Synthesis of Multiporous Carbons from the Water Caltrop Shell for High-Performance Supercapacitors

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ABSTRACT: In this study, an economic, sustainable, and green synthesis method of multiporous carbons from agricultural waste, water caltrop shell (denoted as WCS), was presented. To prepare the WCS biochar, the dried WCS was first carbonized to a microporous carbon with a surface area of around 230 m² g⁻¹ by using a top-lit-updraft method. Then, the microporous WCS biochar was directly mixed with an appropriate amount of ZnO nanoparticles and KOH as activating agents via a solvent-free physical blending route. After further activation at 900 °C, the resulted carbons possess both micropores and mesopores that were named as WCS multiporous carbons. The carbon yield of the prepared WCS multiporous carbons with high surface area in the range of 1175−1537 m² g⁻¹ is up to 50%. Furthermore, the micropore/mesopore surface area ratio can be simply tuned by controlling the ZnO content. For supercapacitor applications, the as-prepared WCS multiporous carbon electrodes showed high specific capacitance (128 F g⁻¹ at 5 mV s⁻¹) with a good retention rate at 500 mV s⁻¹ scan rate (>60% compared to the capacitance at 5 mV s⁻¹) and low Ohmic resistance in a 1.0 M LiClO₄/PC electrolyte. In addition to the ZnO nanoparticles, CaCO₃ nanoparticles with low environmental impact were also used to prepare the WCS multiporous carbons. The assembled supercapacitors also demonstrate high specific capacitance (102 F g⁻¹ at 5 mV s⁻¹) and good retention rate (~70%).

1. INTRODUCTION

During the last decades, electrochemical double-layer capacitors, also named as supercapacitors, are energy storage devices that store the electrical energy in the interface between the charged surface of the electrode and the electrolyte solution.²,³ The supercapacitors have become noticeable because of their excellent cycle ability, high power density, and high charge/discharge rate performance compared to batteries.³ Although supercapacitors provide higher power in the same volume, they are not able to store the same amount of charge as batteries do. This makes supercapacitors suitable for those applications where power burst is needed, but high energy storage is not required.³ However, the limitation of its low energy density increases both the volume and cost of the device. Because of their low pore volume, the commercially available microporous carbons (pore size < 2 nm) are not very attractive.³ Therefore, it is a key issue to design a nano-structured porous carbon with pore properties specifically tailored for the supercapacitor application.⁶

Nowadays, porous carbon materials are widely utilized as electrode materials for supercapacitors owing to their low cost, excellent cycle stability, and easy manufacturing.⁷ Among them, multiporous carbons with three-dimensional mesoporous/microporous structures have become popular in recent years.⁸ Multiporous carbons have high potential in applications such as fuel cells, hydrogen storage devices, dye adsorption, and energy storage devices.⁷ Many methods have been used for the preparation of porous carbon materials, including catalytic activation, polymer blend carbonization, organic aerogel carbonization, and nanocasting.¹⁰,¹¹ Nanocasting involves using various templates (colloids or mesoporous silica), which has proven to be particularly efficient.¹² However, the removal of silica requires the toxic hydrofluoric acid, which renders the complex and nonenvironment-friendly process. Consequently, recent studies have investigated the feasibility for synthesizing porous carbons using nanoparticles as templates, for example, magnesium and calcium salts, such as magnesium acetate,¹³ calcium citrate,¹⁴ and calcium carbonate.¹⁵ These methods yield carbons with mesopores ranging from 2 to 20 nm. However, they usually use either sucrose or formaldehyde resin as a carbon precursor. Sucrose requires acid to catalyze polymerization, while formaldehyde resin produces tar during pyrolysis.¹⁶ Thus, finding more suitable carbon precursors is still required. Furthermore, these traditional synthesis procedures are complicated, expensive, time-consuming, and toxic. Hence, they cannot be commercialized. Development of simple low-cost strategies for the
synthesis of multiporous carbons remains a significant challenge.

Previously, our group has used ZnO nanoparticles as hard templates to prepare mesoporous carbons by using petroleum pitch as the carbon precursor. The effects of the carbonization temperature and ZnO/pitch weight ratio on the physical properties of the multiporous carbons were studied in detail. These results showed that the specific surface area and pore volume can be easily improved by adjusting the ZnO/pitch ratio. Although industrial residual petroleum pitch shows good potential as the carbon precursor, we still tried to find other cheap and natural carbon precursors. For the sustainable purpose, biochar derived from agriculture waste is an alternative because of its rich abundance and availability. Recently, activated carbons have gained great interest for their utilization as supercapacitor electrodes because they can be readily prepared from cheap biomass residues and wastes.

