Chemistry

Query paper:

Title: Polymeric Graphitic Carbon Nitride as a Heterogeneous Organocatalyst: From Photochemistry to Multipurpose Catalysis to Sustainable Chemistry

Abstract: Polymeric graphitic carbon nitride materials (for simplicity: g-C3N4) have attracted much attention in recent years because of their similarity to graphene. They are composed of C, N, and some minor H content only. In contrast to graphenes, g-C3N4 is a medium-bandgap semiconductor and in that role an effective photocatalyst and chemical catalyst for a broad variety of reactions. In this Review, we describe the “polymer chemistry” of this structure, how band positions and bandgap can be varied by doping and copolymerization, and how the organic solid can be textured to make it an effective heterogenous catalyst. g-C3N4 and its modifications have a high thermal and chemical stability and can catalyze a number of “dream reactions”, such as photochemical splitting of water, mild and selective oxidation reactions, and—as a coactive catalytic support—superactive hydrogenation reactions. As carbon nitride is metal-free as such, it also tolerates functional groups and is therefore suited for multipurpose applications in biomass conversion and sustainable chemistry.

Candidate papers:

1. **Title:** Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts

   Abstract: Graphitic carbon nitride, g-C3N4, can be made by polymerization of cyanamide, dicyandiamide or melamine. Depending on reaction conditions, different materials with different degrees of condensation, properties and reactivities are obtained. The firstly formed polymeric C3N4 structure, melon, with pendant amino groups, is a highly ordered polymer. Further reaction leads to more condensed and less defective C3N4 species, based on tri-s-triazine (C6N7) units as elementary building blocks. Due to the polymerization-type synthesis from a liquid precursor, a variety of material nanostructures such as nanoparticles or mesoporous powders can be accessed. Due to the special semiconductor properties of carbon nitrides, they show unexpected catalytic activity for a variety of reactions, such as for the activation of benzene, trimerization reactions, and also the activation of carbon dioxide. Model calculations are presented to explain this unusual case of heterogeneous, metal-free catalysis. Carbon nitride can also act as a heterogeneous reactant, and a new family of metal nitride nanostructures can be accessed from the corresponding oxides.

2. **Title:** Photodegradation of Rhodamine B and Methyl Orange over Boron-Doped gC3N4 under Visible Light Irradiation

   Abstract: Graphitic carbon nitride (g-C3N4) and boron-doped g-C3N4 were prepared by heating melamine and the mixture of melamine and boron oxide, respectively. X-ray diffraction, X-ray photoelectron spectroscopy, and UV–vis spectra were used to describe the properties of as-prepared samples. The electron paramagnetic resonance was used to detect the active species for the photodegradation reaction over g-C3N4. The photodegradation mechanisms for two typical dyes, rhodamine B (Rh B) and methyl orange (MO), are proposed based on our comparison experiments. In the g-C3N4 photocatalysis system, the photodegradation of Rh B and MO is attributed to the direct hole oxidation and overall reaction, respectively; however, for the MO photodegradation the reduction process initiated by photogenerated electrons is a major photocatalytic process compared with the oxidation process induced by photogenerated holes. Boron doping for g-C_3N_4 can promote photodegradation of Rh B because the boron doping improves the dye adsorption and light absorption of catalyst.

3. **Title:** Novel group 14 nitrides
   Abstract: In recent years, a lot of work has been focused on the synthesis of novel carbon nitrides, especially crystalline C_3N_4 phases. Numerous attempts to synthesise the theoretically predicted solids have been published. This review summarises the theoretical work as well as the attempts to prepare carbon(IV) nitrides by chemical and physical vapour deposition, and in particular on the concepts and results of bulk synthesis routes. Although very interesting materials have been obtained, a comprehensive characterisation of a crystalline C_3N_4 phase is still missing. In 1999, a novel class of nitrides, which posses the spinel structure, has been discovered. The synthesis and properties of the high pressure phases γ-M_3N_4 with M = Si, Ge and the first tin nitride γ-Sn_3N_4 are reviewed. Related oxide nitride spinel compounds, other ternary phases such as Si/C/N as well as subnitrides, sialons and amorphous phases are mentioned briefly.
4. **Title:** Origins, current status, and future challenges of green chemistry
   Abstract: Over the course of the past decade, green chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Significant progress is being made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable feedstocks. Current and future chemists are being trained to design products and processes with an increased awareness for environmental impact. Outreach activities within the green chemistry community highlight the potential for chemistry to solve many of the global environmental challenges we now face. The origins and basis of green chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world.
5. **Title:** Boron-and nitrogen-doped carbon nanotubes and graphene
   Abstract: Multi-walled, single-walled and double-walled carbon nanotubes as well as graphene can be doped with boron and nitrogen. B_2H_6 has been generally used as the boron source while NH_3 or pyridine is employed as the nitrogen source. Doping carbon nanotubes and graphene with boron and nitrogen brings about significant changes in the electronic structure and properties. Such doping not only results in desirable properties but also allows manipulation of properties for specific purposes. Doping with boron- and nitrogen-causes marked changes in the Raman spectra of the carbon nanostructures. In this article, we present the synthesis, characterization and properties of boron- and nitrogen-doped carbon nanotubes and graphene.
6. **Title:** Preparation and characterization of novel microporous carbon nitride with very high surface area via nanocasting technique
   Abstract: A novel microporous carbon nitride material (Mic-CN-1) with very high surface area and pore volume has been prepared for the first time by nanocasting technique using MCM-22 zeolite as a template through a simple polymerization reaction between ethylenediamine and carbon tetrachloride. The material has been thoroughly characterized by XRD, N_2 adsorption, TGA, HRSEM, HRTEM, XPS, FT-IR, and UV–vis spectroscopy. It has been found that the surface

