Cellulose-Derived Highly Porous Three-Dimensional Activated Carbons for Supercapacitors

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ABSTRACT: A novel “selective surface dissolution” (SSD) method was successfully utilized in previous research to prepare “all-polymer composites” aiming to structural applications. In the current study, this simple, cost-effective, and environmentally friendly method was employed for the first time to synthesize cellulose-derived highly porous three-dimensional (3D) activated carbon materials to assemble superior electrodes for supercapacitors. ZnCl₂ aqueous solution was used to partially dissolve the surface of cellulose fibers. The partially dissolved cellulose I crystalline phase at the fiber surface can be consolidated into fibrillar cellulose polymorphs (e.g., cellulose II) which connects remaining fibers together. By a carefully controlled SSD method, a highly porous 3D cellulosic skeleton with interconnected bridge-like fibrillar linkages and hierarchical pore structures can be created. After carbonization, the 3D fiber construct with interconnected fibrillar linkages and hierarchical pore structures remains and highly porous activated carbons were obtained. The effects of various processing parameters (e.g., solvent concentration, immersion time, etc.) on the morphology of the as-formed activated porous carbons and their electrochemical performance as electrodes in supercapacitors were systematically investigated and discussed. It was concluded that the SSD method is a promising chemical approach to produce large-scale cellulose-derived activated porous carbons in an environmentally friendly manner.

1. INTRODUCTION

Emerging environmental problems and excessive energy consumption makes cutting-edge research in eco-friendly and efficient energy storage devices to be urgently needed. Electric double-layer capacitors (EDLC) also known as supercapacitors are one of the most attractive energy storage devices for versatile applications such as urban rail transportation, electrical vehicles, and portable device, thanks to their high power density, fast charge/discharge rate, and excellent stability features.¹ In EDLCs, opposite charges accumulate on the interfacial regions of electrode and electrolyte by electrostatic physical interaction, which leads to highly reversible performances and a long cycle life. Therefore, the surface characteristics of electrode materials will strongly influence the capacitance of EDLCs.²

Active carbons (ACs) have been widely used as electrode materials for EDLCs because of their large surface area, good electrical conductivity, and relatively lower cost. In recent years, biomass-derived porous carbon materials have attracted significant attention. As a renewable resource, biomass shows many advantages, such as an abundant and sustainable raw materials source, environmental friendliness, and low cost. A number of inspiring works have been carried out to synthesize porous carbons from different biomass raw materials for EDLCs.³⁻¹⁵ However, there are still various uncertainties for the utilization of biomass-derived porous carbons in EDLCs. Besides, harsh alkaline and heat treatments are often needed to increase surface area of these carbon materials, which may put more burden on the environment. More researches have to be performed to develop a simple and environmentally friendly technique to produce biomass-derived porous carbons.

The concept of “all-polymer composites” or “self-reinforced composites”, which are based on similar or identical materials for both matrix and reinforcement, was first brought up in 1970s.¹⁶ Since then, this topic has become a fast-growing research area in polymer composites.¹⁷⁻²⁴ Because of their distinct advantages in lightweight, interfacial properties, and recyclability, such composites are therefore used in a wide range of applications, such as automotive, protective materials, sport products, and so forth. In recent decade, a novel
"selective surface dissolution" (SSD) method has been proposed by Nishino and Arimoto to prepare eco-friendly "all-cellulose" composites.25 In their study, the surface layers of cellulose fibers were selectively dissolved and transferred into a matrix by consolidation to bond the remaining fiber cores together, all-cellulose composites were then formed.25 Inspired by this SSD method, a range of all-polymer composites based on ligno-cellulose, regenerated cellulose, bacterial cellulose and even aramids have been developed so far, which expands these composites into high performance applications.26–32 It was noticed in morphological observations that when applying the SSD method to prepare all-polymer composites, interfibrillar voids would appear in the later formed matrix phase when solvent immersion time was not sufficient.27–29 In the case of insufficient immersion times, interfibrillar voids existing in the matrix phase would lead to premature failure of the composites. This situation needs to be much more carefully avoided when preparing all-polymer composites by the SSD method for structural applications. However, for functional applications (e.g., as electrodes for EDLCs), porous materials with high surface area are preferred. Inspired by previous researches on all-cellulose composites, we suggest that by carefully controlling the SSD process parameters, the interfibrillar voids together with remaining fiber cores and as-formed matrix can help to build a beneficial three-dimensional (3D) porous cellulosic skeleton to further synthesize highly porous 3D activated carbon materials.

