Controllable Preparation of 3D Graphene with Different Morphologies for High-Performance Electrode Materials

Yanyun Liu,* Ling Ma, and Yongqiang Chen*

1. INTRODUCTION

In the past decades, supercapacitors have attracted much attention because of their higher power density, higher cycle efficiency, shorter charging time, and longer service life than batteries.1–16 They also have higher energy density than conventional dielectric capacitors. Accordingly, supercapacitors are regarded as the most promising green energy storage devices in this century. Graphene (GN), as a new type of carbon material, has high specific surface area and excellent conductivity and is an ideal electrode material for supercapacitors.17–25 Nevertheless, the surface energy of two-dimensional (2D) graphene sheets is high, and it is easy to agglomerate.24 Therefore, the prevention of restacking has become an important issue in the development of GN-based high-performance materials.

A widely proven method is to construct a three-dimensional (3D) graphene electrode, which can enhance the transport of ions and electrons and improve mechanical stability. Three-dimensional graphene can be basically divided into graphene foam (GF) and vertically aligned graphene (VAGN).23 Various synthetic methods and precursors have been used to prepare GF.24–34 In recent years, VAGN, another type of three-dimensional graphene, has attracted more and more attention as an electrochemical electrode because of its excellent reaction kinetics and mass-transfer capability.31–34 VAGN is generally prepared by chemical vapor deposition with a gaseous carbon source, in which 2D graphene nanosheets grow perpendicular to the substrate to construct a 3D ordered interconnection array structure.28–31 However, this method would suffer from the limitations of tedious procedures or requirement of special equipment. In this paper, VAGN has been prepared by a simple one-pot hydrothermal method, followed by a directional vacuum freeze-drying treatment. Directional vacuum freeze-drying is a process in which water evaporates toward a fixed direction near triple-point conditions. In addition, the possible growth mechanisms of the VAGN nanostructure have been studied based on the experimental results. Furthermore, the effects of morphologies on their electrochemical performances have been investigated. The result shows that the VAGN-based supercapacitor has a higher specific capacitance ($C_s$) of 182 F g$^{-1}$ at 0.5 A g$^{-1}$ than that of GF (160 F g$^{-1}$ at 0.5 A g$^{-1}$). The supercapacitors prepared by VAGN and GF retain about 95.7 and 92.7% of $C_s$, respectively, after 2000 charge–discharge processes. When the power density of the supercapacitor prepared by VAGN is about 50.3 W kg$^{-1}$, its maximum energy density can reach 7.05 Wh kg$^{-1}$, which is higher than that of GF. This shows that VAGN has better electrochemical performance than GF. It might be because the aligned structure of VAGN plays an important role in reducing the internal resistance of the electrodes and accelerating ion and electron transport. Three-dimensional graphene with different morphologies might have potential applications as electrode materials for supercapacitors.
Diffraction peaks located at about 23.9° are observed in the obtained VAGN and GF, indicating that the intergranular distances of the VAGN and GF are becoming smaller. The calculated layer distance of the two samples is about 0.37 nm. This means that GO has been successfully reduced, and there is no obvious difference in the XRD patterns of the two samples VAGN and GF.

The reduction of GO has been also characterized using X-ray photoelectron spectroscopy (XPS). The two peaks located at 284.5 and 531.1 eV correspond to C 1s and O 1s, respectively (Figure 2A). In the samples VAGN and GF obtained by reaction, the content of C 1s increases, while the content of O 1s decreases, revealing that both the samples obtained are successfully reduced. Figure 2B–D displays C 1s XPS spectra of GO, VAGN, and GF, respectively. The C 1s XPS spectra are mostly the same in the two samples, which indicates that the preparation method has little effect on the reducibility of GO, and the prepared VAGN and GF have similar element composition and content.