In Guantian District, Tainan, Taiwan, the annual yield of water caltrop is around 3400 tons. For storage and sale, farmers and merchants peel off the shell from water caltrop. Because of the high lignin content in the water caltrop shell (denoted as WCS), it takes about 7.79 million NT dollars to deal with the discarded shells every year. In practice, the lignin in the WCS can be converted into carbons after pyrolysis. Thus, WCS has been carbonized already to biochar at Guantian District by using a top-lit-updraft (TLUD) method via a suitable carbonization furnace. To introduce the mesopores and micropores into the WCS biochar after high-temperature pyrolysis. The electrochemical properties of the WCS multiporous carbons for supercapacitors in an organic electrolyte were evaluated in this study.

2. RESULTS AND DISCUSSION

2.1. Using WCS as the Carbon Precursor. WCS was previously carbonized to biochar in a TLUD carbonization furnace at Guantian District, Tainan, Taiwan (see Supporting Information, Figure S1). After washing with an appropriate amount of H2O to remove the inorganic residuals in the WCS biochar, the physical properties of the biochar were analyzed. The scanning electron microscopy (SEM) image shows that the WCS biochar exhibits many macropores (the pore size is about 30–60 μm) (Figure 1a). However, as can be seen in the SEM image (Figure 1b), a smooth surface of WCS biochar presents no micropores even at high magnification. The N2 adsorption−desorption isotherms of the WCS biochar show type I isotherm with a specific surface area up to 230 m2 g−1 (Figure 1c, curve I). This indicates a mainly microporous structure (pore size < 2 nm).

In this paper, we provided a simple synthetic method by directly blending the WCS biochar with inorganic ZnO or CaCO3 nanoparticles and activating agents (KOH) to introduce the mesopores and micropores into the WCS biochar after high-temperature pyrolysis. The electrochemical properties of the WCS multiporous carbons for supercapacitors in an organic electrolyte were evaluated in this study.

Figure 1. (a,b) SEM images of the WCS biochar; (c) N2 sorption isotherms of the WCS biochar (I) and the WCS multiporous carbon (II); the inset shows a pore size distribution curve (Horváth–Kawazoe model) for curve II; and (d) SEM and (e,f) HR-TEM images of the WCS multiporous carbon.
The detailed textural properties of the WCS multiporous carbons synthesized with different compositions are listed in Table 1. The thermogravimetric analysis (TGA) curve (Figure S3) shows that the WCS multiporous carbons exhibit good thermal stability even at 500 °C and the inorganic residual is less than 3 wt %. In brief, these results show that the WCS biochar can be activated by ZnO nanoparticles and KOH to produce high surface area multiporous carbons with yield up to 48 wt %.

### 2.2. Effect of the ZnO/WCS Biochar Ratio on the Meso-/Micropore Surface Area

Interestingly, the content of the meso-/micropore surface area can be easily controlled by adding different amounts of ZnO nanoparticles at a fixed KOH/WCS biochar weight ratio. As the weight ratio of ZnO/WCS biochar increases from 0.5 to 2.5, both specific surface area and mesopore surface area increase significantly (Figure 2). This phenomenon can be ascribed to the reaction between ZnO and KOH/water, using easily removable ZnO nanoparticles and KOH as activating agents. The merangonic reaction (eqs 1–3).

\[
2\text{ZnO} + \text{C} \rightarrow 2\text{Zn} + \text{CO}_2 \tag{1}
\]

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} \tag{2}
\]

\[
\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2 \tag{3}
\]

Figure 4a shows the Raman spectrum of the WCS biochar and WCS multiporous carbons. Two broad peaks at 1350 cm\(^{-1}\) (D-band) and 1580 cm\(^{-1}\) (G-band) can be observed. To analyze the defect level of the carbons, the integrated intensity ratio of the D band to the G band was calculated. The high I_D/I_G values (0.71 and 0.75) reveal similar defect level in these carbon materials. The surface composition of the WCS biochar and WCS multiporous carbons was investigated by X-ray photoelectron spectroscopy (XPS), as shown in Figure 4bc. The high-resolution C 1s spectra were deconvoluted into three main peaks. The peak at 284.8 eV can be attributed to the sp\(^2\) hybridized carbon (sp\(^2\) C--C). Meanwhile, the peaks at 285.8 and 288.4 eV demonstrate the presence of C--O and C=O bonds, respectively. From the XPS results, both WCS biochar and WCS multiporous carbon show high carbon content (77.3 and 85.9%). This indicates that after further pyrolysis of the WCS biochar, the unstable oxygen functional groups and defects in the WCS biochar were eliminated, which is consistent with the Raman results.

