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Biomass derivative/graphene aerogels for binder-free supercapacitors

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ABSTRACT

Advanced self-supported electrode materials of various morphologies have recently presented bendable, stretchable and processable features with exceptional application potential in flexible and wearable energy storage devices. Although biomasses and related wastes as abundant natural sources are the ideal low-cost raw materials, their derivatives generally suffer from insufficiently electrically conductive or inadequately mechanically robust, which is generally required to be further processed into electrodes with binders and conductive agents. To break through such barrier, in this contribution, a universal approach is reported to manipulate the three-dimensional (3D) biomass-derived carbon networks into binder-free supercapacitors using in situ graphene aerogel. Such interfacial management has shown remarkable improvements in the chemical composition, surface area and pore size distribution, enabling the self-supported biomass-derived carbon network/graphene aerogel of hierarchical 3D interconnected structures to deliver considerable enhancement in the charge transfer and capacitive storage (up to 320 and 200 $F\,g^{-1}$ at 0.1 and 10 $A\,g^{-1}$, respectively). The results of the binder-free flexible all-solid state devices and electrical power based on three devices in the series circuit promise an exceptionally universal stage for engineering advanced energy storage devices with rich natural sources as well as recycling biomasses and wastes for extended applications.

1. Introduction

There is an increasing demand for energy storage with tremendous applications in portable electronic devices and electric vehicles, which requires advanced materials that are low-cost and large-scale in fabrication with high efficiency in energy storage [1–4]. Among the two typical capacitors of pseudocapacitors and electrical double-layer capacitors (EDLCs), carbon-based EDLCs are able to operate at relatively high charge and discharge rates with excellent capability in long-term sustainable energy storage [2,5].

In the past decades, biomass-derived carbon materials have drawn significant interest since such abundant natural sources could be easily converted into conductive carbon of great potential in energy storage, which highlights a low-cost and efficient approach for recycling and managing biomasses and derived wastes [6–9]. As typical examples, supercapacitor electrodes (usually assembled with binders and conductive agents) based on carbonization of chitosan and glucosamine [6], dead leaves [7], waste papers [8], and human hairs [9] have been explored separately, which indicates that high-performance supercapacitors can be constructed using these low-cost renewable sources.

Recently, EDLCs of binder-free electrodes are increasingly pursued owing to the unique advantages in the reduced cost, simple processing, facile dimensional design and full utilization of electrode mass via avoiding the additional process coupled with binders and conductive agents [10–13]. On this stage, electrically conductive graphene-based nanostructures have been fabricated into a variety of hierarchical configurations, including one-dimensional (1D) fibers [11], two-dimensional (2D) films [14–18] and three-dimensional (3D) frameworks [19–25], for achieving advanced binder-free electrodes with various morphologies. These variable self-supported electrodes of bendable, stretchable and processable features have shown exceptional application potential in flexible and wearable energy storage devices. For instance, Yu et al. have designed 1D hierarchically structured conductive carbon nanotube–graphene fibers of large specific surface area ($396\ m^2\,g^{-1}$) [11]. In the absence of binders, current collectors and separators, the as-fabricated fiber-like supercapacitors afford capacitance of 300 $F\,cm^{-3}$ (at 26.7 $mA\,cm^{-3}$ in a two-electrode cell) in the polyvinyl alcohol (PVA)/H_3PO_4 gel electrolyte, indicating great potential in multifunctional textiles and flexible energy devices. Apart from the employment of various spacers into graphene-based precursor solution for obtaining 2D pliable graphene-based film structures with the vacuum technique [15,18], recent advancement has been made in the utilization of 3D mechanically robust graphene-based frameworks to support electrochemically active nanoparticles, aiming to directly

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fabricating flexible electrodes of adequate charge transfer paths as well as providing sufficient electrical path for the hetero-particles [22–24]. In the work by He et al., graphene was grown with the assistant of Ni foams (as the templates), followed by depositing MnO_2 nanoparticles coupled with subsequently removing the Ni substrates. The as-fabricated flexible electrode composed of graphene supported MnO_2 nanoparticles offers a maximum specific capacitance up to 130 F g^{-1} (at 2 mV s^{-1} in 0.5 M Na_2SO_4 aqueous solution) with a power density up to 2500 W kg^{-1} [23].

Apparently, the essential criteria for achieving binder-free electrodes is the implementation of the interconnected porous matrices that are sufficiently conductive and mechanically robust simultaneously, thus allowing them to realize fast ionic and electronic transport processes without presence of additional binders or conductive agents [11,14–25]. Unfortunately, the major challenges in the biomass derivatives of active carbon mainly involve poor electrical conductance and insufficient mechanically robust. Consequently, they are generally required to be further fabricated into the mixed slurries with binders and conductive agents [6–9].

