Hierarchical Micro/Mesoporous Carbons Synthesized with a ZnO Template and Petroleum Pitch via a Solvent-Free Process for a High-Performance Supercapacitor

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Supporting Information

ABSTRACT: Hierarchical micro/mesoporous carbons were prepared using ZnO nanoparticles as hard templates and a petroleum industrial-residual pitch as the carbon source via a solvent-free process. The ZnO templates can be easily removed using HCl(aq), thereby avoiding limitations present in conventional porous silica templating approaches that require highly corrosive HF(aq) for template removal. Notably, the proposed solvent-free synthetic method from low-cost pitch to high-value porous carbons is a friendly process with respect to our overexploited environment. With the combination of ZnO nanoparticles and pitch, the surface area (76–548 m² g⁻¹) of the resultant mesoporous carbons increases with an increase in the weight ratios of ZnO to pitch. Furthermore, the hierarchical micro/mesoporous carbons with a large surface area (854–1979 m² g⁻¹) can be feasibly fabricated by only adding an appropriate amount of an activating agent. Meanwhile, N-doped hierarchical porous carbons can be achieved by carbonizing the blend of these materials with melamine. For supercapacitor application, the resultant carbons exhibit a high capacitance up to 200.5 F g⁻¹ at 5 mV s⁻¹ using LiClO₄/PC as the electrolyte in a symmetrical two-electrode cell. More importantly, the coin-cell supercapacitor based on porous carbons achieved a capacitance of 94 F g⁻¹ at 5 mV s⁻¹ and 63% capacitance retention at 500 mV s⁻¹, thereby holding the potential for commercialization.

1. INTRODUCTION

Recently, porous carbons with large surface areas, high electrical conductivity, high chemical inertness, and tunable pore size have become attractive materials in nanoscience and commercial business. The porous carbons have been in use in many applications, for example, as absorbent materials, for gas absorption and storage, for catalyst support, and as electrode materials for fuel cells, Li-ion batteries, and supercapacitors.¹⁻³

In general, porous carbons with high surface areas and porosity are commonly synthesized using siliceous templates,⁴,⁵ with tunable structures, mesopore sizes, and morphologies. However, such procedures relying on the fabrication of silica templates are complicated, time-consuming, and unsuitable for large-scale production.⁶⁻⁸ Furthermore, the silica templates can be completely removed only by using highly corrosive hydrofluoric acid, HF(aq), which is extremely environmentally hazardous. On the contrary, nonsiliceous metal-oxide templates are chemically inert during high-temperature carbonization; therefore, using such templates, which can be removed by an acid solution, is a possible alternative method to prepare porous carbons.⁹,¹⁰

In past research studies, resins have been usually used to synthesize porous carbons.¹¹⁻¹³ Though many attractive and meaningful developments have been made regarding porous carbons synthesized with resin, the complicated synthetic procedures and electrical conductivity of the resultant porous carbons need to be improved. On the contrary, pitch, an industrial residue of petroleum, is cheap and abundant. The aromatic hydrocarbons abundant in pitch, featuring sp²-hybridized carbon atoms, can be polymerized and further aromatized to form carbons with a high carbon yield at high temperatures.¹⁴⁻¹⁷ Porous carbons synthesized using pitch possess a high specific surface area and tunable porosity after the carbonization and activation process and can perform a critical role in a supercapacitor.

Various synthesis approaches such as the nanocasting method with porous silica as the hard template and the self-assembling method with amphiphilic surfactant as the soft template have been widely used for the preparation of porous carbons.¹⁸⁻²¹ However, in these methods, it normally takes a long time for the formation of the mesostructured composite between the carbon precursor and the template separated from the diluted solution, which leads to low efficiency and high solvent waste. For comparison, a solvent-free route has many advantages, such as reduced pollution, low cost, and simplicity in process and handling, which are especially important in the
industry. Considering these merits, recently, a solvent-free route has been developed to prepare nanomaterials, such as zeolites, N- and B-doped graphitic carbon, and carbon nanotube.\textsuperscript{22,23} Obviously, it is very desirable to develop a solvent-free approach for the synthesis of porous carbons with a high surface area and tunable porosity.

