Ionothermal synthesis of carbon nitride paved the way to a new structural allotrope—polytriazine imide. In this work, we screen available precursors for pristine polytriazine imides and for their graphitic analogs narrowing it to the melamine—urea mixture as the most promising starting material. Photocatalytic activity of materials verified in reaction of benzyl alcohol oxidation to benzaldehyde, which is known to be highly requested chemical with thousands of tons of annual production. Therefore “green” and selective route of production is highly desired. Developed PTI-LiCl was tested for selective photooxidation of benzyl alcohol to benzaldehyde, demonstrating precious conversion and selectivity rates—96.3% and 91.6%, respectively after 5 hours of UV irradiation. Detailed physical-chemical characterization revealed that PTI materials possessed more ordered and highly condensed structure which grant them improved photocatalytic properties in comparison to graphitic carbon nitride polymorph.

Keywords. Carbon nitride; PTI; photocatalyst; selective oxidation.

1. Introduction

Carbon nitride (CN) as a semiconducting platform continues providing lots of photocatalytic materials for various applications. Its soft nature allows for multiple structural and allotrope modifications, serving excellent material for adaption, and improvement, depending on its ultimate use.1,2 The molecular structure based on triazine or heptazine subunits creates linear, branched, or 2D polymers with almost infinitely delocalized p-electrons, strongly shortening bandgap of the polymeric electronic structure.3

The molecular origin of CN allows for the bottom-up construction of various carbon nitride prototypes based on structurally similar to melamine surrogates4,5 and in situ molecular doping.6–8 CN layered structure gave rise to various exfoliating approaches leading to the delamination of layers, thus increasing specific surface and electron mobility.9–11 Delaminated 2D CN nanosheets exhibit favorable band potentials and
exposed active sites, reduced surface defects, increased lifetime of charge carriers, and stronger reduction potential of the photoexcited electrons. Aside from delamination various intercalation techniques provided novel materials with increased charge separation and reactivity. \[^{11,12}\] Thermal exfoliation aka thermal oxo-degradation of CN organic network yields material with an increased specific surface, something that inorganic semiconductors are not capable of. \[^{13,14}\] Another advantage of the semi-organic nature of carbon nitride is the ability to form various nano- and micro-structures based on various types of templating providing a plethora of mesoporous materials with various applications. \[^{15,16}\]

A significant breakthrough in carbon nitride developments was the introduction of ionothermal synthesis. This invention strongly widened the already vast area of carbon nitride research as it provided a highly crystalline material without the need for special pre-operational adjustment or chemical gimmicks. Simply prepared in a crucible within eutectic salt melt polytriazine imide yields hexagonal nanocrystals of layered triazine imide polymer with intercalated Li and Cl atoms. Depending on the eutectic salt melt used one could obtain various intercalated ions of alkaline metals and halides: chlorides and bromides. \[^{17,18}\] In plane organization forms a ring of six triazine imide subunits with the central void overlapped by chlorine. \[^{19}\] Stacking of the chlorine atoms and in-plane voids creates a channel within the crystal lattice, resembling the zeolite type motif.

Ionothermal approach was also proved to be useful in the preparation of heptazine-imide based carbon nitride with intercalated metal and halide ions. Ionothermal treatments of aminotetrazoles provided highly crystalline nanoparticles composed of the hexagonally symmetrical planar structures resembling original PTI (polytriazine imide). \[^{20}\]

Excellent periodic structure, usually unattainable for carbon nitride at regular thermal condensation conditions dragged much attention of material scientists, some of them already adapted it for gas filtration. \[^{21}\] Yet the photocatalysis remains to be the major utilization of PTI. It served as a photocatalyst for water splitting, alkane reduction, alkane oxidation, chromium reduction, and organic dye decoloration, with advanced activity compared to graphitic analog. However, PTI-LiCl bears the legacy of carbon nitride family: as-prepared material still has a low specific surface and comparatively wider bandgap. The major way to overcome this issue is a deposition of noble metals to create Schottky-junction for increased electron drainage.

A literature review on the PTI photocatalytic applications clearly shows the dominance of the single-step proton reduction to produce molecular hydrogen. \[^{22–24}\] On the other hand, the second major photocatalytic testing of PTI-based materials is a non-specific decoloration of organic dyes. \[^{19,25,26}\] Very few reactions with more than one step requiring higher selectivity have been reported so far. Those include solitary reports on alkene hydrogenation, \[^{27}\] cyclohexane, \[^{28}\] and benzyl alcohol \[^{29}\] oxidations. These studies show higher efficiency compared with graphitic carbon nitride. Worth mentioning is the cyclohexane oxidation did not require noble metal deposition on photocatalyst and the oxidation process was done by using pristine material, although benzyl alcohol oxidation and alkene reduction required doping with sophisticated Ni-based chelate and Pt nanoparticles deposition, respectively.

Inspired with the bare PTI-LiCl photocatalysis of cyclohexane selective oxidation we decided to develop similar photocatalytic material for another oxidation reaction of practical relevance. Investigation of UV-irradiated oxidation gives possibility to perform it under natural solar radiation without any other sources of energy—this is the most cheap and “green” way to perform chemical reactions. In the future for these processes there is no need in expensive equipment and also the wastes are scarce in contrary to industrial processes. The majority of commercial benzaldehyde (7000 tons per year) is produced through partial oxidation or chlorination of toluene—this is connected to waste formation and needs additional chemicals. \[^{30}\] Therefore, photocatalytic process is undoubtedly the highly promising and should be intensively developed.