Hence, for the first time, we propose to apply the SSD method to synthesize highly porous 3D activated carbons for electrodes in EDLCs. Zinc chloride (ZnCl₂) aqueous solution is widely acknowledged as a facile, environmentally friendly solvent for cellulose. In this paper, we utilized ZnCl₂ aqueous solution to partially dissolve the surface of cellulose fibers. When cellulose I is immersed in 5, 10, 20, and 40 wt % ZnCl₂ solutions, the partially dissolved cellulose I on the fiber surfaces can be consolidated into fibrillar cellulose polymorphs (e.g., cellulose II), exhibiting a highly porous 3D structure with bridge-like fibrillar linkages that connect remaining cellulose fiber cores together. After carbonization, a 3D fiber construct with interconnected fibrillar linkages remains and highly porous activated carbons were obtained. The effects of various processing parameters (e.g., solvent concentration, immersion time, etc.) on the morphology of the as-formed activated porous carbons and their electrochemical performance as electrodes in EDLCs will be systematically investigated and discussed in this paper.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Filter papers were first cut into 30 mm × 30 mm squares and immersed into 5, 10, 20, and 40 wt % zinc chloride (ZnCl₂) aqueous solutions for the partial fiber surface dissolution process. The treated filter papers were
then consolidated in water and then dried in an oven at 80 °C for 2 h. In a following carbonization step, the dried samples were placed in a furnace which was heated to 650 °C at a heating rate of 5 °C/min under the protection of argon gas, and the samples were held at 650 °C for 2 h before cooling down to room temperature naturally to finally obtain black and highly porous carbon materials. The samples were designated as CF0 (without the SSD process) and CF-X-Y, where X represents solvent concentration and Y represents immersion time.

2.2. Characterization. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Belsorp mini II (BEL Co. Ltd, Japan). Brunauer–Emmett–Teller (BET) method was used to analyze the surface area ($S_{BET}$). The pore size distribution was analyzed using the density function theory model. Raman spectra were recorded on a Raman spectrometer (Nanophoton, Japan) at a laser excitation of 532 nm. Scanning electron microscopy (SEM) was performed on a JSM-6500F (JEOL, Japan) using an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) was performed on a JSM-2100Plus (JEOL, Japan). X-ray diffraction (XRD) profiles were investigated from 5° to 90° at a scan rate of 5°/min using a MiniFlex600 Rigaku (Japan).

In addition, electrodes for EDLC were assembled by mixing as-prepared carbon materials (72 wt %) with carbon black (18 wt %) and poly(tetrafluoroethylene) (10 wt %) and then uniformly filtered onto a flexible microporous film. Electrochemical measurements were carried out in 2032-type coin cells with these two symmetrical electrodes, with a glass fiber film as separator, and 1 M H$_2$SO$_4$ as electrolyte. Cyclic voltammetry (CV) was recorded on a potentiostatic electrochemical workstation with a two-electrode configuration (VSP-300, Bio-Logic, France). Galvanostatic charge/discharge (GCD) was performed on CT2110A, Land Battery Testing System, China.

The specific capacitances are calculated based on GCD data according to following eq 1

$$C_{\text{cell}} = 4C_{\text{electrode}} \times \frac{I \times \Delta t}{M \times \Delta V}$$

where $C_{\text{cell}}$ [F/g] is the specific capacitance of the supercapacitor, $C_{\text{electrode}}$ [F/g] is the specific capacitance of single electrode, $\Delta V$ [V] is the potential change within the discharge time $\Delta t$ [s], and $M$ [g] is the total mass of active materials on the two electrodes of the capacitor.

