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Template growth of porous graphene microspheres on layered double oxide catalysts and their applications in lithium–sulfur batteries

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ABSTRACT

The wise integration of individual two-dimensional graphene nanosheets into three-dimensional (3D) macroscopic architectures is essential for full exploration of their potential applications in electrochemical energy storage. Graphene microspheres (GMSs) with hierarchical porous architectures and high 3D electrical conductivities are highly expected to be the host carbon to accommodate sulfur cathode for lithium–sulfur batteries. Herein we reported the direct synthesis of GMSs assembled by 3D interconnected graphene with hierarchical pores by template chemical vapor deposition (CVD) on layered double oxide (LDO) microspheres. The LDO templates were derived from conformally calcined layered double hydroxide microspheres produced by spray drying. After methane-CVD, graphene was catalytically grown on LDO templates. Subsequent routine chemical etching of the LDO templates enabled as-obtained GMSs with a large diameter of *ca.* 11 μm and a high surface area of 1275 $m^2 g^{-1}$. The GMS was employed as carbon scaffold to accommodate sulfur for rechargeable lithium–sulfur batteries. An initial areal discharge capacity of 2.67 mAh cm^{-2} was obtained at a current density of 0.83 mA cm^{-2} on flexible GMS paper electrode with an areal sulfur loading of 2.5 mg cm^{-2}.

1. Introduction

Carbon materials have been extensively utilized in various electrochemical energy storage arouse by their diverse micro-/nanoarchitectures and extraordinary properties of covalent bonding [1]. Particularly, porous carbon obtained by organic casting methods on hard/soft templates afford abundant ion channels and very high surface area (>800 $m^2 g^{-1}$ in most cases) but poor electrical conductivity (less than 1 S m^{-1}). The sp^2 carbon (*e.g.* graphene, carbon nanotubes (CNTs)) delivers outstanding mechanical strength and very high electrical conductivity (larger than 100 S m^{-1}) but normally limited external accessible surface area due to its poor macroscopic dispersion. If the sp^2 carbon is rationally integrated into monolithic porous architectures with high three-dimensional (3D) electrical conductivity, their bulk applications will be further extended [2–5]. The involving complex material chemistry can also be revealed to fully demonstrate their potential properties in device scale.

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Spherical particles are widely accepted by material industries for batteries and supercapacitors. Active materials with a spherical shape are favorable to minimize viscous effects, increase integrating homogeneity, and display better electrochemical performance due to their shorter but more uniform diffusion pathway as well as better flow characteristics against other irregular anisotropic particles. Carbon spheres are highly concerned forrecently electrochemical energy storage. For instance, the use of silica hard templates as well as the extensive Stöber method [6] to prepare monodisperse carbonaceous nanospheres has been reported. Carbon spheres derived from resin with hierarchical porous nanostructures were emerging novel nanocarbon for advanced supercapacitors [7], lithium ion batteries [8], lithium–sulfur batteries [9], as well lithium–selenium batteries [10]. However, the graphitic domains in these carbonaceous nanospheres were always very small and their electrical conductivities were expected to be enhanced for better device performance.

