3D printed structures for photo- and electro-chemical applications

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Highlights

- 3D printing of g-C_3N_4 structures via DLP and DIW at high loading.
- Up to 76.6% methylene blue removal in photocatalytic tests.
- Relatively high sensitivity for electrochemical Pb^{2+} detection.
- Stable multifunctional structures for pharmaceutical applications.

1. Introduction

Graphitic carbon nitride (g-C_3N_4), a metal-free polymer n-type semiconductor, has emerged as a promising candidate due to its distinctive electrical, optical, structural, catalytic and physiochemical properties, as well as its biocompatibility.(1) Since Wang et al. demonstrated the photocatalytic capability of g-C_3N_4 for H_2 and O_2 evolution in 2009, g-C_3N_4-based materials have been increasingly explored as multifunctional nanoplatforms in a vast range of energy and environmental applications, including photocatalytic and electrochemical conversion, electrochemical sensing, pollutant degradation,(2) CO_2 reduction,(3) hydrogen production, piezoelectric catalysis and many other fields, due to its good chemical stability, corrosion resistance, optical properties, environmental friendliness and lower cost. Additionally, with a relatively narrow bandgap of 2.7 eV, g-C_3N_4 exhibits strong visible light absorption, further enhancing its potential as an ideal photocatalyst for various applications, including water splitting, pollutant degradation, and carbon dioxide reduction.

Three-dimensional (3D) printing technologies have emerged as pivotal tools for the design and fabrication of complex geometries and devices that are easy to operate across multiple areas of application such as clean energy, environmental and sustainable chemistry.(4, 5) Considering these important aspects, in order to further enhance the efficiency of the C_3N_4-based photocatalytic materials, in this study we have integrated 3D printing, specifically Digital Light Processing (DLP) and Direct Ink Writing (DIW), into the materials fabrication process. Both the DLP and DIW methods presented in this work demonstrated facile 3D printing of structures with significantly higher catalyst concentrations of 5 wt% (for DLP) up to 88.5 wt% (for DIW), without employing the more complex engineered inline systems (blades and wipers) for mixing during the printing, broadening the scope of potential applications.

2. Methods

g-C_3N_4 powder was synthesised by thermal polymerisation using melamine as precursor. The procedure was described as follows: 5.0 g of melamine (Aldrich, 99% purity) were heated up to 550 ℃ for 6 h with a heating rate of 5 ℃/min in the air environment. The g-C_3N_4 nanosheets were obtained by thermal exfoliation of bulk g-C_3N_4 under He flow (100 sccm) at 550 °C for 3 h (10 °C/min). Mesoporous g-C_3N_4 was synthesised via thermal polymerisation of cyanamide using colloidal silica (Ludox AS-30) as template, followed by calcination at 550 °C (4 h) and subsequent silica removal in NH_4HF_2 solution.

To 3D print the different powders, in DLP two commercially available resins were used (The Standard Resin Neutral developed by Real, and the Water-Wash Resin developed by Anycubic), while for the DIW four different binders were tested (methyl cellulose (MC), hydroxypropyl cellulose (HPC), silica (SiO_2), polysulfone (PSF)).

3. Results and discussion

The photocatalytic performances of the synthesised C_3N_4 samples were evaluated based on their methylene blue (MB) removal efficiency after 180 minutes of irradiation (Figure 2). The low-performance category includes 3D printed bulk g-C_3N_4/MC and 3D printed mpg-C_3N_4/SRN, both of which exhibited less than 40% MB removal, indicating low photocatalytic activity. The averageperformance category consists of four samples: 3D printed mpg-C_3N_4/WWR with 55.3% MB removal, bulk g-C_3N_4 in powder form showed 63.4%, 3D printed g-C_3N_4 exfoliated (He)/WWR with 68.6% MB removal, while the best performing sample was the 3D printed bulk g-C_3N_4/PSF structure, with 76.6% MB removal (Figure 2). Additionally, the DLP 3D printed g-C_3N_4 composites were shown to have excellent sensitivity for the detection of a model heavy metal, Pb^{2+}, further enhancing their potential for applications in new areas, such as electrochemical sensors for other heavy metal ions.

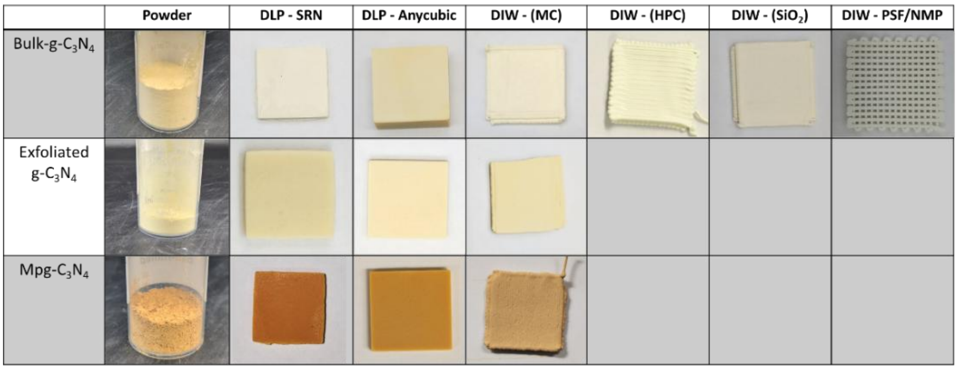

Figure 1. Various 3D printed formulations with different powders and DLP and DIW specific polymers/binders.

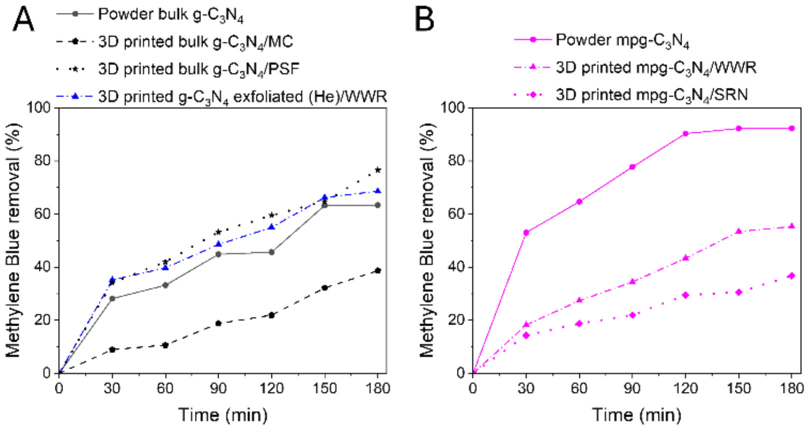

Figure 2. The percentages of the dye removal (Photodegradation + adsorption) using the 3D printed g-C_3N_4 formulations (panel A), mpg-C_3N_4 formulations (panel B) as well as the starting powders under solar simulator with the intensity of 1 kW/m^2.

4. Conclusions

Both the developed DLP and DIW formulations were printable into desired geometries with a high resolution. The resulting structures showed multifunctional properties and chemical stability that offer novel opportunities for the design of tailored systems and their deployment across diverse fields, including the chemical and pharmaceutical industries.

References

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Keywords

3D printing; DIW, DLP, g-C_3N_4; Photocatalysis.