Figure 3A displays the schematic illustration for the preparation of VAGN and GF. The differences of the preparation methods of the two samples are mainly reflected in the freeze-drying process. The morphology of VAGN has been observed by scanning electron microscopy (SEM) in Figure 3B,C. It can be clearly observed that VAGN is stand-up and has a uniform, dense, and porous network. The possible formation mechanism for VAGN can be explained as follows: the water entrapped in the graphene would be impacted by a directional force during directional vacuum freeze-drying, and then rush out from the fixed direction after sublimation. This eventually leads to an upright shape of VAGN. The SEM images (Figure 3D,E) of GF show that the prepared GF just has a well-defined and 3D network structure. This may be because the sublimation direction of wrapping water is random during the normal freeze-drying process, so the obtained GF could just form a 3D porous framework structure, not an upright shape. Different morphologies of the samples will lead to different electrochemical properties.

Cyclic voltammetry (CV) curves for VAGN- and GF-based supercapacitors are shown in Figure 4A–B. Both curves are rectangular-like over the entire voltage range, which indicated ideal electric double-layer capacitance behavior. The current can reach the maximum value when the voltage changes direction, and there is no obvious redox peak in the whole potential window. Galvanostatic charge/discharge (DC) curves for VAGN- and GF-based supercapacitors are shown in Figure 4C,D. In both curves, the DC curves are all symmetrical, reflecting the good reversibility of the electrode materials. Figure 4E shows the DC curves for VAGN- and GF-based supercapacitors at 0.5 A g⁻¹. Compared with GF-based supercapacitors, the supercapacitor assembled by VAGN has a longer discharge time and a smaller voltage drop at the same current density, which indicates that VAGN has a larger capacitance and a smaller internal resistance according to the capacitance calculation formula. This might due to the special aligned structure of VAGN, which could reduce the internal resistance of the electrode and increase the thickness of the region of the effective electron double layer. The specific capacitance (Cₑ) of the VAGN and GF electrode can be calculated based on the DC curve, and the obtained results are plotted in Figure 4F. From this graph, we can note two facts: one is that the electrode of
VAGN possesses relatively higher $C_{sc}$ than the other GF electrodes, which indicates that the structure of the VAGN facilitates the diffusion of solution in electrochemistry; the other is that the $C_{sc}$ values will decrease slightly when current densities increase in both cases, while the VAGN electrode decreases much faster. This means that VAGN could maintain excellent electrochemical performance at high current densities. It might because the special aligned structure of VAGN could play a key role in accelerating ion and electron transport and increasing the thickness of the region of the effective electron double layer.

Figure 4. CV curves of supercapacitors assembled by VAGN (A) and GF (B). DC curves of supercapacitors assembled by VAGN (C) and GF (D) at different current densities. DC curves of supercapacitors prepared by VAGN and GF at 0.5 A g$^{-1}$ (E). Relationships between $C_{sc}$ and current densities (F).

Figure 5. (A) Nyquist plot of VAGN and GF; the inset shows the corresponding equivalent circuit diagram. (B) Ragone plots of energy density versus power density for supercapacitors prepared by VAGN and GF.
The electrochemical performances of the VAGN and GF have been further studied by electrochemical impedance spectrometry (EIS) measurements, and the results are shown in Figure 5A (the inset shows the corresponding equivalent circuit model). Here, C and R_a are the capacitance and charge-transfer resistance; R_s is the total resistance. The diameter of the semicircle in the curve represents R_s, which is the resistance of the charge transfer between the electrode surface and the electrolyte. The intercept between the curve and the X-axis represents R_x, which is associated with all resistances of the current collector, electrolyte, and electrode. The values of R_s and R_x for VAGN are both smaller than that of GF, which is in agreement with the results obtained from the DC curve (Figure 4E). The aligned structure of VAGN plays a key role in reducing the internal resistance of the electrode and accelerating ion and electron transport.

According to the discharge curve, the power density and energy density of the supercapacitor have been calculated based on formulas 2 and 3; the results are shown in Figure 5B. When the power density of the supercapacitor prepared by VAGN is about 50.3 W kg⁻¹, its maximum energy density can reach 7.05 Wh kg⁻¹, which is higher than that of GF.

