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Review

Synthesis, decoration and properties of three-dimensional graphene-based macrostructures: A review

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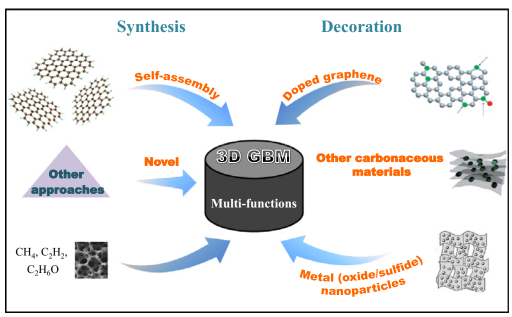
HIGHLIGHTS

- This review summarizes the synthesis, decoration and properties of 3D GBMs.
- Self-assembly, template-directed method and other novel approaches are introduced.
- Decoration operation includes doped graphene, co-construction, and incorporation.
- The structure and properties of 3D GBM are illustrated and emphasized.
- Provides theoretical guidance to design 3D GBM for applications in various fields.

GRAPHICAL ABSTRACT



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ABSTRACT

As the first two-dimensional atomic crystal, graphene possesses many superior physical and chemical properties and justifies its nickname of “miracle material”. The assembly of two-dimensional (2D) graphene nanosheets into three-dimensional (3D) macrostructures has gained great attention in the last four years, mainly due to their unique structures and superior properties. An increasing number of 3D graphene-based macrostructures (3D GBMs) with excellent functions has been reported for different applications. This review aims to provide an overview to summarize the structures and properties of 3D GBMs derived from diverse synthesis methods and decoration types. In the synthesis method section, the self-assembly method, template-directed method and other novel approaches are introduced according to the classification. We generalized the second part on decoration into three aspects, including doped graphene sheets within 3D GBMs, 3D GBMs co-constructed with other carbonaceous materials, and incorporation of metal (oxides/sulfides) nanoparticles into 3D GBMs, all of which endow 3D GBMs with new physiochemical properties. This work will provide theoretical guidance for the special design and synthesis of 3D GBM for applications in various fields, such as electronics, photonics, sensors and metrology, bioapplications, and environmental pollutant management.

Contents

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1. Introduction

As the first two-dimensional (2D) atomic crystal available, graphene possesses many superior physical and chemical properties, such as a large specific surface area [1], high electronic and thermal conductivity [2,3], excellent mechanical strength [4] and is readily chemically functionalized [5,6]. All of these characteristics justify its nickname of "miracle material" [7].

Before graphene was discovered by Novoselov and Geim in 2004 [8], there was a hypothesis about a hierarchical self-assembly process of 3D carbon foam from nanostructured graphite [9]. Subsequently, several 3D architectures based on other carbon nanomaterials were reported, such as carbon nanotubes [10,11]. However, graphene-based aerogels were firstly created until 2009 via freeze-drying by Vickery et al. [12] and Wang et al. [13]. Later, multifarious 3D graphene-based macrostructures (3D GBMs) were prepared using various methods aiming to develop their superior properties, such as low density, high porosity, large specific surface area, super hydrophobicity, excellent mechanical strength, and excellent electrochemical performance [14–17].

The assembly of graphene into 3D hierarchical architectures has been recognized as one of the most promising strategies for "bottom-up" nanotechnology and has become one of the most active research fields in the last four years [18]. With the tremendous ascent, 3D assembled macrostructures possess new collective physiochemical properties, which are remarkably different from both the individual building blocks and their bulk materials, which further extend their application capabilities [19]. Note that the majority of studies concerning 3D GBMs occurred in the last two years. The 3D network prevents aggregation and guarantees mass transport, consequently enhancing performance, offsetting the main disadvantage of nanoparticles in practical application [20]. In addition, another important advantage is the integrated morphology of a graphene-based monolith, which facilitates its manipulation and collection.

Hydrogels, organogels, and aerogels are the main forms of 3D GBMs usually as products of the self-assembly process, and aerogels are obtained from hydrogels and organogels via freeze-drying or supercritical CO_2 drying. Aliases such as graphene foam or graphene sponge are also used for 3D GBMs.

Much work has been performed to investigate the self-assembly of 3D GBMs and their various applications. Although there have been a few reviews on 3D graphene architectures [18,21–26], introducing their preparation, functionalization and application, this review aims to provide an overview on the synthesis and decoration of 3D GBMs, which mainly focuses on the structure–property relationship of 3D GBMs using various synthesis and decoration approaches, with the aim of providing a theoretical basis and technical guidance for their wide applications in the future, such as electronics, photonics, composite materials, energy generation and storage, sensors and metrology, bioapplications, and environmental applications [7,27–31].

2. Synthesis and structure of 3D graphene architectures

2.1. Self-assembly for preparation of 3D GBMs

2.1.1. Direct self-assembly of graphene oxide

Graphene oxide (GO) is preferred over graphene for preparing homogeneous aqueous suspensions as the precursor for 3D GBMs [31] because the abundant oxygen-containing groups on the GO surface result in a highly hydrophilic property and avoid the irreversible agglomeration of hydrophobic graphene [32]. In a previous study conducted by Li et al. [33], chemically converted graphene (CCG) was observed to self-gelate without any additional gelators

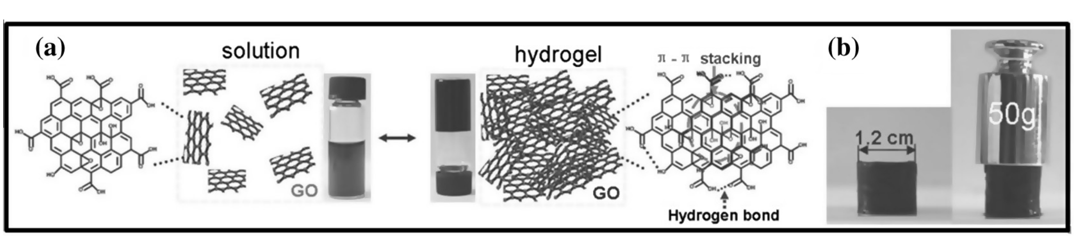

Fig. 1. (a) Proposed mechanism of the graphene oxide hydrogel (GOH). (b) Photographs of the strong GOH permitting easy handling and the ability to support weight. Reprinted with permission from Ref. [35]. Copyright 2012 Wiley.