Flexible Supercapacitors Prepared Using the Peanut-Shell-Based Carbon

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ABSTRACT: In this work, we report the fabrication and performance of supercapacitors made from carbonized peanut shells, which are renewable materials with a huge annual yield and are usually discarded directly by people. With proper treatment, peanut shells could be used for many applications. Herein, we demonstrate that the peanut shells treated with carbonization and activation processes not only possess an extremely high surface area but also provide a hierarchical structure for energy storage. The performance of the electrode can be further improved by nitrogen doping and adding graphene oxide to the electrode. The electrode shows a specific capacitance of 289.4 F/g, which can be maintained at an acceptable level even at a high scanning rate. In addition, a good capacitance retention of 92.8% after 5000 test cycles demonstrates that the electrode possesses an excellent electrochemical property.

1. INTRODUCTION

With the rapid development of technology, there is a demand for devices with high efficiency for energy storage. Supercapacitors, a promising candidate for high-performance energy storage devices, have drawn intensive attention because they possess many advantages, such as high power density (PD), long cycle life, short charging time, low maintenance cost, and wide thermal operating range. However, supercapacitors have their drawbacks: for example, a low energy density (ED) of about 3–30% for a battery. Because of their different energy storage mechanisms, supercapacitors can be divided into two types: electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs).

According to the Helmholtz model, the Gouy–Chapman model, and the Stern model, an electric field is generated at the interface between the electrode and the electrolyte to store energy for the EDLCs. With more surface area of the electrode materials, the electrodes can attract more ions and thus possess higher capacitance. On the other hand, PCs utilize the reversible multielectron faradic redox reactions with charge transfer to store energy and generally exhibit a higher energy density and better capacitance than EDLCs. Nevertheless, the poor electrical conductivity of the electrode restricts the faradic redox reactions, thus lowering the power density and resulting in poor stability.

In contrast, EDLCs have a better power density because of the good conductivity of the electrode materials. Some common materials for EDLCs include activated carbons (ACs), carbide-derived carbons (CDCs), graphene oxide (GO), and carbon nanotubes (CNTs). Among them, AC is the most widely adopted material owing to its high specific surface area, low cost, excellent chemical stability, and abundance in raw materials. However, ACs have a microporous structure with a narrow distribution in the range of 0.5–1.5 nm, which lacks larger pores and limits the electrolyte impregnation into the interior of the electrode materials. The hierarchical structure is a crucial factor for energy storage, especially at a high scan rate or current density. Improper pore size distribution and microstructure will lead to poor power density. To overcome this problem, it is imperative to design electrode materials with a proper microstructure for better properties. By introducing larger pores like mesopores or by improving the conductivity of the electrode materials, the routes for ion transport are increased and the electrical resistance of the electrode is reduced, thereby enhancing the power density. In this regard, the porosity of the structure must be preserved and a significant fraction of micropores need to be maintained to increase the high specific surface area for achieving high energy density.

Besides pore structure design, nitrogen doping also enhances the electrochemical performance of the supercapacitors by way of introducing surface functional groups. The nitrogen atoms...
are mainly from four types of functional groups in the graphite lattice: pyrrolic-N (N5), pyridinic-N (N6), pyridinic-N\(^+\)–O\(^-\) (NX), and quaternary-N (NQ). These four functional groups can improve the conductivity of the electrode materials and also participate in the Faraday reaction, thereby contributing to the pseudocapacitance.\(^{13,15−18}\)

Peanut is a nutritive food with plenty of sources throughout the world. Its annual global production exceeds 40 million metric tons. At the same time, millions of tons of peanut shells are discarded every year.\(^{19,20}\) If these peanut shells can be reused, it would not only be good for the environment but also be beneficial to develop new applications for modern devices, such as energy storage devices. Many biomasses were adopted as starting materials of carbon sources,\(^{21−29}\) such as kelp,\(^{24}\) tong cao pith, molasses,\(^{25}\) bamboo leaf,\(^{26−28}\) and bodhi leaf.\(^{29}\) Among them, kelp, tong cao pith, and molasses provided functional groups for increasing the capacitance, while bamboo leaf and bodhi leaf provided a hierarchical structure to the electrode.