Graphene, two-dimensional (2D) sp^2 carbon allotrope, has been strongly considered into macroscopic multi-dimensional assemblies as fibers, spheres, foam, sponges, and films toward multi-functional properties and vast applications [11,12]. Among a family of macroscopic graphene architectures, graphene spheres were highly concerned for their unique structures and emerging applications in energy storage, water treatment, environmental protection, composites, as well as biosensors [13–18]. For instance, Chen and co-workers reported the electrospray-assisted self-assembly of erythrocyte-like graphene microspheres with perfect exterior doughnut shape and interior porous network for rapid and recyclable removal of oil and toxic organic solvents from water [13]. Wang and co-workers fabricated porous pyrolyzed polyacrylonitrile–sulfur@graphene nanosheet with a size of 1–10 μm by spray drying with a very impressive performance for lithium–sulfur batteries [14]. Yan and co-workers firstly reported the facile synthesis of nitrogen-doped graphene microspheres *via* poly(methylmethacrylate)-assisted chemical vapor deposition (CVD) graphene growth on nickel microspheres and following urea-assisted hydrothermal reaction at 200 °C for nitrogen doping with a diameter of 5–10 μm for electrochemical biosensors of glucose oxidase [15]. 5–10 μm porous nitrogen/sulfur-codoped graphene-like microspheres were fabricated using nickel microspherical templates with poly(vinylpyrrolidone) carbon sources and $(NH_4)_2S_2O_8$ nitrogen/sulfur precursors for lithium ion batteries with superior capacity and cycling stability [16]. Jiang et al. explored the nitrogen-doped holey graphene hollow microspheres of *ca.* 200 nm through template reduction of graphene oxide on silica spheres for high rate anode materials of lithium ion batteries [17]. The use of spray-assisted deep-frying [18] and spherical hard templates (*e.g.* polystyrene [19], poly(methylmethacrylate) [20]) were efficient routes to assemble of graphene oxide into hollow graphene microspheres with unexpected properties and applications. Very recently, we proposed a mesoscale approach to fabricate graphene nanoshells with quite small diameters of 10–30 nm through a catalytic self-limited assembly of nanographene on *in situ* formed nanoparticles for high-rate lithium–sulfur batteries [21]. If the graphene microspheres (GMSs), especially with large surface area and high 3D electrical conductivity, could be bulk synthesized in a controllable manner, the ubiquitous properties and emerging applications of graphene monolith would be fully demonstrated, and the mechanistic insight into the synthesis of macroscopic graphene assembly could be detailed explored.

In this contribution, we reported the direct synthesis of GMSs assembled by 3D interconnected graphene with hierarchical pores by template CVD growth on layered double oxide (LDO) microspheres. The reason we selected LDO as templates was aroused from their catalytic activities for template deposition of graphene as well as high thermal stability during high-temperature CVD of CH_4 [22]. The compositions and topologies of LDO templates can be delicately mediated in a wide range, thus affording high tunability of graphene template growth. As illustrated in Fig. 1, spherical porous layered double hydroxide (LDH) assemblies were employed as the template precursors and then conformally calcined to obtain LDO microsphere templates. Graphene was organized and casted on the LDO catalysts through a high-temperature CVD of CH_4 while purified GMSs were obtained after facile chemical etching. The GMSs reported herein inherited a self-supporting nature from template microspheres and composed of 3D interconnected graphene nanocages and nanosheets. Lithium–sulfur batteries, an emerging electrochemical energy storage system with high theoretical energy density of 2567 Wh kg^{-1} held great practical promise while, however, were hindered by poor utilization of active materials, low efficiency, and undesirable service life [23–25]. Herein lithium–sulfur batteries were considered as a probe device to evaluate the performance of GMSs. The GMSs were

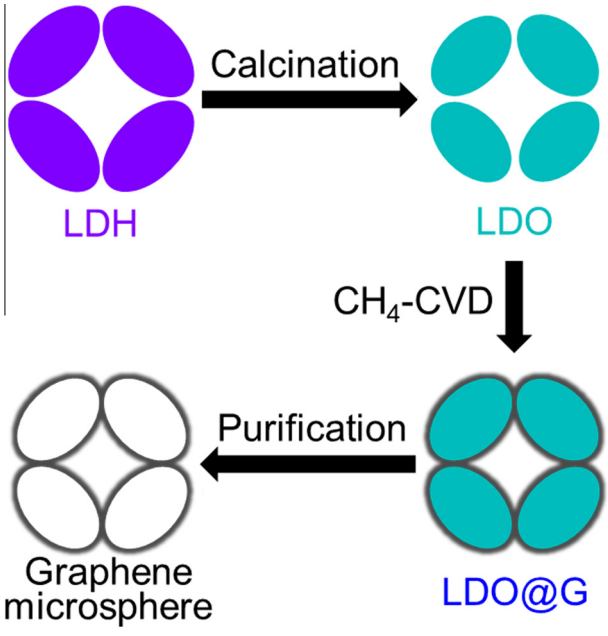

Fig. 1 – Scheme for the synthesis of GMS. A porous microsphere derived from the calcination of spherical LDH assembly was used as the template to cast graphene through CVD. The template was removed by chemical etching, whereas the graphene microsphere was preserved due to the 3D interconnected graphene networks. (A color version of this figure can be viewed online.)