2. Experimental

2.1 Chemicals

Melamine, Urea, Thiourea, Potassium chloride, and benzoic acid of analytical grade were purchased from Lenreactiv JSC. Anhydrous LiCl, p-benzoquinone, methanol, tert-butyl alcohol were purchased from ACROS. Benzyl alcohol and benzaldehyde of analytical grade were purchased from Chimmed Ltd. All reagents were used as received without purification.

2.2 Synthesis

Synthesis of the polytriazine imide (PTI) via ionothermal process was accomplished by previously
reported method. Anhydrous potassium and lithium chlorides were thoroughly mixed in eutectic weight ratio (11 and 9 gm, respectively) \(^{17}\) and then finely ground with the mortar with 4 g of the precursor. Flux was put into the crucible and heated in a furnace. (see heating programs on Figure S1, SI) Reference samples of graphitic carbon nitride (g-CN) based on the same precursors used for Ionothermal batch were synthesized via conventional annealing (powder method) using same heating program. Typically, 20 g of precursor were carefully ground in mortar, put into the crucible, covered with lid and thermodally treated. 

Obtained samples were yellow or pale-yellow powders (see Figure S2, SI). Sample codes of X_Y type were used, where X stands for the precursor used = M(melamine), U(urea), T(thiourea), MU(melamine/urea 50/50), MT(melamine/thiourea 50/50); and Y stands for E—eutectics or P—powder (Table 1).

### 2.3 Characterization

Morphology of materials was studied with Scanning electron microscopy (SEM) using JEOL JSM 7001F. Porosity characteristics were evaluated by \( \text{N}_2 \) adsorption at 77K using an ASAP 2020 Micromeritics apparatus. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer working at Cu K\( \alpha \) radiation (\( \lambda = 0.154 \text{ nm} \)). A Jeol JEM-2100F transmission electron microscope (TEM) equipped with a field emission gun (FEG) was applied for TEM observations. Elemental analysis was performed on a 2400 Elemental Analyzer (PerkinElmer Inc.). Fourier transform infrared (FTIR) spectra were collected using a Shimadzu IR Affinity spectrometer. UV-spectra recorded with Shimadzu UV-vis 2700 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed using monochromatic X-ray source XM1000 mounted on OMICRON ESCA+ spectrometer (Omicron NanoTechnology, Taunusstein, Germany) with the Al-anode (the radiation energy 1486.6 eV and power 300 W (15 kV, 20 \( \mu \text{A} \))). Photoluminescence spectra of the investigated samples were obtained at ambient temperature with an Ocean Optics Maya 2000 Pro CCD spectrometer sensitive within 200–1100 nm. A 365 nm CW LED laser was employed as the excitation source. Electrochemical impedance spectroscopy (EIS) studies were performed with Novocontrol Beta System impedance spectrometer on frequencies: 100 mHz – 10 MHz. The complex impedance spectrum of the samples (\( Z_s = Z' - iZ'' \) (series equivalent circuit)) were measured with the impedance spectrometer Novocontrol Beta system in the frequency range \( 10^2 \) Hz–\( 10^7 \) Hz. \( ^{13} \text{C} \) and \( ^{15} \text{N} \) NMR spectra of carbon nitride were recorded on a Bruker Avance600 spectrometer at 150.9 and 60.8 MHz, respectively. Mott-Schottky plot was built with potentiostat-galvanostat Elins P 45X. Measurement conditions were the following: frequency = 1kHz, oscillating voltage = 10 mV, electrolyte used was 0.1 M \( \text{Na}_2\text{SO}_4 \).

### 2.4 Photocatalytic experiment

The photocatalytic performance of all the compositions was studied in the oxidation reaction of benzyl alcohol in acetonitrile medium in air. The reaction was carried out in a water-jacketed quartz reactor irradiated with eighteen 1 Wt. UV-diodes with sharp luminosity peak at 395 nm. (See Figure S3, SI) Reaction conditions were: initial concentration of benzyl alcohol, 2 mM; volume of a reaction mixture, 30 mL; a quantity of photocatalyst, 50 mg; temperature, 20 °C; involuntary purge with air or argon was excluded. Concentrations of benzyl alcohol (BA), benzaldehyde (BAl), and benzoic acid (BAc) were evaluated by the means of HPLC Shimadzu Prominence LC-20 apparatus with diode array UV detector. Photocatalytic reaction mixtures were analyzed without pre-derivatization. Precise description and layout of irradiation device, actinometry studies, calculation of Conversion, Yield, Selectivity, and Apparent Quantum Efficiency (AQE) are given in the Supplementary Information.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Melamine (4g)</th>
<th>Urea (4g)</th>
<th>Thiourea (4g)</th>
<th>Melamine/Urea 50/50 (2g/2g)</th>
<th>Melamine/Thiourea 50/50 (2g/2g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>M_P</td>
<td>U_P</td>
<td>T_P</td>
<td>MU_P</td>
<td>MT_P</td>
</tr>
<tr>
<td>Powder</td>
<td>M_E</td>
<td>U_E</td>
<td>T_E</td>
<td>MU_E</td>
<td>MT_E</td>
</tr>
<tr>
<td>Eutectic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Mechanistic studies were carried out with the addition of scavengers: tert-butyl alcohol was used as OH• radical scavenger, p-benzoquinone used as O₂•− scavenger, and methanol for “holes” utilization. Tert-butyl alcohol and p-benzoquinone were added in 20 mM concentration—this equals 20 uL per 30 mL reactor. p-benzoquinone concentration was lowered to 1 mM (3.24 mg per 30 mL reactor) to get rid of possible side reactions of hydroquinone formation under the irradiation. All scavengers are soluble in acetonitrile.

Photocatalytic experiment under solar light was kept on a bright day in September in 55th latitude. An experiment under the argon atmosphere was performed after a careful purge by pure argon for 15 min, argon was bubbled through the solution.