A supercapacitor is a useful and widespread device that stores energy by accumulating ions on the interface between the electrolyte and the electrode.\textsuperscript{24–27} Supercapacitors are used in many electric products because of their high power density, long cycle life, and superior safety compared with secondary batteries. Nevertheless, they are limited by low energy density, which causes increased device volume and cost because of the low pore volume of the commercially available microporous carbons (pore size < 2.0 nm). Therefore, it is paramount to design a nanostructured porous carbon with pore properties tailored specifically for the application in supercapacitors.\textsuperscript{28–33}

In this study, novel hierarchical micro/mesoporous carbons using ZnO as the hard template and cheap petroleum industrial-residual pitch as the carbon source have been prepared, as illustrated in Figure 1. The ZnO templates can be almost completely removed by a hydrochloride solution, avoiding the use of highly corrosive HF(aq) for the removal of the silica template. The resultant carbons with a controllable surface area with mesopores can be fabricated by adjusting the ZnO/pitch weight ratio. Furthermore, micro/mesoporous carbons with a large specific surface area and pore volume can be generated by the addition of an activating agent. Meanwhile, the N-doped porous carbons with a high surface area and a micro/mesoporous structure can be approached by further blending melamine, which acts as a nitrogen source. To characterize and evaluate the commercialization potential of the resultant hierarchical porous carbons, tested as the electrode material in the conventional symmetrical two-electrode cell and simulation as commercial coin-cell supercapacitors was conducted. On the basis of the hierarchical micro/mesopore and nitrogen-doped properties of the carbons, these as-synthesized porous carbons exhibit excellent performance as the electrode material for supercapacitors.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Mesoporous Carbon Prepared from Petroleum Pitch. The morphology of the ZnO template and the resultant mesoporous carbon is shown in Figure 2a,b. The ZnO template consists of ZnO nanoparticles with a size of approximately 20–30 nm. After removing the ZnO template by acid solution, one can clearly see that the pore size of the mesopores in the resultant carbon is close to the ZnO particle size, which indicates that the pores of the porous carbon were formed from an integral casting of the petroleum pitch on the ZnO template. Meanwhile, the transmission electron microscopy (TEM) image for the as-prepared carbon was further measured, as shown in Figure S1. Impressively, a highly porous structure with thin carbon walls can be obtained. The thermal gravimetric analyses of the obtained samples are shown in Figure 2c. The thermogravimetric analysis (TGA) curves demonstrate that the ZnO residual content in the mesoporous carbon after HCl etching is approximately 0%. The key point of our synthesis strategy to produce porous carbons is the formation of the high-connectivity ZnO/carbon composite and the use of the easily removed ZnO template. It was also found that the pitch-derived carbon material has high thermal stability with a decomposition temperature higher than 600 °C. To further study the carbon structure in the stable mesoporous carbon from petroleum pitch, we analyzed the defect level of the carbon structure by comparing the intensity ratio ($I_D/I_G$) of the D-band (1350 cm$^{-1}$) and the G-band (1580 cm$^{-1}$) in the Raman spectrum (Figure 2d). The $I_D/I_G$ value for the prepared mesoporous carbons is 0.41, suggesting a low defect level. These results demonstrate that the solvent-free synthesis of the high-value carbon material from ZnO templates blending the petroleum industrial-residual pitch was achieved in our study.

2.2. Effect of the ZnO/Pitch Weight Ratio on the Surface Area of the Mesoporous Carbon. The tunable surface area and the pore volume of porous carbons are key factors for their applications. In this study, it was demonstrated that the surface area and the pore volume of the porous carbons can be easily controlled by adjusting the ZnO/pitch weight ratio. Interestingly, it was observed that the surface areas of the prepared porous carbons increased linearly from 76 to 318 m$^2$ g$^{-1}$ with an increase in the ZnO/pitch weight ratio from 0.5 to 4 (Figure 3). Within this range, the ZnO nanoparticles with nanospaces function as a nanotemplate for the pitch. Above the softening point, the liquid-behavior pitch can penetrate into the textual pores between ZnO nanoparticles via capillary adsorption. Then, the polymerization reaction of the pitch will take place to yield interconnected polymer films made of aromatic structures for integral casting of the ZnO template. This result reveals that the hard templates with textual mesopores play an important role in integral casting of the melting carbon precursors to control the surface area and the mesoporosity of the resultant mesoporous carbons. At a ZnO/pitch weight ratio larger than 4.0, the ZnO content is too high to be completely covered by the pitch, which decreases the pore-formation performance of the ZnO template.