Herein, peanut shells are selected as the primitive material for fabricating supercapacitor electrodes. Through the chemical activation process under optimal conditions, the specific surface area of the material is considerably increased and thus the enhancement of capacitance is achieved.\(^{30,31}\) Graphite papers are used as current collectors by utilizing their high conductivity, stability, and flexibility can be utilized to improve the applicability of the electrode. To further enhance the performance of the supercapacitor, the electrode materials were doped with nitrogen supplied from soy protein; as a result, both the pseudocapacitance and conductivity of the electrode were improved.\(^{32,33}\) In addition, graphene oxide (GO) was added to the materials; as expected, the specific surface area and the electrochemical performance of the electrode were improved further by an accompanying synergistic effect,\(^{34}\) and the reduction in capacitance at a high scan rate was alleviated.

2. RESULTS AND DISCUSSION

2.1. Material Characterization and Electrochemical Evaluation of the AP Materials. Scanning electron microscopy (SEM) was performed to examine the morphology

Figure 1. SEM images of (a) CP, (b) AP-700-imp, (c) AP-800-imp, (d) AP-900-imp, and (e) AP-800-phy.
of the samples synthesized with different activation conditions. Figure 1a–e shows the SEM results of CP, AP-700-imp, AP-800-imp, AP-900-imp, and AP-800-phy samples, respectively. As shown in Figure 1a, the surface of CP is smooth because it was simply subjected to carbonization without further treatment. The flat surface has a low specific surface area, which is detrimental to the energy storage of the capacitor. In Figure 1b–e, we can observe that the samples have porous surfaces because they were subjected to the carbonization and activation processes. A high roughness of the surface morphology increases the specific surface area of the material and thus contributes to the capacitance. Additionally, the morphologies of AP-700-imp, AP-800-imp, and AP-900-imp samples are totally different from each other, while AP-800-phy is somewhat similar to AP-800-imp. This shows that the different activation temperatures are the key factor causing the difference in surface morphology. During the KOH activation process, the following chemical reactions occurred:

\[
\begin{align*}
6\text{KOH} + 2\text{C} &\rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \\
2\text{K}_2\text{CO}_3 &\rightarrow \text{K}_2\text{O} + \text{CO}_2 \\
\text{CO}_2 + \text{C} &\rightarrow \text{2CO} \\
\text{K}_2\text{CO}_3 + 2\text{C} &\rightarrow 2\text{K} + 3\text{CO} \\
\text{C} + \text{K}_2\text{O} &\rightarrow 2\text{K} + \text{CO}
\end{align*}
\]

These chemical reaction equations describe how KOH reacts with carbon, which led to the porous structure and generated products such as potassium carbonate (K$_2$CO$_3$), potassium oxide (K$_2$O), carbon dioxide (CO$_2$), etc. Afterward, these three products kept reacting with carbon to generate more pores. The reaction described in eq 1 can spontaneously occur when the temperature is over 570 °C. However, the reaction described in eqs 2, 4, and 5 can only proceed when the temperature is over 700 °C. Because AP-700-imp samples did not go through the whole activation process, therefore, they kept a relatively smooth surface. Nevertheless, the morphology of the AP-900-imp sample cannot be explained simply based on the participating reactions. To find better explanations, we analyzed the Raman spectra and X-ray diffraction (XRD) patterns of the samples synthesized under different activation temperatures.

Figure 2a shows the Raman spectra of AP-700-imp, AP-800-imp, and AP-900-imp samples; all of them exhibit a D band (disorder band) at ~1350 cm$^{-1}$ and a G band (graphite band) at ~1582 cm$^{-1}$, which are the common features of graphite-based materials. The D band originates from the structural disorders, defects, or edges in graphite, while the G band is related to the in-phase vibrations of sp$^2$ carbon atoms in the basal plane of graphite. The level of graphitization can be examined from the intensity ratio of the D to G band ($I_D/I_G$). A lower $I_D/I_G$ value indicates a higher graphitization level, which indicates lesser disorders or defects in the samples.

