ABSTRACT: MnO2@bamboo leaf (BL) carbon composites have been prepared by a hydrothermal method, wherein, the BL porous carbon structure was based on BLs. The MnO2@BL composites were characterized by SEM, TEM, XRD, Raman, XPS, and TGA. The electrochemical properties of the composites were investigated in a three-electrode system using 1 M Na2SO4 aqueous solution as an asymmetric supercapacitor electrolyte. Electrochemical measurements showed that the MnO2@BL composites can be applied in asymmetric supercapacitors and exhibited a good cycling stability with a capacitance retention ratio of 85.3% after 5000 cycles (at 0.5 A g⁻¹). The MnO2@BL composites were promising materials for application in supercapacitors.

1. INTRODUCTION
To meet the growing demand for charge storage, there is an urgent need for an efficient, reliable, and cost-effective electrochemical energy storage (EES) device. In various emerging EES equipment, because of their high power, high reliability, high safety, and low cost, supercapacitors have been widely used.¹⁻⁵ To date, the rapid development of supercapacitors has an important impact on many fields, and has huge advantages of providing high energy and high power density instantly.⁶⁻¹³ Although supercapacitors have a high power density, their characteristic low energy density is still a problem that needs to be solved.¹⁴ Therefore, how to maintain high power density and stable cycling ability, while increasing energy density is a key issue.

Much effort has been devoted to the study of pseudocapacitor materials with a suitable working potential and a high specific capacitance. These materials include transition metal oxides (RuO₂, MnO₂, Fe₃O₄, Co₃O₄, CoMoO₄, etc.),¹⁵⁻¹⁷ hydroxides (Ni(OH)₂, Cu(OH)₂, etc.),¹⁶¹⁸ sulfides (NiCo₂S₄, Ni₃S₄, MoS₂, etc.),²⁰⁻²⁲ and conductive polymers (polyaniline, polypyrrole, polythiophene, etc.).²³²⁴ Among these electrode materials, MnO₂ is an ideal electrode material. MnO₂ itself is cheap and environmentally compatible and has a high theoretical capacitance value. However, MnO₂ does not have a high electron-transporting capacity, which largely limits the capacitive efficiency of the material, resulting in the material not exhibiting a high power performance, which limits its application in energy storage devices.²⁵⁻²⁷ In general, a way to overcome its shortcomings is to improve its electrochemical conductivity, in conjunction with a carbon material, so it can provide a large specific surface area and a high conductivity, provide a low resistance channel to ions, and reduce the agglomeration and charging distance of materials. In this way, various composite structures combined with this material have been developed, such as: carbon nanotubes, graphene, and porous carbon.²⁸⁻³⁰ These carbon/MnO₂ composites with a specific surface area and a pore structure exhibit good capacitance performance. Therefore, it follows that these carbon composite materials can significantly improve the electrochemical performance of MnO₂.

It is still an important challenge to prepare a carbon material with a suitable pore size distribution and a large specific surface area in a simple and environmentally friendly manner. Biomass material is one of the most economical and environmentally friendly materials; it not only shows better electrochemical performance but also is relatively less costly; thus it can solve all the above problems.³¹,³² More importantly, the effective use of biomass resources has become a hot topic because biomass resources are available in large quantities every year. Many biomass carbons have been reported, such as banana,³³ tobacco,³⁴ soybean stalk,³⁵ and so on. In fact, the inherent structure of biomass makes it an ideal precursor for the production of porous carbon. What’s more, as the most economic material, biomass carbon not only possesses relatively...
high electrochemical properties but is also cost-effective, thus can solve the above problems.

Li\textsuperscript{36} reported that the MnO\textsubscript{2} nanoplates derived from catkins anchored on biomass-derived CCNs (MnO\textsubscript{2}@CCNs) have been prepared using a two-step synthesis, and an asymmetric supercapacitor assembled by employing MnO\textsubscript{2}@CCNs as a positive electrode and CCNs as a negative electrode exhibits a superb energy density. Ren\textsuperscript{37} chose watermelon as the research object, after hydrothermal carbonization and freeze-drying processes, porous carbonaceous aerogels can be obtained. Further functionalization of the carbonaceous aerogels with precursors of MnO\textsubscript{2} is adopted, which exhibited excellent electrochemical performance.