### 2.3. WCS Multiporous Carbons as the Electrode Material for Supercapacitor Applications

Although various activating agents or nanotemplating methods have been used to prepare porous carbons with high surface area (>2000 m\(^2\) g\(^{-1}\)), the low tap density (0.3–0.4 g cm\(^{-3}\)) and carbon yield\(^{12}\) make it difficult to employ them as electrode materials for supercapacitor applications. In contrast, for WCS multiporous carbons, the tap density can be well controlled at around 0.6–0.7 g cm\(^{-3}\), which is suitable for the preparation of supercapacitor devices. Herein, WCS multiporous carbons were used as electrode materials and 1.0 M LiClO\(_4\)/PC was used as an electrolyte to assemble supercapacitors.

As can be seen from Figure 5a, the cyclic voltammetry (CV) curves of these electrodes show a quasi-rectangular shape at a fast scan rate, suggesting the ideal capacitor behavior and reversible redox reaction. The specific capacitance of the WCS multiporous carbons was calculated by integrating the CV curve area in a 0–1.5 V voltage window with a scan rate varying from 5.0 to 500.0 mV s\(^{-1}\). Owing to the high specific surface area, the WCS multiporous carbon supercapacitor has capacitance up to 128 F g\(^{-1}\) at a slow scan rate (5.0 mV s\(^{-1}\)). The gravimetric capacitance of the samples at different scan rates is shown in Figure 5b. As the scan rate increases from 5 to 500 mV s\(^{-1}\), the decrease in capacitance is less than 40%. Furthermore, Figure 5c shows the cycling performance of the WCS multiporous carbons. At a scan rate of 100 mV s\(^{-1}\), the above-mentioned electrodes show a high initial specific capacity of 98 F g\(^{-1}\) and retain 98 F g\(^{-1}\) (>99%) after 10,000 cycles. Thus, these specific capacities and retention...
rates of the WCS multiporous carbon are comparable to those of many reported literature studies in the organic electrolyte systems.\textsuperscript{21−25} This demonstrates that the WCS multiporous carbon electrodes exhibit high capacity values, high rate performances, and good capacitance retention, which can be ascribed to the high pore accessibility in the meso-/microporous structure.\textsuperscript{26−28}

The galvanostatic charge/discharge (GCD) curves of the WCS multiporous carbon electrode under different current densities all reveal nearly symmetrical triangular shapes (Figure 6a). Furthermore, as can be seen from the Nyquist plot (Figure 6b), in a high-frequency region, the semicircle of the WCS multiporous carbon electrode has a small diameter, which confirms the low ionic diffusion resistance within the multiporous carbon matrix. To evaluate the energy storage performance of the WCS multiporous carbon supercapacitor, Ragone plots (energy density vs powder density) are shown in Figure 6c. The gravimetric values exhibit a high power density of 6564 W kg\textsuperscript{-1} at 4.35 W h kg\textsuperscript{-1} energy density. To further explore the feasibility of the WCS multiporous carbon, a 1500 F-class pouch cell-typed supercapacitor has been prepared to evaluate its electrochemical performance (Figure S4).

2.4. WCS Multiporous Carbons Prepared by CaCO\textsubscript{3} Nanoparticles. Apart from ZnO nanoparticles, WCS multiporous carbons can also be prepared with CaCO\textsubscript{3} nanoparticles and KOH via the same activation procedure. The dimension of CaCO\textsubscript{3} nanoparticles is around 50 nm, as shown in Figure S3. As shown in Figure 7a, the CaCO\textsubscript{3} nanoparticles are also capable of increasing both the pore volume and surface area. At WCS biochar/CaCO\textsubscript{3}/KOH weight ratio = 1.0:2.0:0.8, the porous carbon exhibits a specific surface area up to 1305 m\textsuperscript{2} g\textsuperscript{-1} (Figure 7b and Table 1). For the CaCO\textsubscript{3} activating agent, the decomposition of CaCO\textsubscript{3} to CaO (eq 4) produces CO\textsubscript{2} for physical activation (eqs 4 and 5).

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]
The CV (Figure 7c) of the as-prepared WCS multiporous carbon also shows quasi-rectangular curves with symmetric shape. The capacitance values were 102 and 73 F g\(^{-1}\) at 5 and 500 mV s\(^{-1}\) scan rates, respectively, with a retention rate up to 70%. The Nyquist plots present similar impedance behavior to that of the ZnO activating agent, in which the resistance is only 1.0 Ω (Figure 7d).