AP-900-imp with AP-700-imp, Figure 2a depicts the Raman spectrum of the AP-900-imp sample and shows the lowest $I_D/I_G$ value, implying that the graphitization degree of the AP-900-imp sample is increased after being subjected to a relatively high temperature of 900 °C.

Figure 2b shows the XRD patterns of AP-700-imp, AP-800-imp, and AP-900-imp samples. AP-700-imp and AP-800-imp samples do not exhibit obvious peaks indicating amorphous structures, while the diffraction pattern of the AP-900-imp sample depicts the characteristic peaks of graphite at ~26° (002) and ~42° (100), demonstrating graphitization of the AP-900-imp sample owing to higher processing temperature. In short, both the Raman spectra and the XRD patterns show that AP-900-imp was graphitized at an activation temperature of 900 °C, which would restructure the porous surface and even cause the pore to collapse, thereby forming the morphology as shown in Figure 1d.

Figures 3 and S1 show the isotherm plots of the samples, demonstrating that all of the samples belong to Type I of the International Union of Pure and Applied Chemistry (IUPAC) with well-defined plateaus. Type I represents the samples possessing a micropore structure.
Notably, the isotherm of AP-900-imp shows an evident hysteresis loop, indicating that AP-900-imp possesses a certain amount of mesopores as well. This result matches with the morphology shown in Figure 1d. Table 1 summarizes the pore volume and the Brunauer–Emmett–Teller (BET) specific surface area of all of the samples. The optimal condition for the KOH activation process is found to be the impregnation method for obtaining a uniform mixture followed by the activation process at 800 °C.

Figure 4a shows the comparison of cyclic voltammetry (CV) curves for the samples at a scan rate of 10 mV/s. The results indicate that the AP-800-imp sample has the highest $C_{sp}$ of 181.4 F/g. Figure S2 shows the CV curve of each sample at different scan rates that varied from 10 to 100 mV/s. All curves exhibit a nearly ideal rectangular shape, indicating excellent reversibility during the charge/discharge processes as for all of the samples. Figure 4b compares the galvanostatic charge/discharge (GCD) measurements of the samples at a current density of 0.4 A/g. Again, the AP-800-imp sample shows the longest discharge time with the highest $C_{sp}$ of 253.9 F/g. Figure S3 shows the results of GCD measurements for each sample at different scan rates that varied from 0.4 to 3.2 A/g. Both curves present symmetric isosceles triangles, which indicate excellent capacitive behavior.

Figure 4c shows that the electrochemical impedance spectroscopy (EIS) plot of AP-800-imp depicts a vertical line in the low-frequency region, indicating an ideal capacitive behavior owing to rapid diffusion in the electrolyte and adsorption at the electrode/electrolyte interface. In the high-frequency region, a $Z'$ intercept, corresponding to the equivalent series resistance (ESR) and also known as the total Ohmic resistance or the internal resistance, of 1.27 Ω is obtained. ESR is defined as the sum of the contact resistance at the interface of the electrode/current collector, the bulk electrolyte resistance, and the electrode resistance. There is no apparent semicircle in the high-frequency region, implying that the charge-transfer resistance ($R_{ct}$) is substantially low. $R_{ct}$ is defined as the sum of the electrolyte resistance in the porous structure of the electrode, the electrode resistance, and the contact resistance at the interface of the electrode/current collector. Apparently, AP-800-imp

| Sample      | $V_{micro}$ (cm$^3$/g) | $V_{meso}$ (cm$^3$/g) | $V_{meso}/V_{micro}$ | $S_{BET}$ (m$^2$/g) |
|-------------|------------------------|------------------------|-----------------------|---------------------|
| AP-900-imp  | 0.582                  | 0.134                  | 0.230                 | 1276                |
| AP-800-imp  | 0.735                  | 0.063                  | 0.090                 | 1852                |
| AP-700-imp  | 0.132                  | 0.037                  | 0.028                 | 452                 |
| AP-800-phy  | 0.387                  | 0.067                  | 0.170                 | 911                 |

$V_{micro}$: micropore volume, $V_{meso}$: mesopore volume, and $S_{BET}$: specific surface area.