3. RESULTS AND DISCUSSION

To analyze the composition and structure of the materials, samples were characterized by XRD. Before any surface treatment, the diffraction profile of filter paper in Figure 1a shows a typical cellulose I structure (chains aligned in a parallel conformation), exhibiting an intense sharp reflection at 2θ = 22.5° and two overlapping weaker diffractions at 2θ = 14.5°.

![Figure 2. Raman spectra of CF0, CF5-30, CF10-30, CF20-30, and CF40-30, indicating higher $I_D/I_G$ by increasing ZnCl$_2$ solvent concentration from 5 to 40 wt %.]
and 16.3°, which are assigned to the [002], [101], and [101] lattice planes of cellulose I, respectively. Cellulose I crystalline structure is less stable than cellulose II (an antiparallel conformation, see Figure 1b), therefore, during the carbonization process of sample CF0 for example, cellulose I was first transformed into cellulose II, and the disordered carbon structure formed was based on cellulose II as indicated by the appearance of broadened and overlapped diffraction peaks at around 2θ = 22° ([002], [101]) and a diffraction peak at 2θ = 12.5° ([101]) (Figure 1a).

Figure 1c shows different XRD diffraction profiles for samples prepared with various ZnCl2 solution concentrations. All these XRD diffraction patterns possess three relatively broad peaks around 2θ = 12.5°, 22°, and 44°, which correspond to the [101], [002]/[101], and [100] lattice planes of disordered graphitic carbon. It is also noticed in Figure 1c that a slight decrease in diffraction intensity occurred for the [002] plane. To make a clear comparison, XRD diffraction profiles of CF0 and CF40-30 were plotted separately in Figure 1e. After applying suitable curve fitting, we can clearly see that the [002] peak intensity decreased for CF40-30, indicating a decrease in crystallinity with partial surface dissolution. Lateral crystal size (D) normal to [002] plane can be calculated by means of Scherrer’s equation

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where K is a dimensionless shape factor, \(\lambda = 1.5418 \text{ Å}\), \(\beta\) is corrected integral width, and \(\theta\) is Bragg angle for the [002] diffraction. Therefore, lateral crystal size decreases slightly due to an increase of the integral peak width. Crystallinity in the [002] plane also decreases with increasing ZnCl2 solvent concentration and more disordered carbon structures were therefore formed by the SSD process.

We also studied samples treated by relatively low (10 wt %) and high (40 wt %) solvent concentrations with different immersion times. As shown in Figure 1d, by increasing immersion times, the diffraction angle slightly decreased for both low- and high-solvent concentrations which indicates a small decrease in crystal size.

In Raman spectra, two characteristic peaks are present centered at around 1330 and 1586 cm\(^{-1}\) affiliated with the D-band and G-band of polycrystalline carbon materials, respectively (Figure 2). The intensity ratio between D-band and G-bands (i.e., \(I_D/I_G\)) can reflect the graphitic degree of the carbon materials. As shown in Figure 2, \(I_D/I_G\) of samples increased with higher solvent concentration, indicating a more defective structure and lower degree of graphitization created by more cellulose dissolution in ZnCl2 solvent. Table 1 shows \(I_D/I_G\) data for samples with different immersion times, indicating that more defects are induced by increasing the immersion time in the SSD process. The “more defective structure” is attributed to the as-formed porous cellulosic skeleton with bridge-like fibrillar linkages (i.e., partially dissolved and consolidated fibrillar cellulose polymorphs) that connect remaining cellulose fiber cores together.

| Table 1: \(I_D/I_G\) Data for Samples with Different Immersion Times for Low (10 wt %) and High (40 wt %) Solvent Concentrations |
|-----------------|-----------------|-----------------|-----------------|
| sample          | \(I_D/I_G\)     | sample          | \(I_D/I_G\)     |
| CF10-30         | 0.92            | CF40-30         | 0.94            |
| CF10-60         | 0.94            | CF40-60         | 0.96            |