Here, we report the MnO\textsubscript{2} nanosticks adhered to bamboo leaf (BL) carbon (MnO\textsubscript{2}@BL) prepared by hydrothermal deposition synthesis, and by employing MnO\textsubscript{2}@BL as a positive electrode and nitrogen-doped BL (NBL) porous carbon as a negative electrode, the asymmetric supercapacitor exhibited an excellent energy density of 11.47 Wh kg\textsuperscript{-1}, significantly higher than those of other MnO\textsubscript{2}-based asymmetric supercapacitors.

Figure 1. (a,b) SEM image of BL-3, (c) TEM image of BL-3, (d,e) SEM image of MnO\textsubscript{2}@BL-3 h, (f) TEM image of MnO\textsubscript{2}@BL, and (g) MnO\textsubscript{2}@BL-3-6 h EDS map.

Figure 2. (a) XRD patterns of MnO\textsubscript{2}@BL-3-6 h, MnO\textsubscript{2}@BL-3-8 h, MnO\textsubscript{2}@BL-3-10 h, and MnO\textsubscript{2}@BL-3-12 h, (b) XRD patterns of MnO\textsubscript{2}@BL-1-6 h MnO\textsubscript{2}@BL-2-6 h, and MnO\textsubscript{2}@BL-3-6 h, (c) Raman spectra of MnO\textsubscript{2}@BL-3-6 h, MnO\textsubscript{2}@BL-3-8 h, MnO\textsubscript{2}@BL-3-10 h, and MnO\textsubscript{2}@BL-3-12 h, (d) XRD patterns of MnO\textsubscript{2}@BL-1-6 h, MnO\textsubscript{2}@BL-2-6 h, and MnO\textsubscript{2}@BL-3-6 h.
The porous carbon-based composite material prepared from BL has certain application prospects in the field of supercapacitor electrode materials.

2. RESULTS AND DISCUSSION

2.1. Materials characterization. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the structure and morphology of the samples. As shown in Figure 1a, the carbonized BL had a plant fiber structure, mainly composed of cellulose and lignin. During the high-temperature annealing process, KOH melts and corrodes the carbonaceous material. After pyrolysis and KOH activation treatment, the carbon material produced many pore structures, as shown in Figure 1b. The presence of these micropore structures provided sufficient space for growth of MnO2. In addition, the pore structure of the BL-3 sample was further studied by TEM. As shown in Figure 1c, the 3D network structure of carbon could be used as a substrate for electrode materials, carrying a large amount of active materials, and the carbon structure could also improve conductivity. In addition, it could greatly increase the contact area with the electrolyte, which allowed the electrolyte to penetrate and better transfer electrolyte ions. The morphology and microstructure of MnO2@BL-3-6 h were investigated using SEM and TEM, and the images are shown in Figure 1d–f. It could be seen that after hydrothermal deposition, MnO2 was densely and uniformly dispersed on the surface of porous carbon. At the same time, the energy-dispersive spectroscopy (EDS) elemental map in Figure 1g also shows the distribution of C, O, and Mn elements, which also proved the successful synthesis of a MnO2@BL-3-6 h composite electrode material.

As shown in Figure 2a,b, the crystal structure of the samples with different activation levels and different hydrothermal times was studied by X-ray diffraction (XRD) measurement. The four peaks of the MnO2@R composites at 28.7, 37.4, 42.6, and 56.5° corresponded to the (001), (100), (101), and (431) crystal planes of MnO2 (JCPDS no. 44-0141). It could be proved that through simple hydrothermal synthesis, high-crystallinity and high-purity MnO2 were formed. The Raman spectra of MnO2@R in Figure 2c,d showed that there are two D and G peaks belonging to porous carbon at 1350 and 1584 cm\(^{-1}\), respectively. In addition, in the low-wavenumber region, three peaks close to 525, 572, and 650 cm\(^{-1}\) were attributed to the birnessite MnO2.