Figure 4. Comparison of (a) CV curves and (b) GCD curves. (c) Nyquist plot of AP-800-imp. (d) Comparison of $C_{sp}$ for the samples.
exhibits the lowest ESR and $R_{ct}$, matching the results of CV and GCD measurements.

Despite the high $C_{sp}$ at a low scan rate, the AP-800-imp sample exhibits poor $C_{sp}$ at a high scan rate. From Figure 4d, one can clearly observe that the $C_{sp}$ of the AP-800-imp is worse than that of the AP-900-imp at 100 mV/s scan rate. It is probably due to the fact that the electron did not have enough time to transport from the deep interior of the sample to the collector to store energy at a high scan rate. In addition, based on the data shown in Table 1, it depicts that AP-800-imp lacks larger pores to enhance the transportation of the electrolyte into the sample. On the contrary, the AP-900-imp has enough mesopores to provide effective paths and it assists the transportation of the electrolyte into the sample. Therefore, the strategy to improve the capacitance under a high scan rate would be to tune the porous structure and improve the electrical conductivity.

2.2. Further Enhancing the Electrochemical Performance of Porous Bioactive Carbon Materials. To improve the low performance of the electrode at a high scan rate, soy protein was added to the peanut shells before the carbonization process, while the activation condition remained the same. Figures 5a and S4 show the results of the CV tests, and Figures 5b and S5 show the results of the GCD measurements. Both results show that AP-800-imp-5 exhibits the best capacitance of 207.9 F/g at a scan rate of 10 mV/s and 284.1 F/g at a current density of 0.4 A/g. Table S1 shows a comparison between the capacitance of the samples tested under different scan rates. From the data shown in Table S2 and Figure S6, it is found that the mesopore volume of the samples slightly increases with the amount of the introduced soy protein. Meanwhile, the micropore volume decreases, which causes a reduction of the BET specific surface area. In spite of the lower surface area, soy protein introduces nitrogen doping and, as a result, enhances the capacitance.

To investigate the generated functional group via nitrogen doping, the X-ray photoelectron spectroscopy (XPS) test was performed on AP-800-imp-5-1.5 (Figure 6). It is observed that the surface is composed of carbon, nitrogen, and oxygen in the ratio of 84.9:13.5:1.6. The three peaks in the N 1s spectrum, as shown in Figure 6a, correspond to the three types of N-species in the graphite lattice, including pyrrolic-N (N5) at 400.0 eV,
pyridinic-N (N6) at 398.2 eV, and quaternary-N (NQ) at 401.0 eV.\textsuperscript{47–49} The presence of these three groups improves electron transfer in the electrolyte to enhance pseudocapacitance and also enhances the electron mobility.\textsuperscript{50} The C 1s spectrum was deconvoluted into three peaks, including C–C at 284.5 eV, C–N at 285.2 eV, and C–O at 286.0 eV. The presence of C–N bonds indicates successful nitrogen doping of the graphite lattice.\textsuperscript{47–49}

To further improve the performance of the electrode, GO was also added to the peanut shells before carbonization and subsequently treated by the same activation process as for the AP-800-imp-5 sample. Figure S7 shows the Raman spectrum, the XRD pattern, and atomic force microscopy (AFM) image of the sample containing GO. As can be seen, the Raman spectrum and the XRD pattern exhibit characteristic features of GO, and the AFM image illustrates the thickness of the single-layer GO flake to be 1.06 nm. Figures 7a and S8 show the results of CV tests for the samples having different amounts of GO, while Figures 7b and S9 depict the results of GCD measurements. Both results show that AP-800-imp-5-1.5 shows the best capacitance of 214.0 F/g at a scan rate of 10 mV/s and the best capacitance of 289.4 F/g at a current density of 0.4 A/g. Based on the data shown in Table 2 and Figure S10, it is found that the mesopore volume dramatically increases with GO. Among the samples, AP-800-imp-5-1.5 has a certain amount of mesopores to assist the carbonization and also enhances the electron mobility.\textsuperscript{50} The C 1s spectrum was deconvoluted into three peaks, including C–C at 284.5 eV, C–N at 285.2 eV, and C–O at 286.0 eV. The presence of C–N bonds indicates successful nitrogen doping of the graphite lattice.\textsuperscript{47–49}

