Green Synthesis of Graphitic Carbon Nitride Materials using Pig Solids Waste and Urea: A Novel Artificial Photosynthesis

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The escalating global demand for energy has exacerbated environmental pollution and heightened the prominence of the greenhouse effect. In response, the scientific community is exploring alternatives for clean and renewable energy generation. This pursuit has led to the development and utilization of solar energy, with photoelectric conversion emerging as a primary and effective form through solar cells. Within these advancements, a novel class of materials known as graphitic carbon nitride (g-C_3N_4) has gained attention as a potential modulator to enhance the performance of conventional solar cells (Yang *et al.* 2021). Based on their unique structural and chemical properties, including semiconductor characteristics, high nitrogen content, and a tuneable porous structure, g-C_3N_4 materials show significant promise as electrode materials in energy conversion and storage devices.

Synthesized as 2D-polymeric materials from rich-nitrogen precursors like melamine or cyanamide, g-C_3N_4 production involves an environmentally friendly thermal condensation process. However, the utilization of hazardous and pollutant starting materials, even when urea is used as an alternative, raises concerns about waste generation and environmental impact (Rajeshwari *et al.* 2022). Exploring new raw materials is imperative to reduce the carbon footprint and waste associated with this promising material's production. The conversion of waste rich in nitrogen compounds, such as urea or nitrogen-containing compounds like NH_4^+, into g-C_3N_4 presents a valuable opportunity for waste valorization, aligning with the principles of a circular economy.

Currently, the disposal of residues from pig farms poses a substantial challenge in Europe and globally. Unexpectedly, these residues, owing to their high urea and nitrogen content, represent a promising option for synthesizing g-C_3N_4 (Yang *et al.* (2021). The integration of g-C_3N_4 as precursors for photoactive semiconductors and electron-conductive materials introduces a pioneering approach to microbial photo-electrosynthesis (photo-MES). This process, involving the recycling of waste materials from pig farms, has not been previously proposed, marking a significant step toward sustainable solid waste management and circular economy practices.

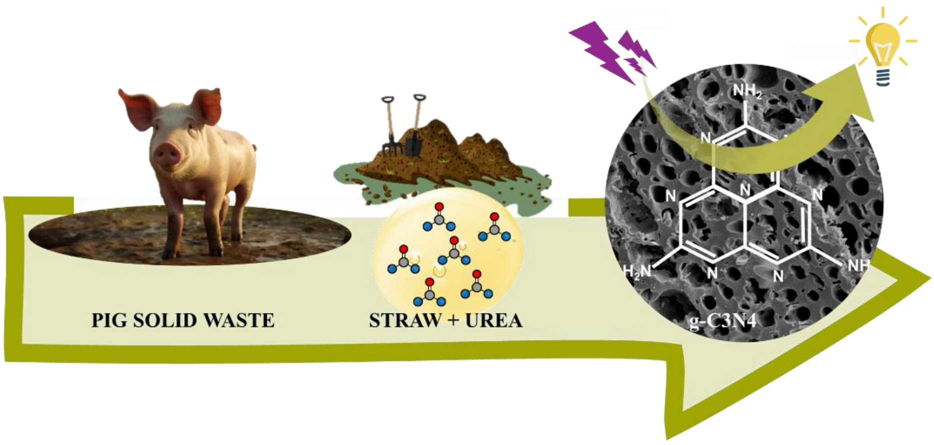

Figure 1. Graphic representation of the valorization process of pig solid waste into graphitic carbon nitride.

To synthesize graphitic carbon nitride (g-C_3N_4), a thermal method was employed, utilizing piggery wastes. The raw materials primarily consisted of lignocellulose material, straw, and residual manure. The synthesis was carried out in a typical furnace without the use of inert gases. Three different maximum synthesis temperatures were investigated: 420°C, 520°C, and 620°C. The synthesized g-C_3N_4 materials underwent comprehensive characterization, including elemental HCNS analysis with emphasis on achieving a desired C/N ratio within the range of 1 to 0.4. Additionally, SEM-EDX was employed to analyze the morphological and elemental composition of the materials. Also, UV–vis diffuse reflection spectroscopy was utilized to investigate the absorption spectra and define the activation wavelength for voltage generation. This process represents a crucial step towards advancing sustainable solid waste management by transforming waste from pig farms into valuable materials for energy applications.