3. CONCLUSIONS

In this research, we proposed a facile solvent-free physical blending method to synthesize the WCS multiporous carbons with high surface area (>1200 m\(^2\) g\(^{-1}\)) from the WCS biochar precursor by using ZnO and CaCO\(_3\) nanoparticles for the formation of mesopores and KOH to produce micropores. Conclusively, the physical blending method provides a facile way to fabricate the multiporous carbons from different carbon precursors. The porous structure can be easily tuned by adjusting the template to biochar weight ratio. With large surface area, high porous connectivity, and appropriate bulk density, the multiporous carbons can be assembled to high-performance supercapacitors with high power density and good retention rate at high scanning rate (>60%). In future, introduction of high content of nitrogen into the carbon matrix of the biochars or multiporous carbons will be studied for catalytic and electrochemical applications.

4. EXPERIMENTAL SECTION

4.1. Synthesis of the WCS Multiporous Carbons via a Physical Blending Method.

To synthesize the WCS multiporous carbons, \(x\) g (\(x = 10.0–50.0\) g) of inorganic ZnO or CaCO\(_3\) nanoparticles, 10.0 g of carbon precursor (WCS biochar, from Guantian District, Tainan), and \(y\) g (\(y = 8.0–20.0\) g) of the KOH activating agent were directly blended into a homogeneous mixture by using a blender. The resulted powder was then sealed in a stainless-steel container and heated in a furnace. The heating rate was set at 8 °C min\(^{-1}\) and held at 900 °C for 2 h. After cooling to room temperature, the sample was washed with water to remove the alkaline oxides and then soaked in 37% HCl solution to remove the residual inorganic activation agents. The following solution was then filtrated, washed, and dried at 100 °C in an oven for 5 h, yielding the WCS multiporous carbons. A scheme of the synthetic process is presented in Figure S5 (see the Supporting Information).

4.2. Structural Characterization.

The thermal stability of the sample was characterized using a TGA (TA Instruments Q50, USA), heated from 100 to 800 °C with a ramp rate of 20 °C min\(^{-1}\) under air. SEM images of the WCS biochar and WCS multiporous carbon were recorded using a field emission scanning electron microscope (JEOL JSM7000F, USA). The N\(_2\) sorption isotherms of the samples were taken at 77 K on a Micrometric TriStar II apparatus to estimate the pore size, pore volume, and surface area. A micro-Raman spectrometer from Renishaw with a He–Ne laser source with a wavelength of 633 nm was used to determine the structure of the carbon samples. The XPS spectra of the samples were recorded using a PHI 5000 VersaProbe ESCA spectrometer with Al K\(_\alpha\) as the excitation source. The XPS analysis results were calibrated against the C 1s peak at 284.8 eV as an internal standard.

4.3. Electrochemical Measurement.

A symmetrical two-electrode capacitor cell was used to examine the electrochemical performance of the carbon electrodes. Both electrodes were made by depositing 2.0 mg carbons on a 1.0 cm\(^2\) stainless foil, which acted as a current collector. The cell consisted of two carbon electrodes, sandwiching a cellulose filter paper as the separator. CV measurements were conducted between 0 and 1.5 V in a 1.0 M LiClO\(_4\)/PC electrolyte at sweep rates ranging from 5 to 500 mV s\(^{-1}\). Plots of the specific capacitance versus the voltage were calculated using the following formula: \(C = \frac{2I}{vm}\), where \(I = \) current (A), \(v = \) scan rate (V s\(^{-1}\)), and \(m\) denotes the mass (g) of the carbon.
material in one electrode. GCD tests were performed in 1.5 V at current densities up to 18.0 A g⁻¹ in a 1.0 M LiClO₄/PC electrolyte. The specific gravimetric capacitance of a single electrode (F g⁻¹) determined from the galvanostatic cycles was calculated by means of the formula: \[ C = \frac{2I}{dV/dt}m \], where dV/dt = slope of the discharge curve (V s⁻¹). Electrochemical impedance spectroscopy measurements were conducted at an open-circuit voltage (0 V) over the frequency range of 1 mHz to 100 kHz with a 5.0 mV amplitude.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01212.

Carbonization furnace systems, SEM image for ZnO and CaCO₃ nanoparticles, TGA curve for WCS multiporous carbons, WCS multiporous carbon pouch cell-typed supercapacitor, and synthesis procedure (PDF)

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Notes

The authors declare no competing financial interest.

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