Table 2. Surface Area and Pore Structure of AP-800-imp-5-G\textsuperscript{a}

| Material      | \(V_{\text{micro}}\) (cm\(^3\)/g) | \(V_{\text{meso}}\) (cm\(^3\)/g) | \(V_{\text{meso}}/V_{\text{micro}}\) | \(S_{\text{BET}}\) (m\(^2\)/g) |
|---------------|-----------------------------------|-----------------------------------|-------------------------------------|--------------------------------|
| AP-800-imp-5-0 | 0.518                             | 0.096                             | 0.190                               | 1263                           |
| AP-800-imp-5-1.5 | 0.501                           | 0.296                             | 0.590                               | 1691                           |
| AP-800-imp-5-3  | 0.407                             | 0.396                             | 0.970                               | 1503                           |

\(V_{\text{micro}}\): micropore volume, \(V_{\text{meso}}\): mesopore volume, and \(S_{\text{BET}}\): specific surface area.

Figure 8a and Table S3 compare the \(C_{\text{sp}}\) of samples under different scan rates. They show excellent capacitance for AP-800-5-1.5, regardless of the scan rates. Figure 8b shows that, by adding the soy protein, the resistance of AP-800-imp-5 is significantly reduced from 1.27 to 0.49 Ω due to the presence of more free electrons. Furthermore, by adding a proper amount of GO, the resistance of AP-800-imp-5-1.5 is further slightly reduced from 0.49 to 0.43 Ω owing to better conductivity of the rGO, which was reduced from GO during the carbonization process under elevated temperature. Figure 8a,b proves that the problem of poor performance under a high scan rate was overcome with these strategies. In addition, we also tested the electroactive surface area (ESA), as shown in Figure S11.

The best sample, AP-800-imp-5-1.5, has a high ESA value, which is 3 times higher than that of CP, indicating that it possesses a hierarchical structure and utilizes the holes effectively. Figure 9a shows the AP-800-imp-5-1.5 electrode having a great cycling performance, which retains 92.8% of its initial capacitance after the test for 5000 cycles. Figure 9b shows the Ragone plot of the AP-800-imp-5-1.5 electrode and the comparison of our results with others fabricated using different biomasses and processes made.\textsuperscript{51–54} The result reveals that the energy density reaches as high as 25.72 Wh/kg with a power density of 160.0 W/kg at 0.4 A/g. In addition, another measurement shows that an energy density of 20.55 Wh/kg with a power density of 1280 W/kg can be attained when the test is performed under a current density of 3.2 A/g.

2.3. Assembling and the Performance Tests of the Flexible Supercapacitor

Using the AP-800-imp-5-1.5 material as the electrode, PVA/H\(_2\)SO\(_4\) as the electrolyte, and a nonwoven fabric as the separator, we assembled a flexible supercapacitor and tested its electrochemical performance, as shown in Figures S12 and 10. Since the gel electrolyte has a poor conductivity (usually less than 10 mS/cm) and low ion mobility as compared with the liquid electrolyte, making the charge and discharge processes slow, and increasing the ESR, it is unable to instantly perform a complete capacitive energy storage process.\textsuperscript{55–57} Therefore, the capacitance is only 10.75 F/g at a scan rate of 10 mV/s. Figure 10a shows the bending test of the flexible supercapacitor. It can be seen that when bent from 0 to 90\(^\circ\), the structure of the electrode is changed due to the applied bending stress over the material, resulting in a slight change in the cyclic voltammetry curve. When bent to 135 and 180\(^\circ\), reverse-bended to ~90\(^\circ\), or re-bended back to 0\(^\circ\), the areas of the CV curves are almost the same, which implies that the flexible supercapacitor can be retained and is stable at different bending angles. Figure 10b shows the retention tests and light-emitting diode (LED) illumination test (inset) powered by three flexible supercapacitors arranged in series. The result shows that after 2000 cycles, the flexible supercapacitor can retain about 82.9% of its initial capacitance. When the flexible supercapacitor is charged for 10 s, the red LED can be illuminated for up to 165 s, indicating that the capacitor has good energy storage performance.