Evaluation of hydrogen concentration in the atmosphere of reactor after the termination of photocatalytic experiment was performed with the aid of Chromatec Crystal 5000 gas chromatograph supplied with a thermal conductivity detector. Probes of gases were taken by gas-tight syringe in the volume of 1 mL, probe separation proceed on NaX 60/80 zeolite chromatographic column, argon was used as carrier gas. The calibration graph was built on the basis of calibration gas mixtures.

3. Results and Discussion

3.1 Material characterization

PXRD analysis of both powder and ionothermal sample batches is presented in Figure 1 a,b shows the strong distinction in diffractometry profiles. Powder samples peaks appeared at 20 values of 12.8° and 27.7°, attributed to the (100) and (002) diffraction planes of the typical g-C₃N₄ motif composed of tri-s-triazine building blocks. The most intensive at 27.7 degrees corresponds to the stacking distance = 3.20 Å, while the weaker one at 12.8 degrees is the evidence of in-plane regularity with a period of 6.87 Å, and is attributed to a melon polymer chain motif. Urea and thiourea powder samples have (002) peak slightly shifted to lower angles demonstrating slightly increased interplanar distance.

Ionothermal samples, with the exception of thiourea based one, displayed a series of moderate to strong diffraction peaks with 20 at 12.0°, 20.9°, 24.2°, 26.6°, 29.3° and 32.2°, which could be ascribed to the poly (triazine imide) (PTI) phase (i.e., triazine-based CN), with major (100), (110), (200), (002), (102) and (210) planes, respectively. Small peak at 28.3° is appropriate to g-C₃N₄ (002) plane with a decreased distance in

![Figure 1.](image-url)
comparison to powder materials (0.316 nm). These phenomena occur because of enhanced interaction between layers.\textsuperscript{34}

Calculated unit cell dimensions are $a = b = 8.48$ Å, and $c = 6.69$ Å, which is a superstructure of the previously reported hexagonal structure.\textsuperscript{33} Peak (002) with the maximal intensity at $26.6^\circ$ corresponds to distance between C$_3$N$_4$ monolayers, which is equal to 3.33 Å. (100) diffraction peak at 12.0$^\circ$ is appropriate to the in-planar size of structure-forming triazine imide motifs, which is equal to 7.33 Å. M$_E$ and MT$_E$ samples exhibited the highest crystallinity. Urea and thiourea are less prone to form a highly ordered crystalline structure in eutectic LiCl/KCl solution than melamine. The main and most obvious feature of PTI is its higher degree of crystallinity, more ordered structure.

All CN samples FTIR spectra display three strong bands around 807/812 cm$^{-1}$, 1100–1700 cm$^{-1}$, and 3000–3600 cm$^{-1}$, which are ascribed to ring-sextant out-of-plane bending vibration of triazine units, the stretching mode of aromatic CN heterocycles, and the N–H stretching vibration, respectively.\textsuperscript{35} (Figure 1c, d) Major distinction separating eutectic and powder IR profiles are the peaks at 887 cm$^{-1}$, which arose from the characteristic bending vibration of tri-s-triazine units in powder batch.\textsuperscript{32} Wide absorption band at 2172 cm$^{-1}$ is the stretching mode of cyano groups, which appear in the eutectic conditions through the process of triazine ring rearrangement in harsh conditions of molten salts.\textsuperscript{32} Formation of cyano groups takes place on the borders of carbon nitride nanosheets, \textit{via} the transition from amino groups to cyano groups promoted by higher salt melt ionic strength.\textsuperscript{36} The presence of O–H bond is less pronounced in the eutectic material—this points to trace amounts of residual hydrogen and subsequently to a more condensed structure of PTI.

Combustion based elemental analysis shown in Table 2 confirms eutectic samples are close to theoretical elemental analysis of the fully lithiated polytriazine imide framework. Increased carbon to nitrogen ratio in ionothermal row is probably attributed to an embedded cyano groups. Powder samples elemental analysis confirms obtaining material with very close to that of polymeric melon structure.\textsuperscript{37} Oxygen share for both eutectic an powder materials is in the same level 1–4% atom. Despite the synthesis proceeds in the protective atmosphere of exhaling NH$_3$, the oxygen can fall within structure of materials from the precursors (which may be humid) and even bleed in small amounts from the leakages of lid.

NMR spectra of melamine based carbon nitride samples dissolved in the sulfuric acid are presented in Figure 2a, b. $^{13}$C peaks of M$_P$ sample matches well with previously reported spectra of g-C$_3$N$_4$.\textsuperscript{38} Three peaks at 152–160 ppm correspond to a heptazine corner atoms of melon and four peaks at 142–146 ppm are denoted to the bay atoms (Figure 2a). $^{15}$N spectrum survey of M$_P$ identified two signals at $-197$ and $-227$ ppm corresponding to tertiary nitrogens of heptazine. Peaks at $-243$, $-249$, and $-251$ ppm correspond to external secondary, tertiary, and primary amines, respectively. $-235$ ppm signal is attributed to a heptazine central nitrogen. Weak triplet at $-265$ ppm ($J = 91.2$ Hz) may refer to a protonated bridge amino groups (Figure 2b).

