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SUSTAINABLE JET FUELS FROM CO₂ BY MICRO-ALGAL CELL FACTORIES IN A ZERO WASTE APPROACH

ALFAFUELS

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1. Executive summary

This deliverable describes synthetic procedures and properties of possible photocatalysts related to the photochemical conversion of isoprene (the fuel precursor) into dimers (the jet fuel molecules) according to the planning in the ALFAFUELS project.

The objective of the deliverable was to synthesise materials based on graphitic carbon nitride (g-CN), a type of material with interesting properties as a photocatalyst for the dimerisation of isoprene. Six compounds were picked as interesting materials due to different properties of interest for the photocatalytic reaction.

All of the six materials were synthesised, purified, and processed to the form that would be required for the catalytic conditions. The materials were then also characterised by a variation of spectroscopic methods to validate that the correct materials had been obtained.

The synthesis of these materials allows for the further development of the photochemical reaction which is a key step in generating the final jet-fuel product.

2. Acronyms and abbreviations

<i>Term</i>	<i>Abbreviation</i>
Graphitic carbon nitride	g-CN
Polyheptazine imide	PHI
Rotations per minute	RPM
Ultraviolet-visible	UV-vis
Infrared	IR
Powderr X-ray diffraction	PXRD
Cyanide-modified graphitic carbon nitride	^{NCN} CN _x

3. Introduction

This document describes deliverable 4.1, focused on the synthesis of graphitic carbon nitride materials, one of the photocatalysts proposed in the ALFAFUELS project. To get the final jet fuel from the isoprene produced by the cyanobacteria, a key step is the light-induced dimerization process of isoprene. The photocatalyst that enables the dimerization reaction requires certain properties such as strong absorption of sunlight, good photostability, and a long-lived triplet state with the appropriate energy to facilitate the dimerisation reaction. Ideally, the photocatalyst should also be cheap, easy to prepare, and made from non-toxic materials so that the reaction is facile to scale up.

A class of photocatalyst that could fulfil all of the requirements are heptazine-based graphitic carbon nitride. These materials are easy to prepare by pyrolysis in an oven by using many cheap starting materials such as melamine and urea [1]. g-CN-based materials have the properties of being both very photostable and chemically stable while absorbing on the border of the visible light spectrum. While the g-CN materials have been mainly explored as photocatalysts for reduction reactions such as hydrogen evolution [2], they have also been shown to facilitate some triplet-based reactions [3,4].

The goal of this part of the project, performed during the first nine months, was to synthesise a wide array of possible catalyst materials. In the coming nine months they will be carefully tested as photocatalysts for the light-induced dimerisation reaction of isoprene, and the results will be described in report D4.2 at month 18. Figure 1 shows the structures of carbon nitride-type photocatalysts synthesised in this project.

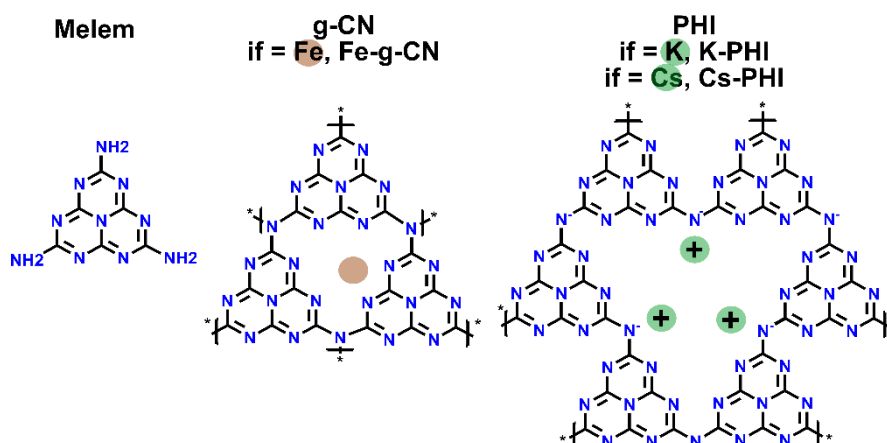


Figure 1: The chemical structures of the materials synthesised and characterised in this project.