area of the Mic-CN-1 is much higher than that of the parent template and the mesoporous carbon nitride. We suppose that the novel CN material with microporous structure could offer great potential for the applications, such as catalytic supports, gas storage, lubricants, the size selective adsorption of small organic molecules such as amino acids and vitamins.

Exemplary analysis:

1. **Relevance:** It discusses how different synthesis conditions lead to materials with varying properties, which is crucial for understanding how g-C3N4 can be tailored for specific catalytic applications. The query paper might reference this to support discussions on the polymer chemistry of g-C3N4, its texturing, and its use as a heterogeneous catalyst.
   Reason for Citation: This paper is likely cited because it provides foundational knowledge on the synthesis of g-C3N4, its structural variations, and its catalytic properties.
2. **Relevance:** This citation supports the claim that doping and copolymerization can enhance the photocatalytic efficiency of g-C3N4, aligning with the query paper's discussion on modifying band positions and bandgap for improved catalytic performance.
   Reason for Citation: The query paper might cite this study to illustrate the practical applications of modified g-C3N4 in photocatalysis, specifically in the degradation of pollutants under visible light.
3. **Relevance:** It might be used to highlight the unique properties and potential of g-C3N4 within the wider family of carbon nitrides, especially in terms of synthesis methods and the challenges in characterizing crystalline phases. This could help frame the significance of the query paper's focus on g-C3N4.
   Reason for Citation: This review could be cited to provide a broader context for the study of carbon nitrides, comparing g-C3N4 with other group 14 nitrides.
4. **Relevance:** It underscores the relevance of metal-free, stable, and functional group-tolerant catalysts like g-C3N4 in achieving sustainable chemical processes. This citation likely supports discussions on the environmental benefits and multipurpose applications of g-C3N4 in sustainable chemistry.
   Reason for Citation: Citing this paper helps the query paper position its research within the broader goals of green chemistry.
5. **Relevance:** It could provide a basis for understanding how boron and nitrogen doping alters the electronic structure and catalytic properties of g-C3N4, relevant to the query paper's exploration of doping and copolymerization techniques..
   Reason for Citation: This article might be referenced to discuss the effects of doping on the properties of carbon-based materials, drawing parallels between g-C3N4 and other carbon nanostructures.
6. **Relevance:** This citation could support discussions on the texturing of g-C3N4 and its implications for catalysis, particularly in applications requiring high surface areas like gas storage or the adsorption of small molecules.
   Reason for Citation: The query paper likely cites this work to highlight advanced methods for enhancing the surface area and porosity of g-C3N4, which are critical factors for catalytic efficiency.

Exemplary ranking: Ranked order: paper 1, paper 2, paper 3, paper 4, paper 6, paper 5

1. **Explanation:** This paper is foundational and provides a comprehensive background on g-C3N4, including its synthesis, structure, and catalytic properties. For a follow-up study, understanding these basics is crucial, especially if the research aims to explore further modifications or applications of g-C3N4. It sets the stage for discussing advancements or new insights in the synthesis and application of g-C3N4 as a catalyst.
2. **Explanation:** Given the emphasis on photocatalysis and the modification of g-C3N4 to enhance catalytic performance, this paper is highly relevant. It provides a specific example of how doping g-C3N4 can improve its photocatalytic activity, which is directly applicable if the follow-up research involves photocatalytic applications or the exploration of doping effects on g-C3N4.
3. **Explanation:** While this paper provides valuable context on the broader class of carbon nitride materials, it might be less directly relevant to a study focused specifically on g-C3N4 and its applications. However, it could still be cited for background information or to discuss potential comparative materials, making it less prioritized in this specific ranking but still important for a comprehensive understanding of the field.
4. **Explanation:** Aligning the research with the principles of green chemistry is essential, especially if the follow-up work focusing on the topic of continuing to emphasize sustainability and environmental friendliness of catalytic processes. This paper would be cited to frame the research within the broader context of green chemistry, highlighting the significance of developing sustainable catalytic materials like g-C3N4.
5. **Explanation:** This paper is relevant for understanding the broader context of doping effects on carbon-based materials, which is important for exploring similar modifications in g-C3N4.
6. **Explanation:** Given the emphasis on enhancing the catalytic efficiency of g-C3N4 through texturing and increasing surface area, this paper is relevant for research focusing on the physical manipulation of g-C3N4 for improved performance.