To understand the high-integrity casting and the feasible removal of the ZnO template, the decomposition profiles of the pure pitch, the ZnO/pitch mixture (4/1 in weight ratio), and the ZnO template were measured by TGA under a nitrogen...
atmosphere, as shown in Figure 4. The carbon precursor/pitch showed a decomposition initiating at approximately 200 °C, and its residual weight percentage at 900 °C is approximately 48%, which means a high carbon yield from pitch sources. In comparison to the TGA profiles of ZnO and the pitch, the ZnO/pitch mixture had an additional weight loss at approximately 800 °C. This decomposition is ascribed to carbothermal reduction of partial ZnO nanoparticles at a temperature higher than 800 °C in the presence of carbon.34 The resultant zinc nanoparticles and carbon monoxide gases lead to foam formations that increase the interconnectivity of the carbon/ZnO matrix (Figure S2). Because of the high connectivity of the carbon/ZnO matrix, ZnO can be almost completely etched in a moderate acidic solution.

2.3. Micro/Mesoporosity Control via the Addition of an Activating Agent. It is well-known that a large surface area is a primary requirement for obtaining a high specific capacitance for carbon electrodes. Therefore, different activating agents, K2CO3 and KOH, were blended with ZnO and the pitch to increase the surface areas of the porous carbons by introducing microporosity.35−37 Table 1 shows the textural parameters of the hierarchical micro/mesoporous carbons activated by K2CO3 and KOH at different activating agents/pitch weight ratios. The resultant carbons activated by K2CO3 were observed to have a large improvement in their surface area up to 1272 m2 g−1 when the ZnO/pitch/KOH ratio was 4:1:3. Furthermore, the porous carbons activated by KOH exhibited a high surface area of 1979 m2 g−1 when the ZnO/pitch/KOH ratio was 4:4:3.
ratio was 4:1:1. At a high temperature, both K$_2$CO$_3$ and KOH can react with carbon to corrode its framework, which creates micropores. This process takes place via a mechanism similar to that operating during the chemical activation of carbonaceous materials with alkali hydroxide.$^{38}$ The reaction mechanism of K$_2$CO$_3$ and KOH activation is as follows

\[
\begin{align*}
K_2CO_3 + 2C & \rightarrow 2K + 3CO_2 (g) \\
K_2CO_3 & \rightarrow K_2O + CO_2 (g) \\
K_2O + C & \rightarrow 2K + CO (g) \\
6KOH + 2C & \rightarrow 2K + 3H_2 + 2K_2CO_3
\end{align*}
\]

Initially, the enhancement of the activating agent increases not only the value of the specific surface area but also the porosity because of the activating agent corroding the carbon structure. However, a larger amount of the activating agent leads to more violent corrosion of the carbon framework, which generally reduces the carbon yield. To estimate the performance of the activation agent, we multiplied the Brunauer–Emmett–Teller (BET) equation surface areas by carbon yields to get the total surface areas (denoted as $S_t$ values). In Table 1, it can be clearly seen that the largest $S_t$ values occur at K$_2$CO$_3$/pitch of 0.5/1 and KOH/pitch of 0.75/1 by using K$_2$CO$_3$ and KOH as activating agents, respectively. At a lower activating agent/pitch ratio, the surface area contributed from microporosity is low. Although the activating agent/pitch ratio is too high, the carbon yield is much reduced, which leads to a low $S_t$ value. Consequently, adding the appropriate amount of the activating agent is critical for controlling the porosity and surface area of the prepared porous carbons. In brief, we provide a simple synthetic method to fine-tune the surface area ratio of the micropore to the mesopore by controlling the amount of the activating agent and the weight ratio of ZnO/pitch.

### 2.4. Structural Characterizations of N-Doped Porous Carbons

It has been confirmed that an appropriate nitrogen content in the carbon framework can significantly enhance both the electronic conductivity and the wettability of the interface between the electrolyte and the electrode, thereby improving