4. Material synthesis

4.1 Synthesis of g-CN and derivatives

The synthesis of g-CN and its derivative materials follows a simple procedure. Melamine and possible additives were placed in an alumina vessel (1 x 2 x 5 cm) with a cover, the vessel was then placed in a tube oven with a continuous flow of nitrogen gas at 150 ml gas per minute. After 30 minutes of gas flow to equilibrate the atmosphere in the tube, the oven was heated to 550 °C at a rate of 2,5 °C per minute. The oven was then held at 550 °C for four hours before the temperature was returned to room temperature at the rate of 10 °C per minute.

The material was then washed with water by centrifugation at 4400 RPM five times, removing the supernatant and re-dispersing the material in fresh water every time. The material was then finally dried after washing the material with acetone.

Without any additives in the initial mixture, the material that is acquired this way is the heptazine-based g-CN, a powder with a dull yellow colour. Derivatives of g-CN can be synthesised by the inclusion of certain additives, such as salts, into the initial powder mixture or by mixing the g-CN powder with an additive and running the process in the oven yet again.

The samples were both directly used in their post-processed form and as nanoparticles prepared with planetary ball-milling. The ball-milling was performed with two 50 ml zirconium oxide (ZrO_2) jars both filled to about one-third with 1 mm ZrO_2 balls and five 5 mm ZrO_2 balls, 0,5 g of a g-CN material was added to the jars with 2 ml ethanol. The jars were then rotated at 600 RPM for two hours in five-minute intervals with 30-second breaks in between the intervals. The nanoparticles were subsequently separated with centrifugation.

4.1.1. Cyanide-modified g-CN

One of the variations of g-CN that has been reported to have a reactive and, long-lived, triplet state is the one having the addition of negatively charged nitrile groups in the structure ($^{NCN}CN_x$) [4]. This material was synthesised by mixing potassium thiocyanate salt (KSCN) with the g-CN powder and then running it in the tube oven again, first at 400 °C for one hour and then at 500 °C for half an hour, all the time under the atmosphere of nitrogen gas.

4.1.2. Polyheptazine imides

Polyheptazine imide (PHI) is the anionic version of graphitic carbon nitride. These materials have been of interest for their photophysical properties in literature including triplet sensitisation [3]. They can easily be synthesised by using large amounts of salt (ten times the mass of melamine) in the reaction mixture [5]. Two variations of PHI were prepared: one with potassium (K-PHI) and one with Cesium (Cs-PHI), by including their chloride salts in the reaction mixture (KCl and CsCl), respectively.

4.1.3. Iron-modified g-CN

Another promising variant of g-CN for triplet sensitisation is a variant modified with iron ions (Fe-g-CN) [6]. The preparation differs from that of basic g-CN in that Melamine and iron chloride ($Fe(III)Cl_3$) (6:1 mass ratio) were dissolved into water and heated to 80 °C while stirring, the water was then evaporated and the powder was put into the oven.

4.2 Synthesis of Melem

Melem is an intermediate in the thermal condensation reaction forming g-CN. The structure of Melem is a heptazine core with three amine groups at the tips, the formal name is 2,5,8-triamino-heptazine. In literature, Melem was shown to have a more stable and long-lived triplet state with a much smaller energy gap between the singlet and the triplet state allowing for higher rates of inter-system crossing (ISC) [7]. Melem was synthesised similarly to g-CN, starting with melamine and using an oven, but at a lower temperature, 425 °C for 6h.

5. Material characterisation

To verify that the materials synthesised were the target compounds, a variety of methods were applied to characterize them. Spectra and other characterization data are found in the appendix, and otherwise available from the WP4 leader (H. Ottosson) upon request.