For addressing such bottleneck, here we demonstrate a simple and universal strategy to engineer the N-doped biomass-derived carbon networks (N–C-Networks) by in situ generating 3D interconnected graphene aerogel interfaces. The established hierarchical 3D interconnected structures impart substantially improvements in the chemical composition, surface area and pore size distribution via the synergetic effects. These exclusive features permits the self-supported N-doped biomass-derived carbon/RGO aerogel networks (N–C–RGO-Networks) to present substantially enhanced energy storage capability (specific capacitance of 320 and 200 F g^{-1} at 0.1 and 10 A g^{-1}, respectively) in the binder-free system, compared to the biomass-derived carbon (specific capacitance of 175 and 80 F g^{-1} at 0.1 and 5 A g^{-1}, respectively) under the same conditions. The associated opportunities based on the as-fabricated flexible all-solid state devices and supercapacitor power have been discussed, suggesting novel concept to effectively recycle and manage biomasses and wastes for extended applications.

2. Experimental section

2.1. Chemicals

Graphite powder was supplied by Sigma-Aldrich. Concentrated sulfuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 70%), sodium nitrate ($NaNO_3$, AR), potassium permanganate ($KMnO_4$, AR), hydrogen peroxide (H_2O_2, 38%), hydrochloric acid (HCl, 38%), ethanol (AR), hydroquinone (AR), melamine, urea and poly (vinyl alcohol) (PVA, M_w: $>80{,}000$, hydrolyzed) were purchased from Beijing Chemicals Co. Ltd.

2.2. Graphene oxide (GO)

GO was prepared based on the modified Hummers method. Briefly, commercial graphite powders (2 g) and $NaNO_3$ (1 g) were added into concentrated H_2SO_4 (120 Ml) in an ice bath and the mixture was kept at 0 °C for 1 h, followed by adding $KMnO_4$ (6 g) gradually. After stirring for 2 h, the mixture was heated and kept at 30 °C for 0.5 h. Subsequently, water (150 mL) was dropwise added, followed by adding H_2O_2 (5%, 50 mL). Finally, the solution was washed with water and HCl (5%) to obtain the GO aqueous solution.

2.3. C-Networks

Without any further pre-treatment, the commercial cotton was directly carbonized at 800 °C for 1 h with a heating rate of 5 °C min^{-1} under N_2 atmosphere.

2.4. C–RGO-Networks

In the typical preparation, a portion of the as-prepared C-Networks (8 mg) were immersed in the mixture of ethanol (8 ml) and GO aqueous solution (8 ml, 2 mg/mL) under 2 h sonication. The mixture was then transferred into an autoclave (25 mL in volume), followed by a hydrothermal process at 180 °C for 18 h. The resultant mixed hydrogel was subsequently washed with water and freeze-dried to obtain C-Networks/RGO aerogel hybrid networks, namely C–RGO-Networks.

2.5. N–C-Networks

Similar to the preparation of C-Networks, a piece of cotton along with melamine and urea (with mass ratio of 1:2:2) was mixed in quartz boat. The mixture was then carbonized at 800 °C for 1 h with a heating rate of 5 °C min^{-1} under N_2 atmosphere.

2.6. N–C–RGO-Networks

In the typical preparation of N–C–RGO-Networks, the as-prepared N–C-Networks were firstly treated under ultrasonication for 1 h with the presence of mixture of HNO_3/H_2SO_4 (v/v=1/3), followed by being washed with distilled water and dried at 90 °C in an oven. Subsequently, N–C-Networks (8 mg) were immersed in the mixture of ethanol (8 ml) and GO aqueous solution (8 ml, 2 mg/mL) under 2 h sonication, followed by similar hydrothermal treatment and post-treatments. The products were assigned as N–C–RGO-Networks. Meanwhile, neat RGO aerogels were obtained according to the same procedure expect for the presence of N–C-Networks.

In the reference samples, the N–C-Networks with different initial masses (16 and 32 mg) were used. All the other conditions for preparing N–C–RGO-Networks maintained the same, except for the N-C-Network mass. The component loadings of the N–C-Networks were estimated via tracking the mass loss in the treatment. In separate hydrothermal processes, the mass losses in neat RGO aerogels and N–C-Networks were calculated to be around 36.8 wt% and 8.1 wt%, respectively. According to the comparison with initial masses of the GO and N–C-Networks, the final component loadings could be obtained via calculating the mass losses. With the initial N–C-Network masses of 8, 16 and 32 mg, the corresponding RGO loadings in the N–C–RGO-Networks were approximately 57.3%, 40.7% and 25.6%, respectively.

2.7. Characterizations

Field-emission scanning electron microscopy (SEM) was conducted on ZEISS supra 55 system and transmission electron microscopy (TEM) was performed on JEOL JEM-2010. X-ray photoelectron spectroscopy (XPS) was acquired on PHI-5300 system. The nitrogen absorption/desorption isotherms associated with specific surface area and pore diameter distribution data were investigated on an Autosorb-iQ2-MP (Quantachrome) analyzer under 77k. The total surface area (S_{total}) and surface area of micropores (S_{micro}) were calculated from multi-point Brunauer–Emmett–Teller (BET) plot and V–t plot, respectively. Surface area of mesopore and macropore ($S_{meso+macro}$) was obtained by subtracting S_{micro} from S_{total}. Total pore volumes (V_{total}) was determined at $P/P_0=0.99$ and micropore volume (V_{micro}) was obtained from V–t plot.

2.8. Electrochemical characterizations (three-electrode system)

The electrochemical performance of the carbon materials was determined in a three-electrode system with basic aqueous solutions. The working electrode was prepared by directly