



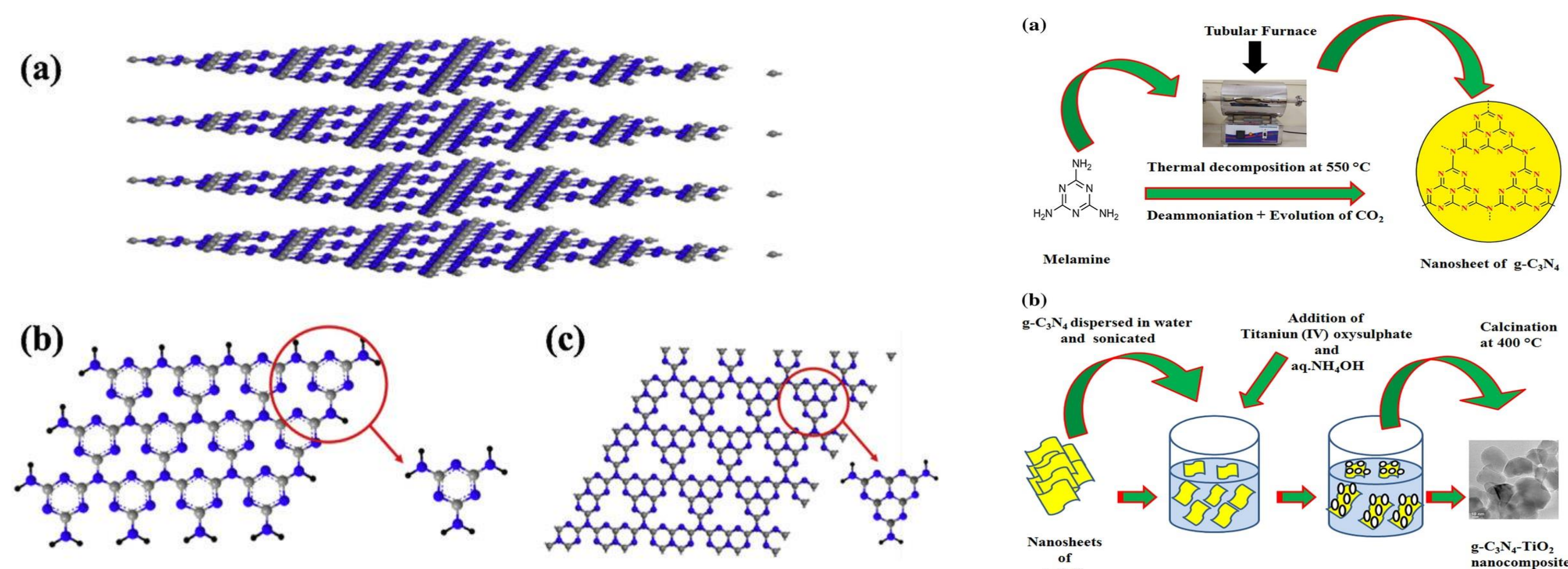
Structural and electronic modifications of g-C₃N₄ through nanostructure engineering applications in supercapacitors and photo-rechargeable devices

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Abstract

Graphitic carbon nitride (g-C₃N₄) has been applied in various fields such as photovoltaics, biosensing, and photocatalysis. As an analog of graphene, it has layers that can be transformed into different morphologies, including nanosheets, nanotubes, and quantum dots. In this paper, surface morphologies are described, and the applications of g-C₃N₄ in catalysis as a functional material to synthesize nanosized metal particles are discussed. We emphasize and elaborate on the underlying mechanisms in the photocatalytic activity enhancement of g-C₃N₄-based nanocomposites. Moreover, g-C₃N₄ exhibits a low specific surface area and a high rate of recombination of photogenerated charges, which enhances its applications in supercapacitors and photo-rechargeable devices.



Introduction

The pursuit of sustainable energy is driving the development of advanced technologies like supercapacitors (SCs), which offer high power and fast charging but suffer from limited energy density. Improving electrode materials is key to overcoming this. Transition metal oxides (TMOs) like Co₃O₄ provide high capacitance but are hindered by poor conductivity and stability, often addressed by forming hybrid conductive composites. Parallel interest exists in integrated energy harvest-and-store systems, such as photo-rechargeable devices, where graphitic carbon nitride (g-C₃N₄) is a critical material. This stable, 2D semiconductor has tunable electronic properties but is limited by low surface area and rapid charge recombination. To address these limitations, g-C₃N₄ is modified through nanostructure engineering (e.g., creating nanosheets and quantum dots) to increase surface area and active sites. Furthermore, forming heterojunction composites with materials like TMOs creates a built-in electric field that enhances charge separation and migration, boosting performance in both electrochemical and photocatalytic applications. This paper explores how such nanostructure engineering and modification of g-C₃N₄ create high-performance materials. We detail the synthesis of g-C₃N₄ nanostructures and examine the mechanisms by which these tailored nanocomposites overcome inherent limitations for use in advanced supercapacitors and photo-rechargeable devices.