To identify the crystal structures of the synthesised materials they were measured using PXRD (Figure 2). All of the materials show a peak at 28° which is the characteristic peak for the 2D layers of g-CN type materials. The amplitude of the peak differs strongly between materials, indicating that the degree of crystallinity and particle size varies among the materials. The highest degree of crystallinity seems to be in the basic g-CN material, with the largest signal-to-noise ratio.

To characterise the electronic properties and the bond structure of the materials, absorption spectroscopy was used to measure the UV-Vis and IR ranges. All of the UV-Vis absorption spectra show that the absorption starts in the range of 400-500 nm within the range reported in the literature (Figure 3). The most shifted into the visible part of the spectra is that of the $^{NCN}CN_x$ with absorption close to 500 nm and a bright yellow colour.

IR absorption (Figure 4, and 5) shows a broad band of absorption in the 3000-3500 cm^{-1} range as well as a multitude of peaks in the range of 1000-1750 cm^{-1} these two ranges of peaks are defining of g-CN type materials. The $^{NCN}CN_x$ structures as well as the PHI materials also have a peak around 2200 cm^{-1} which is the area of the nitrile stretching mode, showing that the modification was successful.

Finally, the emission properties of the materials were tested since they are a good sign of how the photophysics of the materials work. All of the materials are emissive, and the g-CN type materials are strongly emissive with the Fe-g-CN as the exception with considerably lower emission. All of these materials emit around 430-500 nm when excited at 400.

6. Conclusion

Six materials based on g-CN have been successfully synthesised; g-CN, $^{N}CN_x$, KPHI, CsPHI, Fe-g-CN, and Melem. All the materials were synthesised through similar methods based on pyrolysis under inert conditions. The materials were then purified from any residual starting material and processed into nano-particles. The materials were characterised by a variety of spectroscopic methods, showing comparable features to literature data and confirming that the target compounds had been obtained.