| Sample | Activating Agent (AA) | ZnO/pitch/AA (Weight Ratio) | $S_{BET}$ (m$^2$ g$^{-1}$) | $S_{mic}$ (m$^2$ g$^{-1}$) | $S_{mes}$ (m$^2$ g$^{-1}$) | Carbon Yield (%) | $S_t$ (m$^2$ g$^{-1}$) |
|--------|----------------------|-----------------------------|---------------------------|--------------------------|--------------------------|-----------------|---------------------|
| C1     | K$_2$CO$_3$          | 4/1/0.5                     | 1170                      | 397                      | 773                      | 43              | 503                 |
| C2     | K$_2$CO$_3$          | 4/1/1                       | 1231                      | 520                      | 711                      | 37              | 455                 |
| C3     | K$_2$CO$_3$          | 4/1/2                       | 1269                      | 443                      | 826                      | 27              | 343                 |
| C4     | K$_2$CO$_3$          | 4/1/3                       | 1272                      | 396                      | 876                      | 24              | 305                 |
| C5     | K$_2$CO$_3$          | 2/1/1                       | 854                       | 595                      | 260                      | 38              | 325                 |
| C6     | KOH                  | 4/1/0.5                     | 921                       | 541                      | 380                      | 42              | 387                 |
| C7     | KOH                  | 4/1/0.75                    | 1537                      | 543                      | 994                      | 38              | 584                 |
| C8     | KOH                  | 4/1/1                       | 1979                      | 725                      | 1254                     | 21              | 416                 |
| CN     | K$_2$CO$_3$          | 4/1/1/0.5 melamine          | 1375                      | 747                      | 628                      | 33              | 454                 |

$^a$Micropore surface area. $^b$Mesopore surface area. $^c$Carbon yield/% = weight of carbon/weight of pitch. $^d$S$_t$ = $S_{BET}$ × carbon yield.
the performance of carbon as an electrode material in supercapacitors. In this study, the N-doped porous carbons (C_N) were synthesized by simply blending melamine with the aforementioned mixture. For comparison, C2, the carbon without N-doping, was made with the same weight ratio of ZnO, pitch, and K2CO3, as shown in Table 1.

From elemental analysis data, the nitrogen content in the obtained N-doped porous carbon was approximately 3.6 wt % with a weight ratio of ZnO/pitch/activating agent/melamine of 4:1:1:0.5. In Figure S3, the N2 adsorption–desorption isotherms show that significant differences exist between the C_N and C2 curves. C_N has already absorbed abundant nitrogen at low pressure. The specific surface areas of C_N and C2 are 1375 and 1231 m2 g−1, respectively, with microporous surface areas of 747 and 520 m2 g−1. This indicates that C_N has more micropores in the carbon framework and an enhancement of the specific surface area, confirming that melamine changes the distribution of pores via its interaction with K2CO3 and completely binds with the pitch to produce N-doped porous carbons. The presence of nitrogen group on the surfaces of CN and C2 curves. CN has already absorbed abundant nitrogen between the graphitic carbon layers, respectively. It is clear that C_N contains larger percentages of pyridinic and pyrrolic types of nitrogen, which are reported to be responsible for the active sites. Thus, the simple blend with the carbon precursor, nitrogen-containing precursor, and ZnO template via a solvent-free route and pyrolysis at a high temperature led to the effective formation of nitrogen-doped porous carbon materials.