Different carbon and nitrogen spectra profiles have been obtained for ionothermal samples. Additionally, two weak triplets at $-283$ ($J = 96.4$ Hz) and $-289$ ($J = 96.4$ Hz) can be identified as protonated secondary (bridge) amines. Nevertheless, one can certainly

<table>
<thead>
<tr>
<th>Sample name</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Atomic C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_P$</td>
<td>35.46</td>
<td>0.78</td>
<td>61.81</td>
<td>1.22</td>
<td>0.67</td>
</tr>
<tr>
<td>U$_P$</td>
<td>34.03</td>
<td>1.98</td>
<td>59.88</td>
<td>3.71</td>
<td>0.66</td>
</tr>
<tr>
<td>T$_P$</td>
<td>33.80</td>
<td>2.09</td>
<td>59.80</td>
<td>3.31</td>
<td>0.66</td>
</tr>
<tr>
<td>MU$_P$</td>
<td>35.16</td>
<td>0.00</td>
<td>61.14</td>
<td>3.21</td>
<td>0.67</td>
</tr>
<tr>
<td>MT$_P$</td>
<td>35.11</td>
<td>1.81</td>
<td>61.20</td>
<td>1.38</td>
<td>0.67</td>
</tr>
<tr>
<td>M$_E$</td>
<td>27.87</td>
<td>0.39</td>
<td>47.50</td>
<td>3.19</td>
<td>0.68</td>
</tr>
<tr>
<td>U$_E$</td>
<td>27.77</td>
<td>1.05</td>
<td>46.63</td>
<td>3.38</td>
<td>0.69</td>
</tr>
<tr>
<td>T$_E$</td>
<td>26.93</td>
<td>1.84</td>
<td>44.01</td>
<td>3.16</td>
<td>0.71</td>
</tr>
<tr>
<td>MU$_E$</td>
<td>27.45</td>
<td>1.26</td>
<td>46.20</td>
<td>3.32</td>
<td>0.69</td>
</tr>
<tr>
<td>MT$_E$</td>
<td>27.70</td>
<td>0.46</td>
<td>47.00</td>
<td>2.79</td>
<td>0.69</td>
</tr>
</tbody>
</table>
distinct ionothermal and powder samples from each other based on their carbon or nitrogen nuclei resonances. Interestingly, a major spectral pattern of melamine and melamine-urea based carbon nitride samples within the powder preparation method was found almost identical for $^{13}\text{C}$ spectra and somewhat similar for $^{15}\text{N}$ ones (see Figure S5, SI).

SEM images of the carbon nitride samples revealed strong morphological differences between carbon nitride batches synthesized with different methods. Molten salt samples exhibited a curly folded tissue appearance, while powder samples presented rock-like morphology without a certain pattern (see Figure S6, SI).

TEM images of material, prepared from melamine in the eutectic mixture of salts demonstrate the hexagonal shape of particles with sizes of 50 nm (Figure 3a). Particles reveal ordered structure, separate lattice fringes may be seen. Eutectic materials, derived from other precursors (urea, thiourea, mixtures) have similar crystalline structures (see Figure S7, SI). Fast Fourier Transform (FFT) pattern demonstrated in Figure 3b. Distance between structure motifs equal to $1/1.18 = 8.48$ Å—this corresponds perfectly with unit cell dimensions, calculated on the basis of XRD pattern: $a = b = 8.48$ Å.

XPS 1s carbon spectra of MU_P and MU_E samples peak at 284.3 eV corresponds to the surface adventitious carbon (Figure 4). Another significant peak with binding energy value 288.0 eV corresponds to an sp2-hybridized carbon atom in the triazine ring ($\text{N}=\text{C}–\text{N}$). Less intensive peaks with binding energies 285.9 eV (powder sample) and 286.2 eV (eutectic sample) are attributed to different forms of carbon-oxygen bonds. The peaks at 284.9 (powder sample) and 285.1 eV (eutectic sample) are appropriate for different forms of carbon-nitrogen bonds, in the case of MU_E material this bond is triple carbon-nitrogen bonding.

Figure 2. NMR$^{13}\text{C}$ and $^{15}\text{N}$ spectra of sulfuric acid dissolved melamine-based samples.

Figure 3. HRTEM of the eutectic sample. a) microphotograph, b) Fast Fourier-Transform image.
interaction. Eutectic material contains higher share of carbon on the surface, accompanied with the higher share of oxygen (see Table S2, SI), therefore it may be assumed that surface of eutectic material is plenty of carbonyl and lactone functional groups.

N 1S spectra of the MU_P sample consists of 4 peaks. The most intensive peak at 398.6 eV is inherent for triazine nitrogen atoms, connected with carbon atoms (C=N–C). Another type of nitrogen atom, bridging between heptazine motifs—its peak is situated at 399.7 eV. Hydrogen connected nitrogen has peak at 401.0 eV. The last one at 404.1 eV appropriates to 4 coordinated N-atom, donating 1 electron from its free electron pair for the formation of a covalent bond with the neighboring carbon and acquiring a positive charge. Spectra for N 1S of MU_E material precisely deconvoluted into 4 peaks. The most intensive peak with binding energy 397.9 eV is inherent to nitrogen atoms of triazine rings (C=N–C). Peak at 399.6 is attributed to nitrogen atom,
bridging between two polytriazine rings.\textsuperscript{28} The peak at 400.7 eV corresponds to nitrogen involved in N-H bond.\textsuperscript{32} The absorption peak at 403.1 eV caused by 4 coordinated N-atom.\textsuperscript{32} It may be seen that eutectic material contains less amount of N–H bond and therefore the reduced share of hydrogen.

