



REVIEW

Three-dimensional graphene and their integrated electrodes



X.H. Xia¹, D.L. Chao¹, Y.Q. Zhang, Z.X. Shen, H.J. Fan*

School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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Summary Lightweight, flexible electrodes based on three-dimensional (3D) graphene have received increasing attention because of their application potential in electrochemical energy storage and conversion. Integrating 3D graphene networks with other active components endows electrodes with large capacity/capacitance, high energy and power densities, and ultrastable cycling at high rates. This review highlights the fabrication techniques for self-supported 3D porous graphene structures and their integrated electrodes with metal oxides/hydroxides for battery, supercapacitor, and oxygen reduction reaction applications. Merits and demerits of different preparation methods and the associated electrochemical properties are presented. General advantages of graphene-based integrated electrodes are discussed.

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Introduction

Electrochemical energy storage and conversion underpin the fast development of advanced power sources ranging from modern electronics to grid-scale applications. The performance of an electrochemical energy storage device is largely determined by the properties of active electrode materials, which, in turn, are influenced by a number of physicochemical properties (e.g., structure, composition and morphology). As the advancement of new active

materials and processing technologies, in recent years, the concept of lightweight, free-standing, and binder-free and additive-free electrodes has been adopted to boost the power/energy densities of electrochemical energy storage devices. In such a context, it is a straightforward idea to employ light, structurally robust, and highly conductive substrates.

Excitingly, graphene and its derivatives have become the “star” materials for the construction of integrated electrodes to boost the energy storage/conversion performance. This is because of their unique physical/chemical properties such as lightweight ($0.1\text{--}0.6\text{ mg cm}^{-2}$), high porosity (up to 99.8%), high specific surface areas ($\sim 2620\text{ m}^2\text{ g}^{-1}$), and fast mass/electron transport kinetics [1–3]. For the graphene-based integrated electrodes, free-standing superlight and highly conductive graphene architectures are smartly

* Corresponding author. Tel.: +65 6513 7408; fax: +65 6795 7981.
E-mail address: fanhj@ntu.edu.sg (H.J. Fan).

¹ These authors contributed equally to this work.

combined with the electrochemical active materials in an integrated architecture, in which structural features and electroactivities of each component are fully manifested, the interface/chemical distributions are homogeneous at a nanoscale, and a fast ion and electron transfer is guaranteed. The graphene-based lightweight integrated electrodes possess two main advantages as compared with traditional bulk forms. First, no extra preparation process of electrode and avoid undesirable supplementary interfaces (that is, polymer binders and additives). Second, weight advantage and fast reaction kinetics. The lightweight of graphene and its derivatives can effectively reduce the weight ratio of substrate and improve the energy/power density of the whole electrode. In addition, the 3D graphene networks show highly porous structure, which accelerates the reaction kinetics leading to higher energy/power density. In view of these excellent characteristics, the graphene-based integrated electrodes are triggering new research attention and playing more and more important role in the development of high-performance integrated electrodes.

In this review, we will review the recent progress made in the graphene-based integrated electrodes and their application in electrochemical energy storage and conversion. The article starts with preparation methods to different graphene and its derivatives with an emphasis on high surface area 3D network architectures. Our focus is free-standing ones; metal substrate supported graphene nanostructures are not in the scope of this review. After the preparation strategies, we will highlight a few examples of the graphene-based integrated electrodes as high-performance electrodes in batteries, supercapacitors and fuel cells. Finally, conclusion remarks and perspectives are offered. We hope this article provides snapshots of the recent development and future challenges of such unique type of electrodes toward commercial applications.

Preparation of free-standing 3D graphene networks

It is well known that the first graphene is prepared from bulk graphite by micromechanical exfoliation method [4]. Despite of high-quality graphene, this technique cannot meet the requirement for large-scale applications. Following this pioneering work, various alternative methods have been developed to fabricate graphene in large scale, including chemical vapor deposition (CVD), epitaxial growth, and chemical exfoliation of graphite [1,5–7]. The quality and structure of the as-prepared graphene materials are highly associated with the synthetic methods. Among them, scientific researchers start to focus on free-standing 3D porous graphene architectures, which are composed of interconnected graphene sheets (named as self-supported 3D graphene) or continuous interconnected foam structure (named as graphene foam (GF), or ultrathin graphite foam). Advantageous properties of these 3D graphene materials include high flexibility, lightweight, and high electron conductivity. Generally, the various fabrication methods can be classified into two major categories: “template” and “templateless” synthesis methods. We will present a few selected examples of these two methods and address their merits/demerits in the following sections.

Template synthesis of free-standing 3D graphene networks

About 20 years ago, Martin and co-workers demonstrated that template synthesis was a useful method to prepare nanostructured materials with specific structure and morphology [8]. Ever since then, considerable template-directed synthesis methods have sprung up and lots of template-synthesized nanomaterials have been reported for diverse potential applications [9,10]. The beauty is that the template-synthesized products show morphological and structural abundance because of the diversity of templates. The connectivity of the pores of templates strongly affects the final structure and morphology of products [10]. The template synthesis involves three main steps: (1) combing the reaction precursors with the template by impregnation or incorporation; (2) forming solid species on/in the template by reaction, nucleation and growth; (3) obtaining final products after removing the template. Usually, the template acts as a structure/morphology defining agent and can be utilized in various synthetic methods including chemical vapor deposition (CVD), hydrothermal/solvothermal synthesis, electrodeposition, sol–gel synthesis. Similarly, the template synthesis method is also applicable for preparation of self-supported 3D graphene architectures. So far, different templates (such as metal foam, binary metal foam, polystyrene spheres) have been adopted to fabricate 3D graphene architectures with controlled morphology and tunable properties.

CVD-template synthesis

In principle, CVD synthesis of 3D graphene architectures is the catalytic decomposition of hydrocarbon or small organic molecules with the aid of transition metal catalysts. To date, CVD is the most popular method for fabrication of free-standing 3D graphene architectures, especially for the self-supported GF, because of the high quality and low defects. The templates for the CVD-graphene architectures are mainly 3D porous metal (Ni or Cu) foams/films. The porous metal foams/films serve both as template and catalyst. It has been well demonstrated that the structure/morphology of the obtained 3D graphene architectures strongly depends on the metal template. Meanwhile, the carbon source for CVD-graphene architectures covers a wide range such as methane (CH_4), acetylene (C_2H_2) and ethanol. The reaction temperature for CVD-graphene architectures is usually quite high of 900–1100 °C, therefore, the hydrocarbon gas can be catalytically decomposed forming graphene structure on the metal foam templates during the CVD process.

Among all templates, the nickel foam is the most popular one for the construction of self-supported GF and has been dominating in current literature. In 2011, the Cheng group pioneered a CVD-synthesis of self-supported GF using nickel foam template (Fig. 1a–c) [12]. This work opened a new way for fabrication of novel lightweight and highly conductive substrates. The CVD-graphene via Ni foam template has been described as a two-step mechanism including a first stage of carbon atoms incorporation into the Ni substrate [13], followed by out diffusion onto the Ni surface to form graphene layers during the rapid cooling process.

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