2.5. Supercapacitor Performance of the Hierarchical Micro/Mesoporous Carbons

2.5.1. Conventional Symmetrical Two-Electrode Cell Test. It is known that the presence of mesopores among the carbons is helpful for fast mass transport of ions at high charging rates. Figure 5a shows cyclic voltammograms of the conventional two-electrode cell assembled with the hierarchical micro/mesoporous carbon (C7) with the surface area of 1537 m2 g−1. The cells behave similar to an ideal double-layer capacitor with an almost symmetric and rectangular shape at various potential scan rates. Furthermore, the specific capacitance value was high, that is, 200.5 F g−1 at 5 mV s−1. Figure 5b shows the Nyquist plot of the C7 cell measured at 0 V. The semicircle appearing within the high-frequency range in the plots can be accounted for as an Rct equivalent-circuit unit consisting of a double-layer capacitance at the electrode/electrolyte interface in parallel with a charge-transfer resistance (Rct) through the pseudocapacitance process. The intersection of the forefront of the semicircle with the x-axis gives the ionic resistance, R_0, of the electrolyte, whereas the span of the semicircle along the x-axis provides Rct. Accordingly, the R_0 and Rct values for C7 cell are 3.8 and 0.5 Ω, respectively. Both the high specific capacitance and the low resistance confirm the great performance of C7 as an electrode in a symmetric two-electrode cell. In addition, Figure 5c shows the specific capacitance values and capacitance retention of the C7 electrode at various scan rates. The C7 cell delivered 89.6 F g−1 at the largest scan rate of 500 mV s−1, constituting a 46% retention rate. Furthermore, for cycle stability test, the capacitance drops was approximately 5% after the 8000 cycle test, as shown in Figure 5d. The retention in capacity at a high scan rate is ascribed to the mechanical resistance from fabrication and the obstacle of ionic transportation. In addition to effectively increasing the specific surface area of the hierarchical porous carbons, the micropores also play a critical role in creating ion transportation resistance because of their small tunnel size, thereby limiting migration and diffusion of ions. Hence, the hierarchical porous carbon with the optimum ratio of micropores to mesopores is beneficial for a supercapacitor to achieve high electrochemical performance. Figure S5a,b shows the representative galvanostatic charge–discharge curves of C7 cell with organic and aqueous electrolytes, at different current loads from 0.5 to 9.0 A
In this section, coin-cell supercapacitors are fabricated by three symmetric two-electrode cell used in the energy industry. In supercapacitors are more notable than the laboratory-used hierarchical porous carbons, the easy-assembling coin-cell capability and the commercialization potential of the prepared materials, as discussed in the following. The carbons, namely, C5 (micropore is a major portion in carbon framework and thus deliver more e−, respectively, at a scan rate of 5 mV s−1. From a commercial point of view, the C7 cell with an aqueous electrolyte (6.0 M KOH(aq)) are shown in Figure S6. The cells behave similar to an ideal double-layer capacitor with an almost symmetric and rectangular shape at various potential scan rates and delivered an 80% retention rate at the largest scan rate of 500 mV s−1.

2.5.2. Coin-Cell Supercapacitor Test. To evaluate the capability and the commercialization potential of the prepared hierarchical porous carbons, the easy-assembling coin-cell supercapacitors are more notable than the laboratory-used symmetric two-electrode cell used in the energy industry. In this section, coin-cell supercapacitors are fabricated by three different frameworks of as-synthesized hierarchical porous carbons, namely, C5 (micropore is a major portion in carbon materials), C7, and CN, as discussed in the following. The capacitance values of C5, C7, and CN are 67, 94, and 84 F g−1, respectively, at a scan rate of 5 mV s−1. This reveals that a higher specific surface area of hierarchical porous carbons can enhance the specific capacitance.

The CV curves of the coin cells containing the three above-mentioned hierarchical porous carbons are compared in Figure 6. All CV curves exhibit nearly rectangular profiles at various potential scan rates, indicating nearly ideal capacitor behaviors. Furthermore, the C7 cell exhibited a higher capacitance retention at 63% compared with C5 (at 45%) at high potential scan rates, as shown in Figure 7a, which is attributed to its hierarchical micro/mesopores structure. Although mesopores play a limited role in storing charge, they provide suitable space to allow ions of bulky electrolytes to transport smoothly to the carbon framework and thus deliver more effective access than micropores. As such, a balance between micropores and mesopores should be obtained in the supercapacitor. In addition, the retention rate of the CN cell is higher than that of the C5 cell, despite their pore size distribution varying only slightly. Because nitrogen can not only wet the interface between the carbon surface and the electrolyte but also increase the conductivity of CN, nitrogen doped into the hierarchical porous carbon minimizes the resistance of the supercapacitor. The Nyquist plot in Figure 7b also provides evidence for their difference in terms of resistance via the high-frequency part. As seen, the Rs values for the C5, C7, and CN cells are 3.0, 0.8, and 2.9 Ω, respectively. Again, the C7 and CN cells show a lower resistance than the C5 cell. From a commercial point of view, the C7 cell can be applied as the electrode material in a coin-cell supercapacitor with the specific capacitances of 94 F g−1 at 5 mV s−1 and 59 F g−1 at 500 mV s−1 with a retention rate of 63%.

