 10% CN5CT heterojunction complex has good reactivity to visible light, which may increase its photocatalytic activity. The results show that photo-generated electron-hole charge carriers are enhanced, which will boost photocatalytic activity compared to CN5 and CT.

To obtain the band levels of the g-C$_3$N$_5$/Cu$_3$TiO$_4$, the valence band (CB) and conduction band (CB) potentials for g-C$_3$N$_5$ & Cu$_3$TiO$_4$ were calculated with the aid of Equations (1) and (2) [75].

$$E_{VB} = \chi - E_e + (1/2) \times E_g$$

$$E_{CB} = E_{VB} - E_g$$

where, $E_g$-band gap calculated from Figure 6b (2.02 eV for g-C$_3$N$_5$, and 2.15 eV for Cu$_3$TiO$_4$); $E_{CB}$-CB potential; $E_{VB}$-VB potential; $E_e$-energy of free electrons evaluated on the H scale (4.5 eV); $\chi$-electro negativity (6.89 eV for g-C$_3$N$_5$ and 5.63 for Cu$_3$TiO$_4$) calculated from literature [64]. The calculated $E_{VB}$ and $E_{CB}$ were +1.38 and −0.64 eV for g-C$_3$N$_5$, +0.055 and −2.095 eV for Cu$_3$TiO$_4$, respectively.

It is well known that the heterojunction photocatalyst g-C$_3$N$_5$/Cu$_3$TiO$_4$ will be produced when g-C$_3$N$_5$ and Cu$_3$TiO$_4$ are coupled. According to the band gap structures of g-C$_3$N$_5$ & Cu$_3$TiO$_4$, the separation processes of photo-induced electron–hole ($e^{-}/h^{+}$) is conveyed in Figure 7a,b, respectively.

![Figure 7](attachment:image.png)

**Figure 7.** Proposed electron-hole pair transfer mechanism of g-C$_3$N$_5$/Cu$_3$TiO$_4$ nanocomposite (a) type-II, (b) Direct Z-Scheme.

According to the type-II heterojunction (Figure 7a), the holes of g-C$_3$N$_5$ formed by visible-light will transfer to the VB of Cu$_3$TiO$_4$ (0.055 eV). Altogether, $e^{-}$s instantaneously migrate from the CB of Cu$_3$TiO$_4$ (−2.09 eV) to the CB of g-C$_3$N$_5$, (−0.64 eV). However, the potential energy (V vs. NHE) of $e^{-}$s from g-C$_3$N$_5$ is much lower than O$_2$/O$_2^{-}$ (−0.33 V) [76], which designates that these electrons are unable to reducing O$_2$ to ·O$_2$$^-$. Correspondingly, holes of Cu$_3$TiO$_4$ have inadequate potential energy to oxidize H$_2$O to ·OH (-OH/H$_2$O = 2.34 V vs. NHE) [77]. Consequently, the type-II mechanism does not well define the photocatalytic activity by the g-C$_3$N$_5$/Cu$_3$TiO$_4$ heterojunction.

Our photocatalyst works in total tandem with the visible light wavelength from BLUE LED light sources. Both g-C$_3$N$_5$ and Cu$_3$TiO$_4$ can be stimulated to produce electrons and holes when exposed to light. The electrons in CB of g-C$_3$N$_5$ tend to migrate to VB of Cu$_3$TiO$_4$ and recombine with the holes there under the influence of the electron transport.
system, following the Z scheme charge transfer path. As a result, the highly redox active photogenerated electrons in CB of Cu$_3$TiO$_4$ and holes in VB of g-C$_3$N$_5$ are retained to participate in the photocatalytic activity. If the photo-induced charge transfer process follows the direct Z-Scheme mechanism as illustrated in Figure 7b, the photon-induced excited electrons would thermodynamically transfer from the CB of g-C$_3$N$_5$ to VB of Cu$_3$TiO$_4$. Meanwhile, the O$_2$ could be reduced into ·O$_2^-$ (reduction reaction) by the electrons generated by CB of Cu$_3$TiO$_4$ because of the more negative potential (−2.09 eV). Further, the holes of g-C$_3$N$_5$ are arrested by OH to produce the 'OH, and the 'OH are moved to the superficial of the nanocomposite to oxidize molecules, because of the more positive potential (+1.38 eV). This charge transfer process in the direct Z-scheme greatly improves the efficiency of photo-generated electron-hole separation, resulting in the enhancement of the photocatalytic activity [78–80].