X-ray photoelectron spectroscopy (XPS) analysis was used to understand the surface chemical composition and the valence state of MnO2@BL-3-6 h. The XPS spectrum shown in Figure 3a contained characteristic peaks of C, Mn, and O, and the contents were 29.02, 19.07, and 47.66%, respectively. Among them, the high-resolution Mn 2p spectrum showed two peaks at 641.6 and 653.5 eV, as shown in Figure 3b, which could be attributed to Mn 2p\(^{3/2}\) and Mn 2p\(^{1/2}\), respectively. The spin energy separation of 11.9 eV indicated that the oxidation state of Mn was mainly +4. The deconvolution of the C 1s high-resolution spectrum is shown in Figure 3c. The most obvious peak was concentrated at 284.1 eV, corresponding to C\(-\)C and the other three peaks were at 284.9, 286.5 and 288.1 eV, respectively, corresponding to C\(-\)O, C\(-\)O, and O\(-\)C\ (=)O. In Figure 3d, the high-resolution O 1s spectrum could be fitted into three peaks, namely 529.5 eV (Mn–O–Mn), 531.3 eV (Mn–OH), and 532.6 eV (COOH).

The thermogravimetric curve of the product was tested in a N\(_2\) atmosphere, as shown in Figure 4. Weight loss below 400 °C can be attributed to the desorption of surface-adsorbed water.
and evaporation of water molecules bound in the MnO₂ lattice, while weight loss above 400 °C was attributed to the consumption of carbon and MnO₂, the mass loss of samples above 400 °C was 18.6%.

2.2. Electrochemical Measurements. The three-electrode device was used to explore the electrochemical performance of the sample in 1 M Na₂SO₄. The cyclic voltammetry (CV) curves of MnO₂@BL-x-y at various scan rates are shown in Figure 5a. These CV curves showed a quasi-rectangular shape at a low scan rate, indicating that MnO₂@BL-x-y materials exhibited ideal capacitance performance. MnO₂@BL-3-6 h showed the largest CV curve area, which represented the largest specific capacitance performance. Figure 5e shows the CV curves of MnO₂@BL-3-6 h at different scan rates. The CV curves of the surface of the material were close to the rectangular shape, thus the material exhibited ideal capacitance performance. At a higher scan rate of 100 mV s⁻¹, as the density increased, the shape of the CV curves showed some variations from the ideal rectangle, indicating a deviation from the ideal capacitance behavior, which may be because of the increase in the overpotential of the ion migration between the electrolyte and MnO₂.

The GCD curves of MnO₂@BL-x-y were collected using 1 M Na₂SO₄ electrolyte and at various current densities, as shown in Figure 5b,c,d,f. These curves were almost symmetrical during the charging and discharging processes, showing ideal capacitance behavior. Figure 5b–d are the charge–discharge curves of MnO₂@BL-x-y at 0.5 A g⁻¹. The samples with the largest specific capacitance in the three systems were MnO₂@BL-1-10 h (50 F g⁻¹), MnO₂@BL-2-6 h (57 F g⁻¹), and MnO₂.
Figure 5f shows the charge/discharge performance of MnO2@BL-3-6 h at different current densities. The potential window was 0−1 V and the charge/discharge curves almost all showed the ideal triangular capacitor behavior.

In order to further explore the value of MnO2@BL composites for practical applications, MnO2@BL-3-6 h composites were used as the positive electrode and NBL-700 was used as the negative electrode to assemble an asymmetric capacitor device in 1 M Na2SO4 electrolyte. After 12 h of immersion, performance of the asymmetric capacitor was evaluated. The assembly diagram is shown in Figure 6a. Figure 6b shows the CV curves of NBL-700 and MnO2@BL-3-6 h electrode materials at a scanning speed of 30 mV s−1. Among them, the voltage windows of NBL-700 and MnO2@BL-3-6 h electrodes were −1−0 and 0−1 V, respectively.