The oxygen 1s spectra of MU samples are deconvoluted into three peaks. The higher energy of 532.9 eV corresponds to O–H bond of adsorbed water or surface hydroxyl groups.\textsuperscript{40} The most intensive peak at 531.8 eV corresponds to C–O–C double and the least intensive peak with binding energy 530.1 eV is attributed to double bond C=O.\textsuperscript{41} Eutectic sample spectrum also has three peaks with somewhat similar energies: 533.0 eV, 531.9 eV, 530.5 eV, with stronger C–O–C band peak due to enhanced share of surface oxidized carbon of surface functional carbonyl and lactone groups. K2P spectrum of eutectic material demonstrates the two major peaks at 292.1 and 294.9 eV, which is the typical binding energy of K\textsuperscript{+} ions\textsuperscript{32} included in the structure of carbon nitride material obtained through the eutectic procedure (Figure S12, SI). Peaks at 54.3 eV and for Li 1S 197.5 eV for Cl 2P are also present (Figures S13, S14, SI).

![Figure 5.](image)

UV-spectra of carbon nitride samples presented in Figure 5 a,b show major absorption cutoff below 450 nm. In some cases, UV-spectra demonstrate an additional weaker absorption edge in the range of 450–550 nm points. Only U_P sample spectrum reveals a single absorption edge, with the steep transition to absorbance band. UV-vis reflectance spectra of eutectic samples are rather diverse in adsorption edges, showing their profiles are strongly precursor dependent.

The major absorption edge was considered for the band gap calculation.\textsuperscript{42,43} In most of the powder samples band gap values are close to the theoretically calculated band gap for isolated heptazine-based monolayer (2.7 eV). M_E, MT_E samples exhibit a blue shift of absorption spectra and, hence, the rise of band gap values to 2.80–2.87 eV, as PTI-based CN is known to have an absorption edge at lower wavelength numbers.\textsuperscript{1} Several materials show additional optical absorption edges in the visible region of the spectrum, with bandgaps close to 2.20 eV for the powder samples and 2.30 eV for the eutectic ones, (see Table S2, Figure S8) and may be attributed to the stacking or coalescence of the structural units in CN.\textsuperscript{44} (Table 3)

Room temperature photoluminescence (PL) spectra depicted in Figure 5 c,d show a significant difference in radiative recombination of photoseparated charge carriers between powder and eutectic batches, in general compliance with previous reports.\textsuperscript{26,35,45}
Emission maximum of polytriazine imide-based CN samples are significantly blue-shifted from graphitic analogs with a 30 nm average shift. Urea samples demonstrated the strongest in-group redshifts of the emission maxima. All eutectic materials demonstrate lower rate of photoluminescence in comparison to powder ones. This obvious feature shows that more charges, formed in the eutectic materials successfully travel the reaction centers and participate in the chemical reaction.

Regardless of the synthetic approach, all synthesized carbon nitride materials demonstrate 2nd type low-temperature nitrogen adsorption isotherms, referring to mesoporous materials. (Figure 6a,b) Low-pressure nitrogen adsorption is weakly marked—this points to a low volume of micropores. All materials exhibit a hysteresis loop at pressures 0.5–1 P/P₀, which describes them as mesoporous materials. A significant rise of isotherm at P/P₀ pressures close to 1 point at the presence of macropores (>50nm). Higher volume of micropores is common, especially for melamine/urea–derived samples.

Lower volumes of micropores are attributed to the layered structure of CN. Curled and wrinkled nanosheets of carbon nitride have mesoporous-size voids whilst the majority of micropores are attributed to interlayer ranges, which are scarce. Materials with the highest mesopore volumes are melamine/urea and melamine/thiourea derived ones (Table 4).

Mesopore size distributions of both powder and eutectic materials show no interesting features, as they do not reveal any prevailing size (see Figure S9, SI). Meanwhile, the micropores distribution pattern strongly depends on the preparation method (Figure 6 c,d). All powder materials have maximum on 1,1 nm, while eutectic samples, on the other hand, exhibit maximum micropore distribution in the range of 0.8-0.9 nm. Smaller micropores with 0.75–0.90 nm

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band gap energy, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_P</td>
<td>2.62</td>
</tr>
<tr>
<td>U_P</td>
<td>2.80</td>
</tr>
<tr>
<td>T_P</td>
<td>2.63</td>
</tr>
<tr>
<td>M_E</td>
<td>2.84</td>
</tr>
<tr>
<td>U_E</td>
<td>2.65</td>
</tr>
<tr>
<td>T_E</td>
<td>2.56</td>
</tr>
<tr>
<td>M_E</td>
<td>2.67</td>
</tr>
<tr>
<td>MT_E</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Table 3. Band gap energy of synthesized samples, eV

Figure 6. (a, b) N₂ adsorption isotherms, (c, d) micropores size distribution.
sizes are identified as spaces between adjacent heptazine or triazine units of in-plane g-CN and PTI structures, respectively. 1.1 nm pores are inherent to the powder samples only—these are in-plane structural micropores, which are assumed as spaces between neighboring melon chains, connected by the hydrogen bonds. These pores are absent in the structure of eutectic materials because of the higher degree of crystallinity.

### 3.2 Photocatalytic studies

Photocatalysis studies of the PTI-LiCl obtained from different precursors were tested on benzyl alcohol oxidation in anhydrous aprotic UV-transparent solvent—acetonitrile—under irradiation of light-emitting diodes. Pristine carbon nitride was used without additional pre-treatment or doping. Before the photocatalytic experiment adsorption of benzyl alcohol on carbon nitride was studied for 1 hour without irradiation. Adsorption in the acetonitrile is negligible, (see Figure S10, SI) because of the higher eluting strength of acetonitrile.