The nanocomposite exhibited excellent stability, visible absorption nature, high yields, a shortened reaction time, and reusability (Figure S30a). The photocatalyst 10%CN5CT does not affected by the reaction mixture and giving higher yields for the next few runs. Then after recycled catalyst was showing good crystalline nature in XRD analysis shown in Figure S30b. In the presence of visible light, the narrow bandgap feature demonstrates a visible active photocatalyst. In visible light, green synthesis of different heterocycles using CN5CT nanocomposite produced good yields in a short period. The photocatalyst can be used repeatedly without affecting the activity of the catalyst.

3. Materials and Methods
3.1. Materials Information
All of the chemicals and reagents were obtained from Avra Chemicals Private Limited, which is located in Andhra Pradesh, India. The column solvents and other chemicals were brought from Avra chemicals and used without further purification or processing. We purchased the lemons from the Vellore local market in Katpadi, Tamil Nadu, India. The NMR solvents came from Merck and was said to be 99.9% pure by the manufacturer.

3.2. Preparation of Citrus Limon Extract
Fresh lemons were split into half and squeezed to gather the pulp. There is some excess waste in the gathered juice (seeds and peel). To eliminate the additional trash, the pulp was centrifuged at 10,000 rpm. The clear liquid from the top layer was collected and it was stored in refrigerator.

3.3. Preparation of Cu$_3$TiO$_4$ NPs
Copper acetate (1 M) and titanium tert-butoxide (1 M) were taken in two separate beakers with 50mL of deionized water. A titanium tert-butoxide solution was added into the copper acetate solution with constant stirring. Then 5 mL of citrus extract obtained was added and the mixture was kept stirring overnight. Bluish-white coloured residue was separated and washed with a water-ethanol solution to remove the other impurities. The precipitate was heated at 500 °C for 4 h in a silica crucible. Finally, a black precipitate was obtained and subjected to characterization.

3.4. Preparation of g-C$_3$N$_5$ Nanosheets and Composite
In a beaker, 1 mmol of 3-amino-1,2,4-triazole was stirred well with 20 pellets of NaOH for 20 min. The colour of the mixture was altered to light brown after it was ground. For 4 h, the mixture was heated at 550 °C at a rate of 20 °C/min. Finally, grey g-C$_3$N$_5$ was collected and rinsed 10 times with distilled water to eliminate unreacted NaOH before being kept for characterization. The 5%, 10%, 20%, and 30% CN5CT were produced after processing g-C$_3$N$_5$ with Cu$_3$TiO$_4$ at various concentrations.
3.5. General Synthesis of Carbonitriles (1.4a-g) under Visible Light

1,3-cyclohexadione (1 mmol), corresponding aldehydes (1 mmol), malononitrile (1 mmol), CN5CT photocatalyst (20 mg), and 5 mL of ethanol were placed into a 25 mL round-bottom flask in the BLUE LED (12 W, 450 to 495 wavelength) light chamber. The reaction mixture was illuminated, and TLC was tested every minute to identify the result. After reaction completion, the reaction mixture was poured into crushed ice and precipitated out. The solids were removed from the ethanol and recrystallized.

4. Conclusions

In conclusion, we described the fabrication of direct Z-scheme Cu$_3$TiO$_4$/$g$-C$_3$N$_5$ heterojunction and their characterization. The Cu$_3$TiO$_4$/$g$-C$_3$N$_5$ photocatalyst has expressed excellent activity for the synthesis of carbonitriles derivatives. In an as-prepared heterojunction, 10% Cu$_3$TiO$_4$ is dispersed on surface the surface of $g$-C$_3$N$_5$ exhibited better photocatalytic activity. When compared to pure Cu$_3$TiO$_4$ and $g$-C$_3$N$_5$, Cu$_3$TiO$_4$/$g$-C$_3$N$_5$ nanocomposites perform better at photocatalysis due to their distinctive nanostructure and direct Z-scheme heterojunction. Low-energy consumption visible light BLUE LED lights were used for the irradiation. The reaction has been carried out immediately and the photocatalyst was showing excellent activity, reusability, easily recoverable, less recombination rate in visible light and high surface area.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121593/s1, Figure S1: XPS of Cu$_3$TiO$_4$/$g$-C$_3$N$_5$ nanocomposites; Figures S2–S29: FT-IR, $^1$H, $^{13}$C NMR and GC-MS of carbonitrile derivatives 1.4a–g; Figure S30: Reusability and reused XRD.

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