Design and development of Boron-doped graphene materials for environmental applications

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Introduction

Boron engineering of graphene-based materials has emerged as a powerful approach to modulate the intrinsic physicochemical limitations of pristine graphene.[1] While graphene exhibits outstanding electrical conductivity and high specific surface area, its chemically inert basal plane restricts its performance in catalysis, photocatalysis, sensing, and environmental remediation.[2] Substitutional boron doping introduces electron-deficient sites within the carbon lattice, alters charge density distribution, induces p-type characteristics, and generates structural defects that act as catalytically active centers.[3] Such electronic and structural perturbations have been shown to significantly enhance electrochemical activity, surface reactivity, and pollutant degradation efficiency, highlighting boron incorporation as a key strategy for next-generation graphene-based environmental materials.[4] In this work, we develop a systematic materials platform spanning low, medium, and ultra-high boron concentrations in two-dimensional carbon frameworks. Three distinct classes of boron-containing graphene-based materials were synthesized, spanning a broad compositional range from ~1.6 and ~6.5 at% up to 50 at% boron. Beyond conventional boron-doped graphene systems, we investigate a next-generation 2D boron–carbon material inspired by the Zintl phase CaB_2C_2, targeting the experimentally unrealized hydrogenated structure $H_2B_2C_2$. This graphene-analogue material, denoted as borographane, represents a boron-rich 2D network with anticipated high surface area and unique electronic properties. By bridging controlled boron doping with the development of a highly boron-enriched 2D framework, this study elucidates structure–composition–function relationships and advances the implementation of boron-engineered graphene materials in environmental technologies.
Among the contaminants that influence the hazardousness of wastewater, organic pollutants such as pharmaceuticals and dyes, as well as heavy metals are regarded as particularly concerning due to their toxicity, persistence, and potential to bioaccumulate in the environment. Thus, removing these dangerous substances from water is critical because they impair both human health and water quality. Several treatment techniques have been employed, but adsorption has shined out as an easy, efficient and effective method. As model pollutants Rhodamine B, Ketoprofen and Cr(VI) have been selected, due to their toxicity and persistence in wastewaters.

Experimental

Synthesis of B-doped graphene oxide (1.6 at% B). GO was synthesized from graphite via a modified Staudenmaier method .[5] The as-prepared GO was dispersed in water and ultrasonicated to ensure homogeneous suspension. Boric acid was added under continuous stirring, and the mixture was subsequently dried and thermally annealed under vacuum to promote boron incorporation into the graphene oxide framework. The resulting material was redispersed, acid-treated to remove residual boron oxide species, and thoroughly washed to obtain purified B-doped graphene oxide. [2]
Synthesis of B-doped graphene oxide (6.5 at% B). GO was dispersed in water and mixed with boron anhydride under ultrasonication to achieve uniform distribution of the precursor. The mixture was freeze-dried and thermally treated in a vacuum furnace to induce high-level boron doping. The final product was repeatedly washed with hot distilled water to eliminate residual boron oxide, as schematically illustrated in Fig. 1(a). [1]
Synthesis of Borographane (50 at% B). Borographane was pursued via a top-down route from the Zintl phase CaB_2C_2, synthesized by solid-state reaction of Ca, B, and C. [6] Calcium was removed by acid-mediated

deintercalation, followed by EDTA purification. The resulting layered boron–carbon material was exfoliated using biomolecule-assisted liquid-phase exfoliation (lysozyme, glucose oxidase, or caffeic acid), yielding stable aqueous dispersions without toxic organic solvents.

Results and Discussion

A systematic platform of boron-engineered graphene materials was developed, covering low (1.6 at%), medium (6.5 at%), and ultra-high (50 at%) boron concentrations. Low and medium boron-doped graphene oxide materials were successfully synthesized via solution-based and thermal annealing methods, yielding stable black powders with tunable structural and electronic properties (Fig.1a). Representative XRD patterns of pristine graphite, intermediate graphene oxide and the boron-doped graphene (6.5 at%B) are shown in Fig. 1b that reveal the successful synthesis. The novel boron–carbon 2D material, borographane, was obtained from the Zintl phase CaB_2C_2 (Fig. 1c) through acid-mediated deintercalation and biomolecule-assisted liquid-phase exfoliation, producing few-layer boron-rich nanosheets (Fig. 1d).

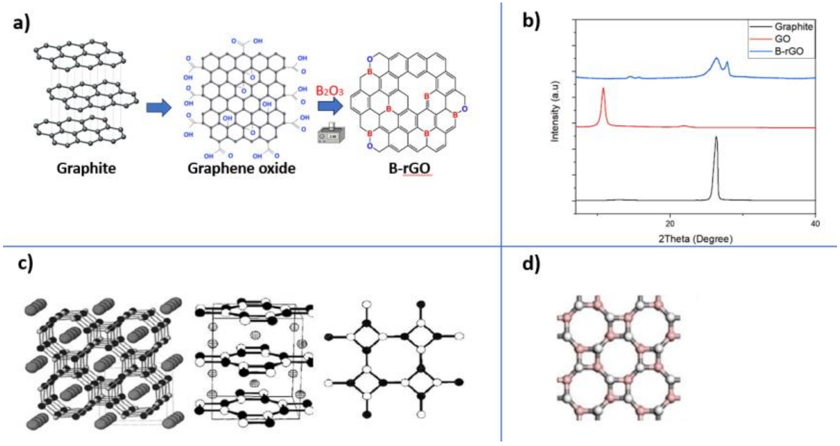

Figure 1. *(a)* Schematic illustration of the preparation of B-rGO. (*b)* XRD patterns of graphite, GO, B-GO. (c*)* Structure of CaB_2C_2 (crystallizes in I4/mcm with Z = 4). (*d)* Theoretical structure of $H_2B_2C_2$

In order to find the optimal conditions for the removal of the aforementioned pollutants, batch studies have been conducted, and several parameters have been examined. These include the effect of pH, contact time, initial concentration of the adsorbate, temperature and the dosage of the adsorbent. The results demonstrated a strong dependence on surface interactions, indicating favorable adsorption behavior. These findings can lead to a better understanding of the adsorption mechanism and the potential application of boron-doped graphene materials for environmental remediation.

Conclusions

This work demonstrates that precise boron incorporation enables controlled modulation of graphene-based materials and provides a foundation for advanced environmental applications, including catalysis, adsorption, and pollutant degradation.

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