Nitrogen adsorption—desorption isotherms were used to analyze the micro- and nano-structure of the samples. As shown in Figure 3a, all CF materials rapidly take up nitrogen at low relative pressures (\(P/P_0 = 0—0.1\)), displaying typical IUPAC type I isotherms, indicating that microporosity plays a major role in these porous structures. Samples from CF5-30 to CF40-30 presents dramatically higher adsorption uptake at low relative pressure (\(P/P_0\)) compared with CF0, which was attributed to the formation of more micro- or meso-pores by the SSD process at higher solvent concentrations. The pore parameters of the samples were listed in Table 2. According to Table 2 and the pore size distribution (Figure 3c), micropores (<2 nm) are dominant in all CF samples, although for samples CF40-30 and CF40-60 larger pores were created. It is proposed that the ZnCl2 solvent can substantially dissolve the outer layers of cellulose fibers during the SSD process. Upon consolidation, dissolved cellulose molecules reoriented and re-crystallized into cellulose II and formed bridge-like fibrillar linkages that connect the remaining fiber cores together. Meanwhile, numerous micro- and meso-pores were created inside these “bridges” during the consolidation process. As indicated in Table 2, with higher solvent concentration, both the specific area and volume of micropores (\(S_{mic}\) and \(V_{mic}\)) increased; the specific area and volume of mesopores (\(S_{mes}\) and \(V_{mes}\)) increased dramatically by 1 order of magnitude for samples CF40-30 and CF40-60, which is also clearly shown in Figure 3c,d. Interestingly, from 5 to 20 wt %, the mean pore size (\(D_{pore}\)) decreased with higher solvent concentration due to more fibrillar linkages and micropores created, but eventually for sample CF40-60, \(D_{pore}\) increased back to the same value as sample CF0. This interesting phenomena is resulted from the amount of large-sized pores (e.g., meso- and macro-pores) increased by higher solvent concentration and longer immersion time. It is noteworthy that the specific surface area (\(S_{BET}\)) of sample CF40-60 are 4 times higher than \(S_{BET}\) of sample CF0. We also investigated the porosity of samples with different immersion times for low (10 wt %) and high (40 wt %) solvent concentrations (Figure 3a,b,d). For low solvent concentration, with increasing immersion time, \(S_{BET}\) and \(V_{total}\) increased due to a continuous formation of fibrillar linkages and micropores. However, for high solvent concentration, \(S_{BET}\) and \(V_{total}\) decreased with increasing immersion time. This can be attributed to the pore amalgamation and closure. The pore amalgamation and closure happened when a fairly large amount of pristine cellulose fibers were dissolved and consolidated into linkages between fiber cores under the circumstances of high solvent concentration and long immersion time. Similar to the formation of large amount of matrix phase in all-cellulose composites, during such a massive dissolution and consolidation process, small-sized pores (e.g., micropores) amalgamated into large-sized pores (e.g., meso- and macro-pores). Therefore, the proportion of large-sized pores increased in the samples CF40-30 and CF40-60 as shown in Figure 3b. Besides, with extended dissolution time, more small-sized pores closed for sample CF40-60. Hence, both \(S_{BET}\) and \(V_{total}\) of sample CF40-60 are inferior than those of sample CF40-30. It is also indicated in Figure 3d that pore sizes in sample CF40-60 are more evenly distributed than in sample CF40-30, which is the result from pore transformation. The phenomena of pore transformation can also explain the
dramatic increase of $S_{mes}$ and $V_{mes}$ for sample CF40-30 and the changes of $D_{pore}$ in Table 2.

It is agreed widely that high specific surface area and wide pore size distribution for activated porous carbons would strongly enhance their electrochemical performance and the performance of EDLCs made by these carbon materials. Therefore, these cellulose-derived highly porous 3D activated carbons with rich and hierarchical pore structures are promising candidates for electrodes in EDLCs.