From Figure 6c, it could be seen that at a scan rate of 30 mV s−1, the materials still maintained a good capacitance state under a voltage window of 0−1.6 V, and polarization occurs at 0−1.8 V. The results showed that the electrode materials still had good reversibility in the voltage window of 0−1.6 V. Therefore, we chose 0−1.6 V as the working voltage window of the MnO2@BL-3-6 h electrode material for an asymmetric capacitor. The CV curves of the MnO2@BL-3-6 h/NBL-700 asymmetric capacitor at different scanning speeds are shown in Figure 6d. It could be seen that the asymmetric capacitor exhibited electrochemical properties similar to those of an electric double layer capacitor and a pseudocapacitor. Under the conditions of a high scanning speed of 100 mV s−1, the CV curve had no significant deformation, which was mainly because of the pseudocapacitive behavior and reversible energy storage capacity of the cathode material.

Figure 7a shows the GCD curve of MnO2@BL-3-6 h/NBL-700 in the voltage range of 0−1.6 V. At a current density of 0.5 A g−1, the asymmetric capacitor exhibited a specific capacitance of 32.25 F g−1. In addition, as shown in Figure 7b, after calculating, the specific capacitance (from 0.5 to 3 A g−1) increased, the energy density became 11.47, 7.86, 2.51, and 1.47 W h kg−1, respectively, power density was 1600, 3200, 6408, and 9621 W kg−1, respectively. This energy density was lower than that of some of the reported porous carbon electrode materials, as shown in Table 1, this result might be the reason that in this composite material mainly MnO2 played the main role in electrochemical performance. Under the condition of a current density of 0.5 A g−1, the cycling stability was tested, and the measurement results are shown in Figure 7c. After 5000 cycles, the specific capacitance is maintained at 85.3%. In addition, the solid capacitor device assembled with MnO2@BL-3-6 h/NBL-700 could light up a yellow light-emitting diode (LED) bulb (Figure 7d).

3. CONCLUSIONS

In conclusion, this article described a simple, environmentally friendly, and inexpensive method for the preparation of composite electrode materials. SEM, TEM, XRD, and Raman were used for structural characterization. The three-electrode and two-electrode systems were used to test their electrochemical performance. By changing the mass ratio of BL carbon to KOH and the hydrothermal time, when the mass ratio of BL...
carbon to KOH was 1:3 and the hydrothermal time was 6 h, the maximum specific capacitance of 76 F g⁻¹ (at 0.5 A g⁻¹) was obtained. The asymmetric supercapacitor, MnO₂@BL-3-6 h//NBL-700, exhibited a large potential range of 0–1.6 V and a high energy density. The energy density of the porous carbon material was 11.47 W h kg⁻¹ at 0.5 A g⁻¹ and it retained 85.3% of the original specific capacitance after 5000 cycles. The porous carbon-based composite material prepared from BLs has certain application prospects in the field of supercapacitor electrode materials.

4. EXPERIMENTAL SECTION

4.1. Preparation of Nitrogen-Doped Porous carbon NBL. The collected BLs were dispersed in ethanol and then treated under ultrasound for 30 min. Next, the BLs were washed with deionized water and stirred vigorously to remove impurities, and dried in an oven at 60 °C for 12 h, and then pulverized into powder using a grinder mill and 0.5 g of BL powder was taken. 0.5 g, 1 g, and 2 g (mass ratio of powder and KOH is 1:1, 1:2, 1:3, respectively) KOH was mixed, 80 mL of deionized water was added, and then the mixture was stirred for 12 h, and then the mixed liquid was kept at 60 °C. The mixed liquid was dried in a 60 °C oven for 24 h, and the remaining mixture was heated to 700 °C in a tube furnace at a heating rate of 5 °C min⁻¹. The reacted samples were neutralized with dilute hydrochloric acid and then repeatedly filtered and washed with deionized water, and then dried in an oven to obtain a porous carbon sample designated as BL-x (x = 1, 2, and 3).

BL powder was mixed with melamine and 1.5 g of KOH, an appropriate amount of deionized water was added, thoroughly stirred and dried in an oven, and then the mixture was kept in a tube furnace at 700 °C for 2 h to obtain a nitrogen-doped porous carbon material, NBL-700.