After 5 hours of irradiation (Table 5, Figure 7) at room temperature most of the PTI samples exhibited at least 76% conversion with fairly high selectivity. The efficiency of powdered samples is significantly less than that of eutectic samples and is consistent with higher photoluminescence rate, higher porosity and significantly less ordered structure (XRD, TEM).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Specific surface area, m²/g</th>
<th>Mesopore volume, cm³/g</th>
<th>Micropore volume, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_P</td>
<td>26.6</td>
<td>0.112</td>
<td>0.008</td>
</tr>
<tr>
<td>U_P</td>
<td>47.2</td>
<td>0.122</td>
<td>0.015</td>
</tr>
<tr>
<td>T_P</td>
<td>12.8</td>
<td>0.049</td>
<td>0.004</td>
</tr>
<tr>
<td>MU_P</td>
<td>63.5</td>
<td>0.236</td>
<td>0.020</td>
</tr>
<tr>
<td>MT_P</td>
<td>40.8</td>
<td>0.167</td>
<td>0.012</td>
</tr>
<tr>
<td>M_E</td>
<td>43.5</td>
<td>0.131</td>
<td>0.013</td>
</tr>
<tr>
<td>U_E</td>
<td>53.5</td>
<td>0.056</td>
<td>0.017</td>
</tr>
<tr>
<td>T_E</td>
<td>39.3</td>
<td>0.107</td>
<td>0.012</td>
</tr>
<tr>
<td>MU_E</td>
<td>43.0</td>
<td>0.151</td>
<td>0.013</td>
</tr>
<tr>
<td>MT_E</td>
<td>53.8</td>
<td>0.141</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The yields of benzoic acid and was also evaluated by the means of HPLC. It was found that benzoic acid forms in small amount, in most cases not exceeding 4.1%. But there are 2 cases when benzoic acid forms in higher percentage—these are: anomalous T_E and most active MU_E. In both cases it was accompanied with highest reaction rates. Benzoic acid never appears in the beginning of the process, but it may be found only after the accumulation of benzaldehyde—therefore it may be assumed as the product secondary oxidation, which occur predominantly in dry solvent and with the presence of oxygen in the atmosphere. Other side products were counted indirectly—as the difference between the conversion and yields of benzaldehyde and benzoic acid. It may be seen that eutectic materials proceed more side products than powder materials. In each case it may be clearly seen correlation with the high reaction rate and side product yields. Side products were not separated and identified. According to the literature data benzyl alcohol photocatalytic conversion may proceed in oxygen free conditions with formation of: dibenzyl ether, 1,2-diphenyl-1,2-ethanediol, 2,3,5,6-tetraphenyl-1,4-dioxane. Presence of oxygen in the reaction atmosphere results in formation of additional compounds: benzoic acid, benzyl benzoate and benzaldehyde dibenzyl acetal. Despite such a variety of possible products, in the present reaction media benzaldehyde forms with high selectivity. Two steps of photoreduction
Table 5. Benzyl alcohol photooxidation after 5 h of irradiation using CN samples as photocatalyst.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BA conversion, %</th>
<th>BAl yield, %</th>
<th>Selectivity to BAl, %</th>
<th>BAc yield, %</th>
<th>Other products, %</th>
<th>Pseudo first order constant, 1/sec*10^-4</th>
<th>AQE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_P</td>
<td>30.5</td>
<td>28.1</td>
<td>92.1</td>
<td>1.1</td>
<td>1.3</td>
<td>0.20</td>
<td>0.105</td>
</tr>
<tr>
<td>U_P</td>
<td>49.2</td>
<td>43.3</td>
<td>88.0</td>
<td>2.9</td>
<td>3.0</td>
<td>0.36</td>
<td>0.161</td>
</tr>
<tr>
<td>T_P</td>
<td>51.2</td>
<td>43.8</td>
<td>85.5</td>
<td>3.5</td>
<td>3.9</td>
<td>0.41</td>
<td>0.173</td>
</tr>
<tr>
<td>MU_P</td>
<td>61.7</td>
<td>53.4</td>
<td>86.6</td>
<td>4.1</td>
<td>4.2</td>
<td>0.52</td>
<td>0.199</td>
</tr>
<tr>
<td>MT_P</td>
<td>46.8</td>
<td>43.0</td>
<td>91.9</td>
<td>2.5</td>
<td>1.3</td>
<td>0.34</td>
<td>0.161</td>
</tr>
<tr>
<td>M_E</td>
<td>76.8</td>
<td>67.0</td>
<td>87.3</td>
<td>0.8</td>
<td>9.0</td>
<td>0.75</td>
<td>0.251</td>
</tr>
<tr>
<td>U_E</td>
<td>85.2</td>
<td>72.5</td>
<td>85.1</td>
<td>3.2</td>
<td>9.5</td>
<td>0.86</td>
<td>0.271</td>
</tr>
<tr>
<td>T_E</td>
<td>97.9</td>
<td>72.8</td>
<td>74.4</td>
<td>11.8</td>
<td>13.3</td>
<td>1.65</td>
<td>0.272</td>
</tr>
<tr>
<td>MU_E</td>
<td>96.6</td>
<td>81.0</td>
<td>83.9</td>
<td>7.4</td>
<td>8.2</td>
<td>1.47</td>
<td>0.329</td>
</tr>
<tr>
<td>MT_E</td>
<td>86.3</td>
<td>72.0</td>
<td>83.4</td>
<td>1.6</td>
<td>12.7</td>
<td>1.09</td>
<td>0.269</td>
</tr>
</tbody>
</table>

BA—benzyl alcohol, BAl—benzaldehyde, BAc—benzoic acid.

Figure 7. The photocatalytic performance of the powder and eutectic samples.

Scheme 1. Photooxidation mechanism.
(Scheme 1) proceeds subsequently one after one without accumulation of free radicals after the first stage and their dimerization, etc.