7. References

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8. Appendix

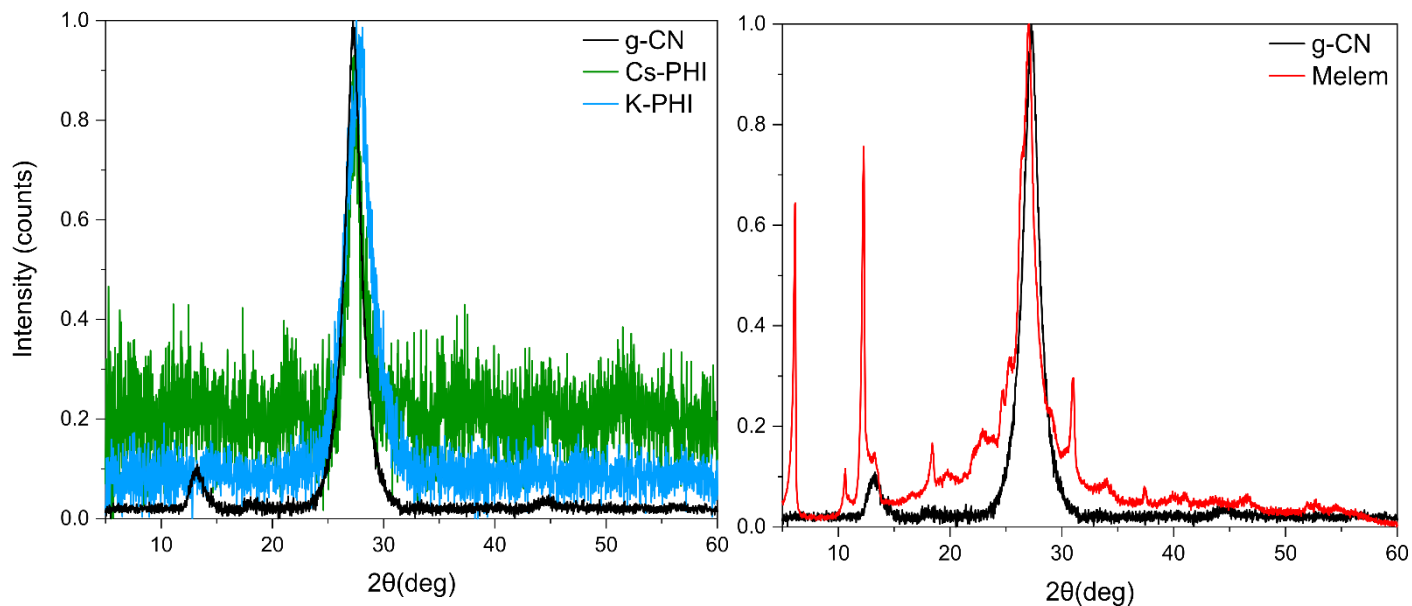


Figure 2: PXR D spectra of 4 of the materials, showing the signature peak at 28° for all of them with some extra features of melem.

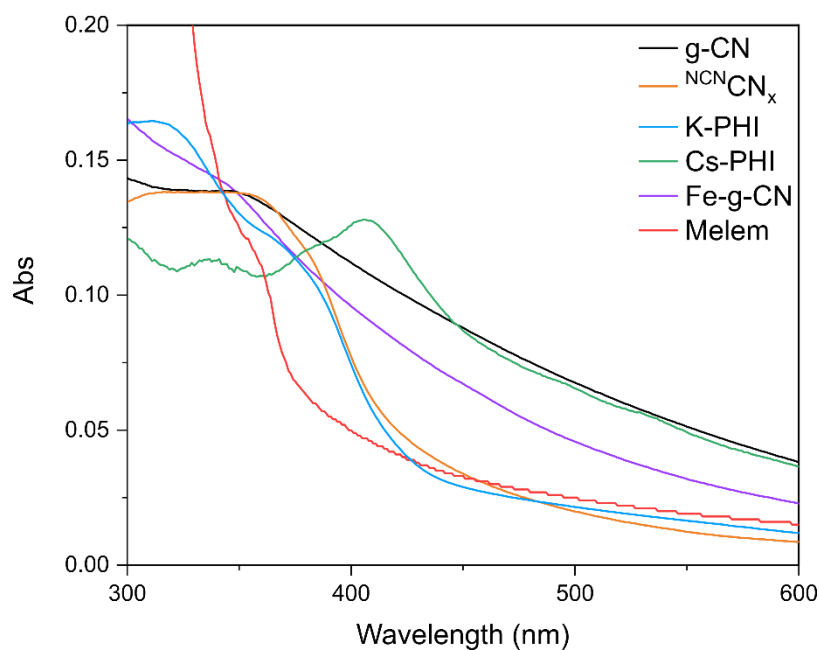


Figure 3: The UV-vis spectra of the six materials suspended of acetonitrile (DMSO for Melem), adjusted for scattering by zeroing at 800 nm.