Service life is an important factor in the supercapacitor electrode. Therefore, the stability of the capacitors prepared by VAGN and GF electrodes has been evaluated by the DC method at 1 A g⁻¹ (Figure 6). It can be seen that the supercapacitors assembled by VAGN and GF retained about 95.7 and 92.7% of C_{sc}, respectively, after 2000 DC treatment, indicating that VAGN and GF have good durability and can be used as ideal electrode materials for electrochemical capacitors.

3. CONCLUSIONS

In this paper, 3D graphene with controlled morphologies has been prepared by changing the freeze-drying process of graphene. The obtained VAGN is stand-up and has a uniform, dense, and porous network, while GF just has a cross-linked 3D porous framework. The VAGN-based supercapacitor has a higher C_{sc} of 182 F g⁻¹ at 0.5 A g⁻¹ than that of GF (160 F g⁻¹ at 0.5 A g⁻¹). The supercapacitors prepared by VAGN and GF retain about 95.7 and 92.7% of C_{sc}, respectively, after 2000 charge–discharge processes. This shows that VAGN has better electrochemical performance than GF. Three-dimensional graphene electrode materials with different morphologies may have significant applications in the field of energy storage.

4. EXPERIMENTAL SECTION

4.1. Preparation of 3D Graphene with Different Morphologies. GO suspension (2 mg mL⁻¹) was obtained by diluting graphite oxide in water under the action of an ultrasonic wave. GO solution (50 mL) was transferred to a 100 mL poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave and heated to 170 °C for 24 h.

After cooling to room temperature, the prepared cylinder sample was taken out and cut in half from the middle. One sample was freeze-dried by directional vacuum-pumping (the bottom and side of the prepared cylinder sample were sealed, leaving only the upper opening); we named this VAGN. The other was prepared under normal freeze-drying (vacuum-pumping from all directions) called GF.

4.2. Characterization. XRD of the samples was performed using an X-ray diffractometer (D/max2550VB+/PC, Rigaku, Japan). XPS tests were carried out using the PHI-5000C ESCA system with Mg Kα radiation. The morphologies of the samples were revealed by field emission scanning electron microscopy (Quanta 200FEG, FEI).

4.3. Electrochemical Measurements. The prepared VAGN and GF were assembled as electrodes into symmetrical supercapacitors. The formation process of the supercapacitor was as follows: 6.0 mol L⁻¹ KOH was used as an electrolyte, foam nickel was used as a collector, and filter paper was used as a membrane to separate two almost identical samples. All components were assembled into a two-electrode test system. Electrochemical performance tests were performed on a CH1660e workstation (Chenhua). In CV and DC tests, the potential window was −0.5 to 0.5 V. The frequency range of the EIS test was 10⁵ to 0.1 Hz, and the amplitude was 5 mV. C_{sc}, power density (P), and energy density (E) were calculated according to the DC curve

\[ C_{sc} = \frac{2I\Delta t}{\Delta Vm} \]  
(1)

where \( \Delta V \) is the voltage drop during discharge, \( m \) is the mass of an electrode, \( I \) is the constant discharge current, and \( \Delta t \) is the discharge time.

\[ E = \frac{1}{2}C_{sc}\Delta V^2 \]  
(2)

\[ P = E/\Delta t \]  
(3)

AUTHOR INFORMATION

Corresponding Authors
Yanyun Liu — College of Chemistry and Chemical Engineering, Jinzhong University, Jinzhong 030619, P. R. China; orcid.org/0000-0001-7359-6739; Email: 312217642@qq.com
Yongqiang Chen — College of Chemistry and Chemical Engineering, Jinzhong University, Jinzhong 030619, P. R. China; Email: chenyongqiang82@126.com

Author
Ling Ma — College of Chemistry and Chemical Engineering, Jinzhong University, Jinzhong 030619, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03507

Notes
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