Material

Graphitic carbon nitride (g-C₃N₄), a metal-free semiconductor with a two-dimensional (2D) structure has garnered significant attention in photoelectrochemistry due to its low cost, straightforward synthesis, and abundance of pyridine-like nitrogen atoms. It resembles graphene with stacked layers of tri-s-triazine (C₃N₃) or heptazine (C₆N₇) units. It has a suitable band gap of approximately 2.7 eV, enabling efficient visible light absorption (typically 460–475 nm), which is crucial for photo-rechargeable applications. g-C₃N₄ demonstrates excellent responsiveness to visible light, making it superior to other semiconductors and increasingly significant in photocatalytic technology.

Methodology

Graphitic carbon nitride (g-C₃N₄) is a two-dimensional semiconducting polymer with a graphene-like layered structure, composed of triazine (C₃N₃) and tri-s-triazine (C₆N₇) building blocks. These units form an sp²-hybridized network with a highly delocalized π -conjugated system, connected via nitrogen bridges. This structure imparts remarkable properties including excellent thermal and chemical stability, tunable electronic properties, biocompatibility, and facile synthesis.

g-C₃N₄ is typically synthesized from low-cost, nitrogen-rich precursors (e.g., melamine, urea, dicyandiamide) through thermal polycondensation at 500–600 °C. Weak van der Waals forces between layers and strong covalent bonds within each layer give rise to its honeycomb structure.

A major challenge for supercapacitor applications is improving energy density. Transition metal oxides such as Co₃O₄ are promising electrode materials due to their high theoretical capacitance (3560 F·g⁻¹), favorable crystal structures, and cost-effectiveness. However, poor conductivity limits their rate capability and cycling stability.

Common g-C₃N₄ preparation methods include thermal polycondensation and template-assisted synthesis (using hard or soft templates), which enables precise control over pore structure and specific surface area. Elemental doping (metal, non-metal, or co-doping) modifies the electronic structure and morphology, enhancing π -electron delocalization, visible light absorption, and charge carrier separation. Furthermore, forming heterojunctions or coupling with co-catalysts improves photocatalytic activity—e.g., by facilitating electron transfer in applications such as tetracycline degradation.

Application

Graphitic carbon nitride (g-C₃N₄) is a versatile material with attractive optoelectronic properties for applications in photovoltaics, biosensing, and catalysis, particularly for energy storage and conversion. Nanostructure engineering can significantly enhance its performance in supercapacitors and photo-rechargeable devices.

Supercapacitors

Supercapacitors (SCs) are crucial green energy devices known for fast charging, long life, and high power density [10]. While g-C₃N₄ composites are promising electrodes, pristine g-C₃N₄ suffers from low conductivity, a small surface area, and rapid charge recombination. Strategies to overcome this include:

