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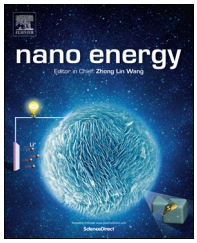

RAPID COMMUNICATION

High-throughput fabrication of strutted graphene by ammonium-assisted chemical blowing for high-performance supercapacitors

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Abstract
Three dimensional graphenes are most desired to deliver the unique nano-sized properties of graphenes to the macro-scale, yet their practical production remains insufficient. Herein we establish a general synthesis approach, *i.e.* ammonium-assisted chemical blowing *via* foaming sucrose into the bubble networks of sucrose-derived polymers, to effectively produce three dimensional strutted graphenes (SGs). SG consists of interconnected mono-/few-layered graphene membranes scaffolded by graphitic struts without restacking or agglomeration, which thus fully exposes the huge surface and possesses appropriate porosity. The SG is further

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applied as additive/binder-free electrodes for supercapacitors, which realize the high energy density of 50 W h kg^{-1} and the high maximum-power-density of 340 kW kg^{-1} due to the large surface area, excellent interconnectivity and porosity. The mass-produced self-supporting SG would open up a wide horizon and enable the abundant potentials of graphenes for promising large-scale applications.

Introduction

Supercapacitors, especially electrical double layer capacitors (EDLC), are promising energy storage devices for pulse charge/discharge and high power supply with 1 million cycle lifetime and low maintenance cost, which benefit from the rapid reversible adsorption and desorption of ions in porous electrodes [1]. Activated carbons have been dominantly used in industry as supercapacitor electrodes for their good conductivity, surface area, stability and low cost [2], although they suffer from the slow kinetics of ion transports in their small pores. Recently, graphenes have been widely explored as supercapacitor electrodes, yet their performances are also limited by laggard ion and electron transports due to the narrow channels of aggregated graphenes and contact resistances respectively. And the ion-accessible surfaces are reduced owing to the re-stacking of graphenes. Three dimensional (3D) graphenes could effectively provide interconnected architectures without those drawbacks, hence to actualize graphene-based energy storage as well as to simplify the device fabrication from a practical viewpoint [3-5].

Currently, the blooming 3D graphenes have been produced generally in three types: assembly of reduced graphene oxide (RGO), foams directed by chemical vapor deposition (CVD) and polymer-derived architectures. RGO hydrogels or aerogels were accomplished by the 3D assembly of graphene oxide coupled with simultaneous or subsequent reduction, by means of hydrothermal gelation [6-8], chemical reduction gelation [9], freeze-drying [10,11], solvent-mediated capillary compression [12,13], casting [14,15], filtration [16-18], breath figure lithography [19], 3D print [20,21], sacrificial templating [22-25], and functional linker/spacer/scaffold-incorporated assembly with organics [26-28], metals [29-31], nickel foams [32,33], carbon nanotubes [34-41], pyrolytic carbons [42], mesoporous carbons [43,44], or carbon weaves [45,46]. 3D graphene foams could be directed by templates, *e.g.* nickel foams, in CVD processes [47-49]. The polymer-derived 3D graphene architectures, strutted graphenes (SG) distinctively integrating continual graphitic struts and membranes, were recently developed *via* the sugar-blowing route [50]. The SG-based aqueous supercapacitors demonstrated the extremely high maximum-power of 1000 kW kg^{-1}. However, the synthesis route succeeding only based on glucose precursors needs to be extended to a general strategy for practical production of SG, and the aqueous supercapacitors with low operation voltage of 1 V and low energy density around 8 W h kg^{-1} needs to be improved [50].

Inspired by our previous work on the self-chemical-blowing method for making boron nitride foams [51] and the sugar-blowing method for making SG [50], herein we propose a general concept, *i.e.* ammonium-assisted chemical blowing, as the universal strategy for making SG. Ammonium-assisted chemical blowing relies on the polymers deriving from diverse sugar precursors such as sucrose and even household sugars coupling with the blowing agents of decomposable residue-free ammonium salts. It is capable of producing cost-effective SG on a large scale. The SG is further directly applied to supercapacitors in organic electrolytes to realize a high energy density of 50 W h kg^{-1}, by improving the operation voltage. In addition, the additive/binder-free SG-based supercapacitors sustain the high maximum-power-density of 340 kW kg^{-1} in the organic electrolyte, taking advantages of large surface area, multi-dimensional electron transport pathways, and minimized resistance of ion transports within bubble cavities of the SG. The electrochemically stable high-performance SG-based supercapacitors thus enable their admirable applications of quick discharging such as the instantaneous startup of electric vehicles.

Experimental section

Sucrose (Wako Chemical Co.) or household sugars was directly mixed with NH_4Cl and $(NH_4)_2CO_3$ with the mass ratio 1:1:1 and heated in a horizontal furnace to 1400 °C at a heating rate of 4 °C min^{-1} and annealed for 3 h under Ar atmosphere. The exhaust was cooled by water to deposit the ammonium salts. The morphology of products was characterized by a scanning electron microscope (SEM, Hitachi S-4800) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-3000F). The structures were characterized by electron energy loss spectroscopy (EELS, attachment of JEOL JEM-3000F), X-ray diffraction (XRD, Rigaku Ultima III) and Raman spectroscope (HORIBA Jobin Yvon T6400). The composition was characterized by an X-ray photoelectron spectroscope (XPS, Thermo Scientific Escalab 250Xi) after Ar^+ ion bombardment for 10 s. Nitrogen adsorption-desorption measurements were carried out at a liquid nitrogen temperature on Quantachrome Autosorb-1.

The SG-based supercapacitors were constructed of symmetric electrodes. The SG was tailored into pieces of 1 mg using a scissor, which were attached into 200 mesh steel grid collectors by folding four corners of steels. The two electrodes were immerged into 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$)/acetonitrile (AN) solution with the separators of 20 mesh cotton to construct a cell under the packaging pressure of 500 Pa. Neither binders nor additives were used here.

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