Benzyl alcohol pseudo-first order oxidation rates using as-synthesized CN photocatalysts presented in Table 5. Both powder and the eutectic materials exhibit similar rates of selectivity, while the conversion is about twice higher for the eutectics. As both powder and eutectic materials have similar values of surface area (see Table 4) and negligible adsorption of benzyl alcohol (Figure S10, SI) the reason is better charges transfer which continuously feeds surface reaction sites. Apparent quantum efficiency AQE calculated based on actinometrical evaluation demonstrated a nice overall ability of the PTI catalyst activity. The calculation of ACQ was explained in the supplementary information, Figure S11, SI.

Photocatalytic material with the best performance MU_E was further investigated in reaction at different temperatures. For that, thermostated reaction mixtures were jacket heated at 0, 20, 40, 60 degrees celsius. Increased temperature positively influenced the kinetics, increasing rate of reaction with significant compromise in selectivity, making temperature rise undesired for the photocatalysis (Table 6).

The activation energy for benzyl alcohol oxidation was calculated using the Arrhenius equation \( E_a = kJ/mol \) (Figure 8):

\[
\ln(k) = \ln(A) - \frac{E_a}{RT}
\]  

Building the graph of the linearized Arrhenius equation in \( 1/T - \ln(k) \) coordinates activation energy is found as the slope of the trend line, taken with the reverse sign and multiplied by the gas constant \( R \): \( E_a = 12.1 \) kJ/mole (Figure 8). Therefore, an increase of temperature results in the rise of side reaction of benzoic acid formation from benzaldehyde as well as directly from the alcohol. Sharp rise of benzoic acid yield with the temperature ascends may be explained by the higher value of activation energy for benzaldehyde → benzoic acid equal to 25.1 kJ/mol (see Figure S15, SI).

Three cycles of regeneration were held for the most active photocatalyst MU_E. The conditions of experiment were the same: 30 mL of 2mM solution of BA and 50 mg of photocatalyst was put into the quartz reactor with the cooling jacket and irradiated for 5 h, after this photocatalyst was washed twice with pure acetonitrile and dried at 180 °C during 2 h, after this it was immediately put into the acetonitrile solution for the next run. For the sake of comparison, an analogous powder sample was investigated. The general trend for reused photocatalysts is the enhancement of BA conversion with the accompanying drop of selectivity for BAl. This phenomenon is strongly pronounced for the powder sample, which gains higher conversion and selectivity than those of the eutectic material after 3 cycles of regeneration. (Figure 9 a,b). This interesting phenomenon is not investigated and may be attributed to processes of photo corrosion, which affect positively the structure of photocatalyst. This is intriguing and needs further study of the evolution of photocatalysts’ structure in the process of UV irradiation.

For the sake of unveiling the mechanism of selective oxidation of benzyl alcohol set of experiment with radicals scavengers were performed (Figure 10). For

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Pseudo-first order constant, 1/sec*10^-4</th>
<th>BA Conversion, %</th>
<th>BAI Yield, %</th>
<th>Selectivity to BAI, %</th>
<th>BAc yield, %</th>
<th>Other products, %</th>
<th>AQE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01</td>
<td>87.6</td>
<td>79.3</td>
<td>90.5</td>
<td>2.7</td>
<td>5.6</td>
<td>0.296</td>
</tr>
<tr>
<td>20</td>
<td>1.47</td>
<td>96.6</td>
<td>81.0</td>
<td>83.9</td>
<td>7.4</td>
<td>8.2</td>
<td>0.329</td>
</tr>
<tr>
<td>40</td>
<td>1.92</td>
<td>100</td>
<td>74.8</td>
<td>74.8</td>
<td>18.0</td>
<td>7.2</td>
<td>0.279</td>
</tr>
<tr>
<td>60</td>
<td>2.69</td>
<td>100</td>
<td>52.4</td>
<td>52.4</td>
<td>34.2</td>
<td>13.4</td>
<td>0.196</td>
</tr>
</tbody>
</table>
In this study, the following compounds were used: tert-butyl alcohol as OH• radical scavenger, p-benzoquinone as O₂•– scavenger, and methanol for “holes” utilization. Under the addition of tert-butyl alcohol, the conversion of benzyl alcohol was the smallest, with a drop from 96.3% to 83.2% with almost negligible decrease in selectivity. This indicates that hydroxyl radical, known to be active in non-selective oxidation, does not play a significant role in the reaction mechanism. The absence of “holes” under the addition of methanol showed a noticeable drop of conversion from 96.3% to 67.8%, with no alteration in selectivity. Therefore, “holes” may be assumed as one of the main driving forces of reaction. The maximum effect among all scavengers is inherent to p-benzoquinone, with a drop of conversion from 96.3% to 67.5%, accompanied by a decrease in selectivity. Reduced quantity of superoxide radicals suppresses the selective oxidation rate and shifts reaction to the alternative directions and undesired products.

Reaction with solar irradiation gave the lowest and negligible conversion of 4.5% due to low intensity of UV irradiation of solar spectrum. The performance of experiment in the argon atmosphere resulted in a drastic drop of conversion. This is in good agreement with the proposed mechanism of photoreaction which is based on O₂•– radicals. Nevertheless, under anaerobic atmosphere, reaction does not stop at all because photocatalyst itself possesses the property for charge separation.

The above-mentioned mechanistic experiments were also subjected to evaluation of hydrogen content in the reaction medium (Table 7). The second column represents the square of hydrogen peak at the chromatogram, which was used for calculation of volume percentage of H₂. Calibration graph and chromatogram for H₂ evaluation are presented in the supplementary file (see Figures S16, S17). Only experiment with methanol addition demonstrated measurable quantities of hydrogen. Other experiments generated only trace amounts of H₂. Methanol addition leads to H₂ formation because of its strongly marked property...
as sacrificial reagent for hydrogen generation.\textsuperscript{54} Nevertheless, that hydrogen content is too low to assume H\textsuperscript{+} as the main oxidative moiety. This obviates that the oxidative function is owned by oxygen but not hydrogen.