3. CONCLUSIONS

In summary, we have synthesized the high-performance electrodes using the biomass converted from peanut shells as the primitive material. With the optimal activation process and the synergistic effect of soy protein and GO, AP-800-imp-5-1.5 exhibits a high \(C_{\text{sp}}\) of 289.4 F/g at a current density of 0.4 A/g and 214.0 F/g at a scan rate of 10 mV/s. Even at a scan rate as high as 100 mV/s, a \(C_{\text{sp}}\) of 131.1 F/g can be attained. It means that the problem of poor performance under a high scanning...
rate has been overcome. In addition, the flexible supercapacitor retains its performance even under bending, and a flexible supercapacitor set containing three supercapacitors arranged in series can illuminate the LED for up to 165 s after being charged for 10 s.

4. EXPERIMENTAL SECTION

4.1. Materials. The materials and chemicals used in this work are of experimental grade and were used as purchased. The peanuts were purchased from a local supermarket.

4.2. Sample Preparation. In this work, the peanut shells were used as the carbon source of the electrode material. They were washed several times with deionized (DI) water to remove unnecessary impurities and then placed in an oven at 90 °C for 24 h before the subsequent carbonization process. Subsequently, they were ground to a fine powder in a pulverizer at 30 000 rpm.

4.2.1. Preparation of the Carbonized Peanut Shell Powder. A quartz boat filled with the peanut shell powder was placed in a tube furnace for carbonization. Argon gas with a flow rate of 500 sccm was channeled into the furnace and vacuumed below 10⁻² mbar. The purging processes were repeated three times to eliminate the residual oxygen in the furnace as much as possible. The peanut shell powder was carbonized at 800 °C for 3 h under an argon flowing atmosphere at a flow rate of 1000 sccm. The product was further ground into a fine powder by a ball mill machine at 250 rpm and the product was designated as CP.

4.2.2. Preparation of the Activated Peanut Shell Powder. A mixture of CP and KOH with a CP/KOH weight ratio of 1:4 was prepared via the physical method and the impregnation method. For the physical method, the mixture was physically stirred for 30 min. As for the impregnation method, KOH was first dissolved in an alcohol solution, and then the CP powder was added to the solution. Subsequently, the mixture was heated at 65 °C for 24 h until the alcohol solution was completely evaporated. The magnetic stirring was applied throughout the process for uniform mixing of KOH and CP.

The dried mixture was placed in a ceramic boat and activated at three different temperatures of 700, 800, and 900 °C for 3 h under an argon flowing atmosphere at a flow rate of 1000 sccm. Subsequently, the final product was ball-milled into a uniform powder and washed with 10 wt % HCl. For ensuring safety, the product was washed with DI water several times until a pH value of 7.0 was reached and was named as activated powder (AP). The final samples were designated as AP-X-Y, according to the activation temperature and mixing method. X stands for the activation temperatures (700, 800, and 900 °C) and Y represents the mixing methods (phy: physical method, imp: impregnation method).

4.2.3. Preparation of Graphene Oxide. GO was prepared by the modified Hummers method, which can be found elsewhere. In short, 1 g of 325 mesh graphite flakes was slowly added to 100 mL of concentrated sulfuric acid (H₂SO₄). The solution was kept in an ice bath, stirred with a magnet for 1 h, and then 4 g of potassium permanganate (KMnO₄) was gradually added followed by stirring at 40 °C for 6 h. The solution was diluted with 50 mL of DI water under stirring for 1 h. Subsequently, 100 mL of DI water and 40 mL of hydrogen peroxide (H₂O₂) were slowly added; the processes were performed under stirring. Once the color of the solution changed from dark purple to brilliant yellow-brown, the solution was placed at room temperature for 12 h for GO precipitation. Finally, the solution was centrifuged and diluted with DI water several times until it became neutral. The precipitated GO was dried in a vacuum pumping system at room temperature.