4.2. Preparation of MnO₂@BL composites. As shown in Scheme 1, to synthesize MnO₂@BL, an aqueous solution containing 50 mg of BL-x, 0.395 g of KMnO₄, 1.25 mL of concentrated HCl, and 40 mL of distilled water was transferred to a 50 mL tetrafluoroethylene-lined stainless steel autoclave, kept at 140 °C for 6, 8, 10, and 12 h. After the reaction, the samples were centrifuged to obtain MnO₂@BL, washed with deionized water, and dried overnight in a 60 °C oven. For comparison, twelve kinds of MnO₂@BL composites were prepared by adjusting the mass ratio of BL to KOH and at different hydrothermal temperatures and named MnO₂@BL-x-y (x = 1, 2, and 3; y = 6, 8, 10, and 12 h).

4.3. Materials characterization. Field emission scanning electron microscopy (Nova NanoSEM450, USA) is a powerful technique for characterizing the structure and surface morphologies of the porous carbons. A transmission electron microscope (TEM, JEOL-2100F, Japan) is used to investigate the morphologies of the samples. The XRD patterns of these samples were collected via a D/max 2550VB+PC diffractometer (RIGAKU, Japan) with Cu Kα radiation (40 kV, 40 mA, and k = 1.5418 Å) between 10 and 80°. X-ray photo-electron spectroscopy (XPS) is a powerful technique for quantitative surface analysis to characterize the elemental analysis of the samples. Raman spectra were obtained on a Senterra R200-L apparatus (BrukerOptics, Germany). Thermogravimetric analysis (TGA) of the samples was performed using a TAQ600 (TGA) analyzer from American TA.

4.4. Electrochemical Measurements. A CHI 760E electrochemical workstation was used to test the constant current charge and discharge, electrochemical CV, electrochemical impedance spectroscopy and cyclic life testing of the carbon materials.

(1) CV test: in the three-electrode system test, according to the voltage window that the material can withstand (ranging from −1 to 0 V), the scan rate is tested according to the setting from small to large steps. Generally, the scan rate we set is 5–500 mV s⁻¹, until the CV curve shows a significant distortion. In the two-electrode system test, the voltage window can be set to 0–1, 0–1.2, 0–1.4 V, and so on. Step by step, large scan rates were tried to evaluate the CV performance of the material.

(2) Constant current charge and discharge (GCD) test: we choose a different current density to test the material rate performance. We increase the current density of the test step by step, from 0.5 to 10 A g⁻¹ or even higher. The test results can be drawn into an intuitive charge and discharge curve, and according to the discharge time and the specific capacitance calculation formula, we can calculate the specific capacity at each current density. Three-electrode specific capacity calculation formula: \[ C_m = \frac{I \Delta t}{m \Delta V} \]

\[ I (A) \] is the discharge current, \( \Delta t (s) \) is the discharge time, \( m (g) \) is the mass of the active material of the working electrode, \( \Delta V (V) \) is the potential window of the test; two-electrode capacitor’s specific capacity calculation formula: \[ C_s = \frac{4I \Delta t}{m \Delta V} \]

\[ C_s (F/g) \] is the capacitance of \( \Delta t (s) \), \( m (g) \), and \( \Delta V (V) \) correspond to discharge current, discharge time, total mass of the electrode active material, and the potential window for testing; the calculation formulas for the power density \( E (W \ h \ kg^{-1}) \) and the energy density \( P (W \ kg^{-1} \ h) \) are \[ E = C_s V^2 / (2 \times 3.6) \] and \[ P = 3600 \times E / \Delta t. \]

(3) Cyclic stability test: this test is to estimate the cyclic life of the material. In these series of experiments, the current density is generally set to 1 or 2 A g⁻¹. Of course, we can set a larger or smaller current density according to different research goals.

(4) Electrochemical impedance spectroscopy test: this characterization is used to evaluate the transport resistance of ions or charges in a three-electrode system. A smaller impedance means faster ion passage and better performance. The test frequency is 0.01 Hz–100 kHz.

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Notes
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