To visualize the microstructure of as-formed pores and bridge-like fibrillar linkages, SEM was performed on samples CF0, CF5-30, CF10-30, CF20-30, CF40-30, and CF40-60. As shown in Figures 4 and 5, more and stable bridge-like fibrillar linkages were created by the SSD process with increasing solvent concentrations. After carbonization, a 3D fiber construct with interconnected fibrillar linkages well remained and highly porous activated carbons were obtained. By controlling the SSD process parameters, more bridge-like fibrillar linkages and micropores are formed with solvent concentrations from 5 to 20 wt %. With higher solvent concentration (e.g., 40 wt %), a large number of micropores are amalgamated into mesopores or macropores, which are in good agreement with pore parameters in Table 2. Besides, a cross-sectional view of sample CF40-60 is inserted in Figure 4, showing large-sized pores underneath the massively dissolved fiber surfaces. All of the micro-/meso-/}

### Table 2. Pore Parameters of the Samples

| Sample | $S_{BET}$ [m$^2$/g] | $S_{mic}$ [m$^2$/g] | $S_{mes}$ [m$^2$/g] | $V_{mic}$ [cm$^3$/g] | $V_{mes}$ [cm$^3$/g] | $V_{total}$ [cm$^3$/g] | $D_{pore}$ [nm] |
|--------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------|
| CF0    | 244.5                | 233.2                | 11.35                | 0.105                | 0.016                | 0.121                | 1.974          |
| CF5-30 | 504.4                | 486.1                | 18.23                | 0.206                | 0.023                | 0.229                | 1.816          |
| CF10-30| 507.4                | 491.6                | 15.80                | 0.209                | 0.019                | 0.228                | 1.796          |
| CF10-60| 570.7                | 553.6                | 17.06                | 0.236                | 0.018                | 0.254                | 1.777          |
| CF20-30| 876.8                | 842.3                | 34.50                | 0.350                | 0.033                | 0.383                | 1.747          |
| CF40-30| 1884                 | 1673                 | 210.4                | 0.742                | 0.155                | 0.897                | 1.905          |
| CF40-60| 1025                 | 856.8                | 168.0                | 0.377                | 0.128                | 0.505                | 1.971          |

![Figure 3](image1.png)

Figure 3. (a) Nitrogen adsorption–desorption isotherms for various samples; (b) specific surface area ($S_{BET}$) by BET method for various samples; (c) pore width distributions for samples prepared with different solvent concentrations; and (d) pore width distributions for samples prepared with different immersion times.

![Figure 4](image2.png)

Figure 4. SEM images for samples CF0, CF5-30, CF10-30, CF20-30, CF40-30, and CF40-60. A cross-sectional view of sample CF40-60 is inserted, showing large pores underneath the massively dissolved fiber surfaces.
macro-pores coexist in the sample, making the highly porous 3D carbon skeleton a desirable structure for application in EDLCs.

TEM was utilized to further investigate the existence of micro-/meso-/macro-pores created by the SSD process for samples CF40-30 and CF40-60. The grinded sample powders were ultrasonically dispersed in ethanol and dripped onto a copper mesh. It can be clearly seen in Figure 6 that a highly porous 3D skeleton with hierarchical pore structures are present in both samples.

Figure 6. TEM images for the samples CF40-30 and CF40-60.

According to the above results, we propose that a highly porous 3D cellulosic skeleton can be formed by the SSD process followed by a consolidation process. After carbonization, the highly porous 3D skeleton with hierarchical pore structures were well maintained to finally obtain activated porous carbon materials. A schematic diagram is demonstrated in Figure 7, revealing how this highly porous 3D skeleton was created and maintained during the SSD, consolidation, and carbonization processes.

Figure 7. Schematic diagram showing the formation of activated porous carbons by SSD, consolidation, and carbonization processes.