4.2.4. Addition of Soy Protein and Graphene Oxide. In this work, the soy protein and GO were used for further improving the electrochemical performance of the electrode that was prepared from APs. Before the carbonization process, the peanut shell powder was mixed with different amounts of...
soy protein (0, 5, and 10 wt %) and GO (0, 1.5, and 3 wt %) were mixed via stirring for 30 min. Then, the mixture was activated with the same conditions as for AP-800-imp. The samples were named as AP-800-imp-S-G, where S and G indicate the weight percentages of soy protein (0, 5, and 10 wt %) and GO (0, 1.5, and 3 wt %) in the mixture, respectively.

4.3. Characterizations. The morphologies, microstructures, and compositions were characterized by X-ray diffractometer (XRD, Shimadzu XRD 6000), field emission scanning electron microscopy (FESEM, Hitachi-SU8010), energy-dispersive spectroscopy (EDS, Hitachi-SU8010), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 VersaProbe II). The microstructures of the samples were examined by a Raman spectroscope (Raman, Horiba Jobin Yvon HR 800 UV) equipped with a laser wavelength of 632.8 nm. The nitrogen adsorption/desorption isotherms were measured using a porosimetry analyzer (Micromeritics Tristar II 3020). The specific surface areas of the samples were determined by using the Brunauer–Emmett–Teller (BET) method at 77 K. The micropore and mesopore volumes were analyzed using the Barrett–Joyner–Helenda (BJH) method based on the nitrogen isotherm data.

4.4. Electrochemical Evaluation. The electrochemical properties of the electrodes were evaluated with a three-electrode system in a 1 M H2SO4 aqueous electrolyte at room temperature. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. The working electrode was prepared using the synthesized active material, poly(vinylidene difluoride) (PVDF), and conductive carbon black in a mass ratio of 7:1:2 as the primary materials. Subsequently, an appropriate amount of N-methyl-2-pyrrolidone (NMP) was adopted as the binder to prepare a slurry, which was coated on a graphite paper by the dipping method for electrode preparation.

Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed by the Potentiostat/Galvanostat Electrochemical Instrument (Autolab PGSTAT30 & FRA2). The specific capacitance ($C_{sp}$, F/g) of the electrodes can be calculated from the CV curve by using eq 6:

$$C_{sp} = \frac{1}{2 \, m \, \nu \, (V_a - V_c)} \int_{V_c}^{V_a} I(V) \, dV$$

(6)

where $V_c - V_a$ represents the applied voltage range (V), $m$ is the mass of the active material (g), $\nu$ is the scan rate (V/s), and $I$ is the response current (A). Additionally, the $C_{sp}$ can also be calculated via the GCD measurement by using eq 7:

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m}$$

(7)

where $\Delta V = V_a - V_c$ corresponding to the applied voltage range (V), $I'$ is the constant discharge current (A), $\Delta t$ is the discharging time (s), and $m$ is the mass of the active material (g).

The energy density (ED, Wh/kg) and power density (PD, W/kg) can be calculated based on eqs 8 and 9, respectively:

$$ED = \frac{0.5 \times C_{sp} \times V^2}{3.6}$$

(8)

$$PD = \frac{ED \times 3600}{\Delta t}$$

(9)

where $V$ is the voltage change during the discharge process (V) and $\Delta t$ is the discharge time (s).

The electroactive surface area (ESA) can be calculated from the CV test using the electrolyte containing 20 mM of K3Fe(CN)6 and 0.2 M of KCl at different scanning rates. According to the Randles–Sevcik equation, ESA can be calculated using eq 10:

$$I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} V^{1/2} C$$

(10)

where $I_p$ represents the peak current (A), $A$ is the ESA (cm²), $D$ corresponds to the diffusion coefficient of [Fe(CN)6]3−/4− in the KCl solution ($6.70 \times 10^{-6}$ cm²/s), $n$ is the number of electrons transferred in the redox event (usually 1), $s$ is the scan rate (V/s), and $C$ is the solvent concentration (mol/cm³).
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