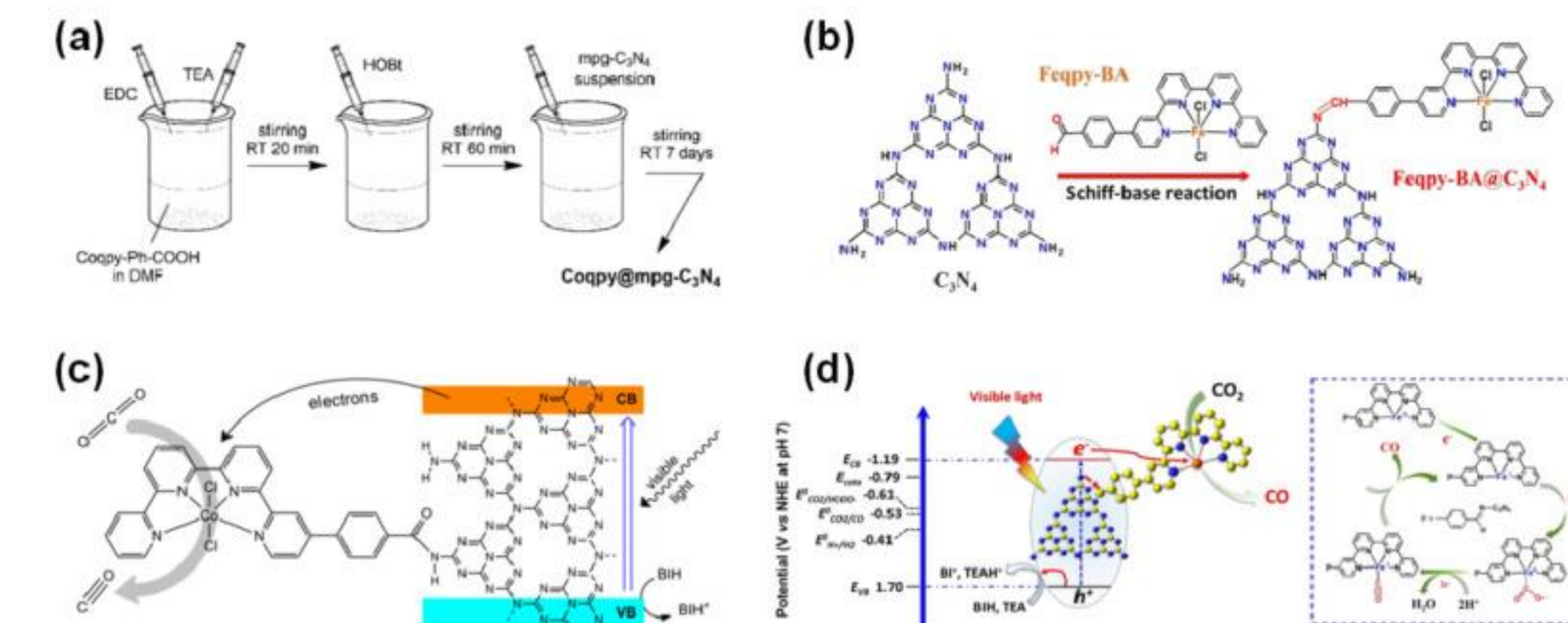
- Nanostructure design (e.g., porous structures) to increase surface area and active sites, achieving a high specific capacitance of 520 F g⁻¹.
- Heterostructure construction to create built-in electric fields that facilitate electron transfer. A Co₃O₄/g-C₃N₄ heterostructure demonstrated a specific capacity of 921.8 F g⁻¹ and, in an asymmetric device, a high energy density of 36.3 Wh kg⁻¹.
- Elemental doping to optimize the electronic structure and surface properties.

Photo-Rechargeable Devices

For photocatalytic H₂ and H₂O₂ production, the efficiency of pristine g-C₃N₄ is limited by charge recombination and low quantum efficiency. Enhancement strategies include:

- Nanostructure design (e.g., ultra-thin porous nanosheets) to increase surface area, active sites, and charge transfer, leading to a 22.24-fold enhancement in H₂ production.
- Elemental doping to tune the band structure and promote carrier separation, with oxygen-doped g-C₃N₄ showing a 9-fold increase in H₂ production.
- Heterostructure construction (e.g., Z-scheme junctions) and cocatalysts (e.g., Au nanoparticles) to improve charge separation, increasing H₂ production rates by up to 111.4 times.
- Piezoelectric photocatalysis, which combines light with mechanical stress to generate a piezoelectric field that drives charge separation. This boosts H₂ production and enables H₂O₂ synthesis at yields up to 4.86 mmol·g⁻¹·h⁻¹, even in the dark with ultrasound.

These strategies address the intrinsic limitations of g-C₃N₄ for advanced applications in energy systems.



Result

Nanostructure engineering has overcome key limitations of g-C₃N₄, such as low conductivity and rapid charge recombination, enhancing its performance in supercapacitors and photo-rechargeable devices.

Supercapacitors

- A porous g-C₃N₄ layer achieved a specific capacitance of 520 F g⁻¹ and stable performance over 10,000 cycles.
- Co₃O₄/g-C₃N₄ heterostructures showed a specific capacity of 921.8 F g⁻¹ (82.88% retention after 10,000 cycles) and an energy density of 36.3 Wh kg⁻¹ in an asymmetric device.

Photo-Rechargeable Devices

- Doping: Elemental doping increased hydrogen production rates by up to 104-fold.
- Nanostructuring: Ultra-thin nanosheets increased surface area by 26-fold and hydrogen production by 22.24-fold.
- Heterostructures: Z-scheme heterojunctions and cocatalysts boosted hydrogen production by up to 111.4 times.
- Piezocatalysis: A g-C₃N₄/PCN-224 heterojunction achieved an H₂O₂ yield of 4.86 mmol·g⁻¹·h⁻¹ under light and ultrasound, with activity in the dark. The highest reported H₂ production rate was 5464 μ mol·h⁻¹·g⁻¹.

Conclusion

Graphitic carbon nitride (g-C₃N₄) is a versatile, low-cost semiconductor. Its limitations have been addressed through modifications like doping, heterostructures, and nanostructuring. These enhance performance significantly: supercapacitors achieved specific capacities up to 921.8 F g⁻¹, and photocatalysis saw hydrogen production rates increase by over 100 times. Piezoelectric catalysis further enabled high H₂ and H₂O₂ production even in the dark. Remaining challenges include scalability, long-term stability, and understanding underlying mechanisms. Future work should focus on computational design, multi-strategy approaches, and multi-field coupling systems to enable industrial applications.

Reference

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