Mechanism of selective photooxidation may be proposed as following: absorption of light causes charges separation, electron passes to oxygen molecule and leads to formation of O\textsubscript{2}•\textsuperscript{–} radical, “hole” oxidizes benzyl alcohol with the formation of radical and H\textsuperscript{+}. Subsequently superoxide radical reacts with benzyl alcohol radical and forms benzaldehyde (Scheme 1).

Photoseparated charge to surface transfer is the rate-limiting step of the photoreaction because it takes up to thousands times longer for charges to get to the surface than photoseparation itself, meaning charge mobility strongly affects photocatalytic activity.\textsuperscript{55} To observe difference in electric properties of these samples the Nyquist (Figure 11a) and Bode (Figure 11b) plots were plotted.

Bode plot shows that the phase shift (Δφ) between the probing voltage and the current flowing through MU_P sample is equal to −90° (practically in the whole frequency range) and modulus of impedance is linear function of frequency (in double logarithmic axes) concluding that MU_P capacitive response is typical for ideal dielectrics. The increase of Δφ in low frequency range could be explained by the influence of boundary effects (e.g. injection of elections from the copper electrode). The purely dielectric behavior MU_P is also clearly seen from Nyquist plot (Figure 11a). The part of the semicirc is probably originated owning to Maxwell relaxation process (discharge of the capacitor with the characteristic time τ = RC, R is resistance of the capacitor and C is its electrical capacitance).

Meanwhile, eutectic sample behaves rather different, exhibiting two processes associated with electric charge carriers motion, that is, charge carrier hopping between two sites in middle frequency range 10\textsuperscript{3}−10\textsuperscript{4} Hz, and the diffusion of charge carriers in the low frequency range 10\textsuperscript{−2} Hz–1 Hz (Figure 10). Significantly lower values of resistance inherent to MU_E compared to MU_P, point to increased charge mobility, confirming the stronger photocatalytic potential of the eutectic material.\textsuperscript{56}

Photocatalytic efficiency is highly affected by the positions of valence and conduction bands. Conduction bang edge potential was calculated via Mott-Schottky route as flat band potential. With this in view capacitance of double layer interface was measured by the impedimetric method and built as a plot versus the potential applied. Crossing between the slope of linear part of graph and absciss axis is known as flat-band potential.\textsuperscript{57} Resulting graphs represented on Figure 12.

Valence potentials were calculated using values of conduction band positions and band gap energies (see Figure 12b), potentials values are given versus SHE (standart hydrogen electrode). For both materials conduction band potential is more negative than H\textsubscript{2}/H\textsubscript{2}O reaction (0 V) while the valence band is more positive than water oxidation potential O\textsubscript{2}/H\textsubscript{2}O, +1.23 V. Accordingly to formation of benzyl alcohol radical. The band gap energies of materials are almost the same, while both potentials of MU_E material are 0.26 V shifted to the positive direction/ This fact points to the improved oxidative capacity of eutectic material including in particular ability for the formation of radical moieties of benzyl alcohol.

\textbf{Figure 11.} a) Nyquist plots of the MU samples; b) Bode plot of the MU samples.
4. Conclusions

Two CN allotropes g-CN and PTI-LiCl were synthesized based on 3 different precursors and two mixtures thereof. Thiourea found to be somewhat problematic in attaining PTI-crystalline lattice as its molten salt heating product strongly resembles graphitic analog. PTI materials, prepared via the ionothermal route exhibited smaller pore sizes that points to higher rate of.

Among five available precursors, melamine-urea mixture provided photocatalysts with the highest efficiency in terms of selectivity and conversion in both graphitic and PTI-batches, with AQE equal to 0.199% and 0.329%, respectively. Reaction of benzyl alcohol oxidation proceed with high selectivity to benzaldehyde with low amounts of benzoic acid and other side products, even in the atmosphere of oxygen. The optimal temperature was found to be 20 °C, enhance of temperature results in rise of benzoic acid yield—this reaction is highly sensitive to temperature.

Photocatalytic oxidation of benzyl alcohol using the pristine PTI based carbon nitrides shows superiority of benzaldehyde yield over graphitic analogs. Accordingly, EIS studies, conclude powder samples as dielectrics, with low charge mobility. Contrary, PTI materials have significantly lower electric resistance according to the Nyquist plot. Mott-Schottky study demonstrate 0.26 V positive shift of PTI valence band, which points to enhance oxidative potential of these materials. Better performance of eutectic materials is attributed to improved charges transfer, reduced recombination of charges.

Funding information

The work was financially supported by Ministry of Science and Higher Education of the Russian Federation, FENU-2020-0019.

Supplementary Information (SI)

Figure S1-S15 are available at www.ias.ac.in/chemsci.

References

2. Patnaik S, Martha S, Acharya S and Parida K M 2016 Overview on modification of g-c3n4 with high carbon containing materials for photocatalytic applications Inorg. Chem. Front. 3 336
10. Tong J, Zhang L, Li F, Wang K, Han L and Cao S 2015 Rapid and high-yield production of g-C3N4 nanosheets via chemical exfoliation for photocatalytic H2 evolution RSC Adv. 5 88149
spectra of carbon-nitride thin films: NEW insights from in situ XPS Carbon N. Y. 108 242
54. Li Y and Tsang S C E 2020 Recent progress and strategies for enhancing photocatalytic water splitting Mater. Today Sustain. 9 100032