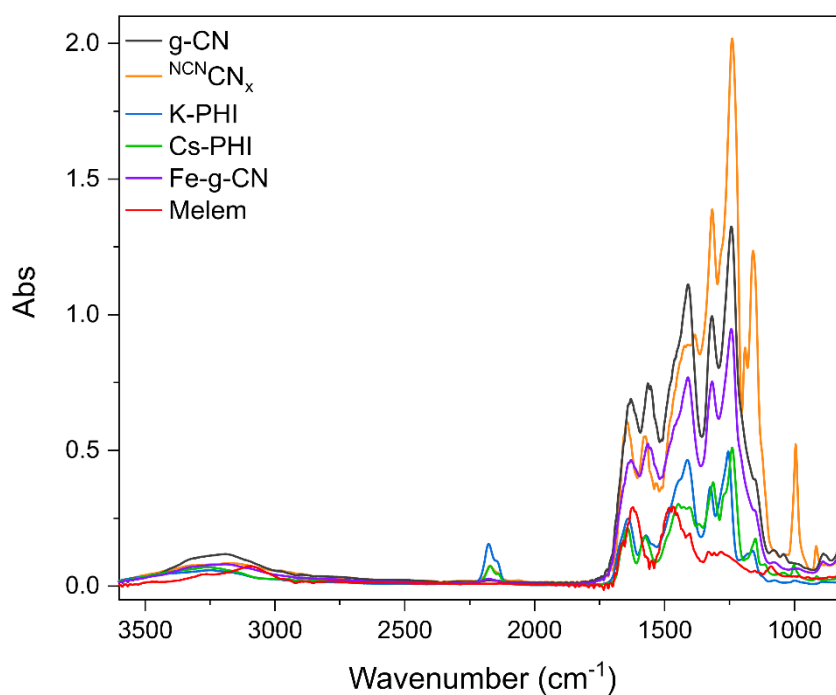


Figure 4: The full IR spectra of the six materials, with absorption bands in the 3000-3500 cm^{-1} range, 1000-1750 cm^{-1} range, and the CN stretching mode at 2200 cm^{-1} for a few materials.

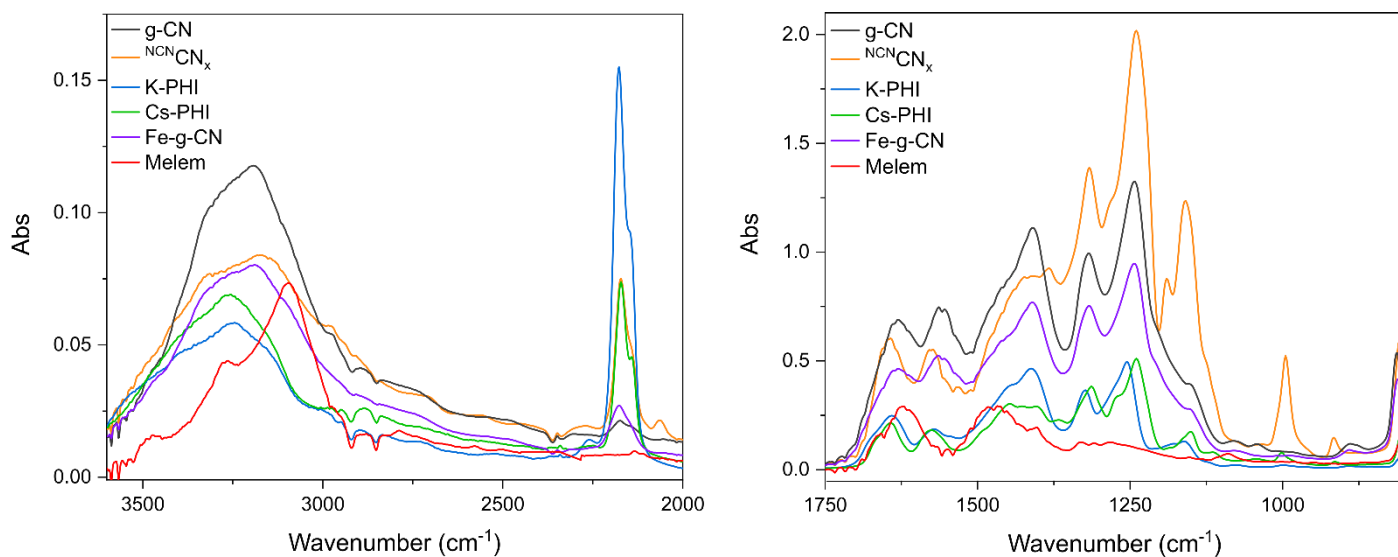


Figure 5: Zoom in on the IR spectra of the six materials. In the right figure: absorption bands in the 3000-3500 cm^{-1} range, and the CN stretching mode at 2200 cm^{-1} . In the left figure: The 1000-1750 cm^{-1} range.