3. CONCLUSIONS

In this study, a simple physical blending method to transform the petroleum industrial-residual pitch into value-added porous carbons with hierarchical pores has been provided. In addition, the ZnO template was simply removed by hydrochloric acid, thereby avoiding the use of highly corrosive hydrofluoric acid. Hierarchical porous carbons with tunable specific surface areas, pore volumes, and micropores/mesopores ratios were feasibly synthesized by changing the ZnO/pitch ratios and activating reagent additions. Although the ZnO nanoparticles are an appropriate template, the Zn2+ ion aqueous solution needs to be recycled rather than discarded. In addition to the ZnO template and the petroleum pitch, other environment-friendly inorganic nanoparticles [such as MgO, Ca(OH)2, CaCO3, Ca3PO4, etc.] and other industrial wastes (e.g., lignin and other biobased residue) can also be considered as hard templates and carbon precursors to prepare the hierarchical porous carbons. The feasibility of using these new inorganic templates and carbon sources needs to be further studied. The hierarchical porous carbons have been used as potential electrode materials in supercapacitors and electrochemical applications.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Hierarchical Micro/Mesoporous Carbons. To prepare the hierarchical porous carbons, the industrial-residual petroleum pitch (CF19, softening point of approximately 120 °C, provided by Chinese Petroleum Corporation, Taiwan), ZnO (AZO900, Diamonchem International Co, Taiwan), and alkaline metal carbonates (K2CO3 and KOH, purchased from Merck) were used as the carbon source, the hard template, and activating agents, respectively. The typical synthesis procedure is as follows: the pitch, the hard template, and activating agents were directly ground into a mixture by using a blender. The weight ratios in the mixture are represented by x/y/z, where x is the template weight, y is the pitch weight, and z is the activating agent weight. The resultant powder was sealed in a stainless steel vessel and then directly heated in a furnace. The heating rate was set at 8 °C min−1 and held at a carbonization temperature of 900 °C for 2 h. After cooling to room temperature, the sample was washed with DI water and soaked in an appropriate amount of 3.0 M HCl solution under stirring for 2 h to remove the alkaline oxides and...
Electrode. The specific and pore size of the resultant porous carbons were examined on a field emission scanning electron microscope (FE-SEM, JEOL JSM7000F, USA). TEM was conducted using a Hitachi H-7500 microscope. The inorganic residue in the resultant porous carbons and the carbon-to-inorganic template ratio of the particle composition was characterized using a TGA (TA Instruments Q50, USA), heated from 100 to 900 °C with a ramp rate of 20 °C min⁻¹ under an air or nitrogen atmosphere. 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 porous carbons. The N₂ adsorption–desorption isotherms of all samples were taken at 77 K on a micrometric TriStar II apparatus to estimate the pore sizes and surface areas. The pore-size distribution curves were obtained from the analysis of adsorption isotherms using the BJH (Barrett–Joyner–Halenda) method.

4.3. Electrode Preparation and Electrochemical Characterization. A symmetrical two-electrode capacitor cell was used to examine the electrochemical performance of the porous carbon electrodes. Both electrodes were made with approximately 2.0 mg carbons on 1.0 cm² stainless foil, which acts as a current collector. This cell consisted of two carbon electrodes, sandwiching a cellulose filter paper as the separator. A coin-cell (CR2032) capacitor was prepared as follows. First, to construct the electrode, the carbon material (90 wt %) and polyvinylidene fluoride (10 wt %) were thoroughly mixed in N-methyl-pyrrolidone. The resultant slurry was coated onto a stainless foam current collector with approximately 3.0 mg cm⁻² for carbon materials and dried under vacuum at 120 °C for 12 h. Finally, the coin cells were assembled in a dry and inert glove box with the two carbon electrodes and the cellulose filter paper as the separator.

Cyclic voltammetry measurements were recorded between −2.0 and 2.0 V in an 1.0 M LiClO₄/PC solution and between 0 and 1.0 V in an 6.0 M KOH solution at sweep rates ranging from 5 to 500 mV s⁻¹. Plots of specific capacitance versus voltage for the symmetrical two-electrode cell were calculated using the following formula

\[ C = \frac{2I}{vm} \]

where \( I \) represents the current (A), \( v \) is the scan rate (V s⁻¹), and \( m \) denotes the mass (g) of the carbon material in one electrode. The specific gravimetric capacitance of a single electrode (F g⁻¹) determined from the galvanostatic cycles was calculated by the following equation

\[ C = \frac{2I}{(dV/dt)m} \]

where \( dV/dt \) is the slope of the discharge curve (V s⁻¹). Electrochemical impedance spectroscopy measurements were recorded at an open-circuit voltage (0 V) within the frequency range of 1 mHz to 100 kHz at a 5 mV amplitude.

■ ASSOCIATED CONTENT

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00308.

TEM image, SEM image, nitrogen adsorption and desorption isotherms, XPS, charge–discharge curves, and cyclic voltammograms (PDF)

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Notes

The authors declare no competing financial interest.

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