We expect that the large surface area and wide pore size distribution of this highly porous 3D skeleton with interconnected bridge-like fibrillar linkages and hierarchical pore structures are beneficial for supercapacitive performances. Thus, the porous carbon samples were utilized to assemble two-electrode type EDLC coin cells and their electrochemical performance was investigated by CV and GCD tests. As shown in Figure 8a, the CV curves of all of the cells exhibit a near-rectangular shape, indicating the apparent supercapacitive behavior for these two-electrode type coin cells. It is noticed that the CV curve of sample CF20-30 shows small redox peaks at around 0.4 V, which is due to the existence of oxygen-containing active groups on the sample surfaces. At a relatively high scanning speed, for example, 20−100 mV/s, CV curve of CF40-30 still shows a good rectangular shape (Figure 8b), indicating the effective electrolyte accessibility and fast ion transportation within this highly porous 3D structure because of the existence of hierarchical pore structures.

It is also noticed in Figure 8c,d that for low solvent concentration (e.g., 10 wt %), the CV curve reveals no apparent changes with increasing immersion time. However, for high solvent concentration (e.g., 40 wt %), the area covered by the CV curve increased with increasing immersion time from 30 to 60 min, indicating a higher capacitance for sample CF40-60. Recalling the results in Figure 3, sample CF40-60 has a high surface area (1025 m²/g) and a relatively wide and even distribution of pore sizes between 1 and 4 nm, which may facilitate the ion transportation and electrolyte accessibility during charging and discharging processes of the cells. Although sample CF40-30 has an even higher surface area (1884 m²/g) than sample CF40-60, it exhibits a lower specific capacitance than sample CF40-60. This can be attributed to the existence of a large amount of micropores (∼1 nm) in sample CF40-30. As indicated in Table 2, \( V_{mic} \) of sample CF40-30 is double that of sample CF40-60. The electrolyte is difficult to access and infiltrate all of these small pores during charge and discharge process. With many unemployed micropores existing, the capacitance of sample CF40-30 is therefore lower than the expected value.

On the basis of this highly porous 3D carbon skeleton with hierarchical pore structures, CF40-60 demonstrates the highest specific capacity in the GCD tests, which is in good agreement with the above CV measurements. A good rate capability makes this carbon material suitable for high power supercapacitor applications. Furthermore, the sample CF40-60 exhibits a much better rate capability than other samples (see Figure 9). The capacitance can retain as high as 94.2% when the current density reached 1 A/g, whereas for CF0 the capacitance dropped significantly to 52.2%. After 5000 cycles, the capacitance of the supercapacitor made with CF40-60 porous carbon materials can have a retention of 75% (Figure 9d).

Table 3 summarizes and compares our results with the specific capacitance of various activated carbon materials. It clearly shows that the activated porous carbons prepared by
the SSD method are very competitive to other carbon-based materials. Meanwhile, the preparation procedure reported in this study is rather simple and environmentally friendly, without the need for an energy-consuming harsh chemical activation process, which will make it even more attractive for industry. Therefore, the SSD method could be a promising way to produce highly porous carbon electrodes on a large-scale for EDLCs or other energy storage devices.

4. CONCLUSIONS

A simple, cost-effective, environmentally friendly SSD method was employed to prepare cellulose-derived highly porous...
activated carbons with a 3D fiber construct, possessing interconnected bridge-like fibrillary linkages and hierarchical pore structures. This highly porous activated carbons exhibit large surface areas (1000–2000 m²/g) and a wide pore size distribution which can strongly enhance the electrochemical performance of supercapacitors (EDLCs) based on these carbon materials. The specific capacitance of EDLCs made with CF40-60 reaches to 263 F/g, which is nearly 5 times the EDLC made from untreated CF0. Noticeably, this is 50% higher than commercial ACs (175 F/g). The capacitance can retain as high as 94% when the current density increases from 100 mA/g to 1 A/g, whereas for CF0 the capacitance dropped significantly to 52%. After 5000 cycles, the capacitance of the EDLCs made with CF40-60 porous carbon materials can have a retention of 75%. In short, it can be concluded that the SSD method is a promising industrial scalable approach to produce highly porous activated carbons in an environmentally friendly manner for the applications in the supercapacitors or other energy storage devices.

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Notes
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