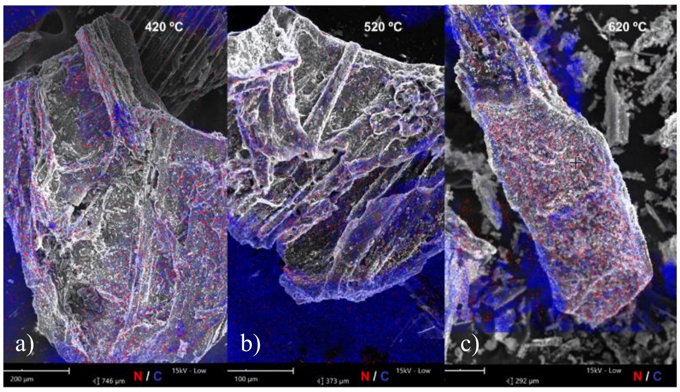

Figure 2. SEM-EDX picture of N-rich materials synthesized at (a) 420ºC, (b) 520ºC and (c) 620ºC.

After a heating process, the N-rich wastes are transformed resulting in condensed aromatic structures like melem, melam, melon, and ultimately g-C_3N_4. These synthesized materials exhibit the proper inclusion of nitrogen into the structure of the straw, Fig. 2 shows the SEM-EDX analysis corresponding to synthesized N-rich materials at 420ºC, 520ºC and 620ºC, where clearly it shows the well dispersion of N into the structure.

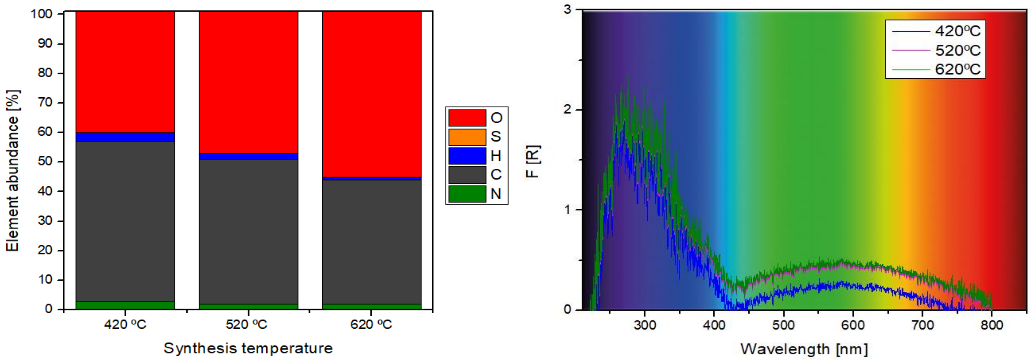

Figure 3. Elemental analysis (left) and UV–vis diffuse absorption spectra (right).

Based on the elemental analysis (Fig. 3 left), N is present in all three synthesized materials, although at temperatures of 520°C and 620°C, the percentage is slightly lower, only around 2%. As expected, carbon is the predominant element in all cases, with its percentage decreasing as the temperature increases. Based on the elemental analysis, the temperature of 620°C can be ruled out as the optimal temperature for g-C_3N_4 synthesis. Regarding the absorbance spectrum (Fig. 3 right), higher temperatures result in increased UV irradiation absorption due to a more ordered structure, evidenced by strong absorption peaks at 300 nm. The presence of straw in the formed materials leads to a reduction in the structural order of the aromatic chains. However, materials with high electrical conductivity are obtained, with conductivity increasing at higher temperatures. Considering all the analyzed parameters, the optimal synthesis temperature is found to be 520°C. This temperature allows achieving a high structural order (high electrical conductivity) without the volatilization of nitrogen.

In summary, g-C_3N_4 were successfully formed through a thermal process using piggery wastes for the first time. The results show that all the materials can be excited by light in the UV range. The described synthesis process, newly developed in this work, provides a new green-pathway to construct the materials based on g-C_3N_4 from waste from the pig industry.

Acknowledgements

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