



Hierarchically porous activated carbons derived from Schefflera octophylla leaves for high performance supercapacitors

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ABSTRACT

Hierarchically porous activated carbons with high specific surface areas are synthesized by chemical activation of the leaves of *Schefflera octophylla*. The specific surface areas of the materials are over 2300 m² g⁻¹ and the specific pore volume is as high as 1.92 cm³ g⁻¹. The optimized material achieves a high specific capacitance of 336 F g⁻¹ in 6 M KOH aqueous electrolyte at a current density of 0.5 A g⁻¹, and it also shows excellent cycling stability with 97.5% capacitance retention after 10,000 cycles at a current density of 10 A g⁻¹. The simple synthesis route of hierarchically porous activated carbon from renewable bio-wastes enables a promising strategy in both reducing wastes and producing useful energy storage materials.

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1. Introduction

Porous carbons are important electrode materials for electrochemical double-layer supercapacitors (EDLC) owing to their high specific surface area, chemical stability, and electrical conductivity. Biomass is an abundant and sustainable source for producing carbon-based materials for supercapacitors [1].

Schefflera octophylla [2] is an evergreen tree widely grown in southern Asia. The leaves of *Schefflera octophylla* contain majorly carbon, nitrogen and oxygen elements. A leaf contains many cells for various biological functions and its microstructure is typically hierarchical. As a bio-waste, *Schefflera octophylla* leaves appear to be a sustainable source to produce a hierarchically structured carbon material.

In this work, the leaves of *Schefflera octophylla* were used to produce hierarchically porous activated carbons (HPACs) for high performance supercapacitors. The process involves carbonization and subsequent NaOH activation. All HPACs had a high specific surface area and a hierarchical pore size distribution (PSD). The optimized HPAC-4.5 material showed superior capacitive performance in 6 M KOH aqueous electrolyte.

2. Experimental

Schefflera octophylla leaves were washed in deionized water and ethanol, and then dried at 80 °C overnight. The dried leaves

were ground and then carbonized at 800 °C for 4 h under argon flow and the product was labelled as C800. The C800 material was mixed with different amounts of NaOH (with C800:NaOH mass ratio being 1:2, 1:3, 1:4, 1:4.5, or 1:5), and the mixture was heated to 800 °C at a ramp rate of 5 °C min⁻¹ and soaked for 4 h in a tube furnace under argon flow. The treated product was washed with 1 M HCl and deionized water by filtration until the filtrate became neutral in pH, and finally it was dried at 80 °C under vacuum overnight. According to the C800:NaOH ratios, the final materials were labelled as HPAC-2, HPAC-3, HPAC-4, HPAC-4.5 and HPAC-5, respectively. Since the performance of HPAC-4.5 was the optimum (Fig. S11), HPAC-4 is not included in the following discussion.

3. Results and discussion

The typical microstructure of the leaf contains stacked layers with pores on the top surface, as shown in Fig. 1b and c. The carbonization temperature was set at 800 °C according to the TGA result (Fig. S3). After carbonization, the laminar structure appeared to shrink and crumple as shown in Fig. 1d. The carbonized C800 material was attacked by NaOH at 800 °C by a process which is known as “activation” [3–4] and a porous structure developed as shown in Figs. 1e–g, and S2. In the XRD patterns (Fig. 2a), there are two broad peaks at around 26° and 44°, which correspond to the (0 0 2) and (1 0 1) planes of graphite, respectively. The structure of HPACs was further analyzed using Raman spectroscopy (Fig. 2b). The two peaks at around 1350 cm⁻¹ and 1590 cm⁻¹ can be assigned to the D and G bands of graphite, respectively. The ratio between the intensities of D and G bands (I_D/I_G) of HPACs

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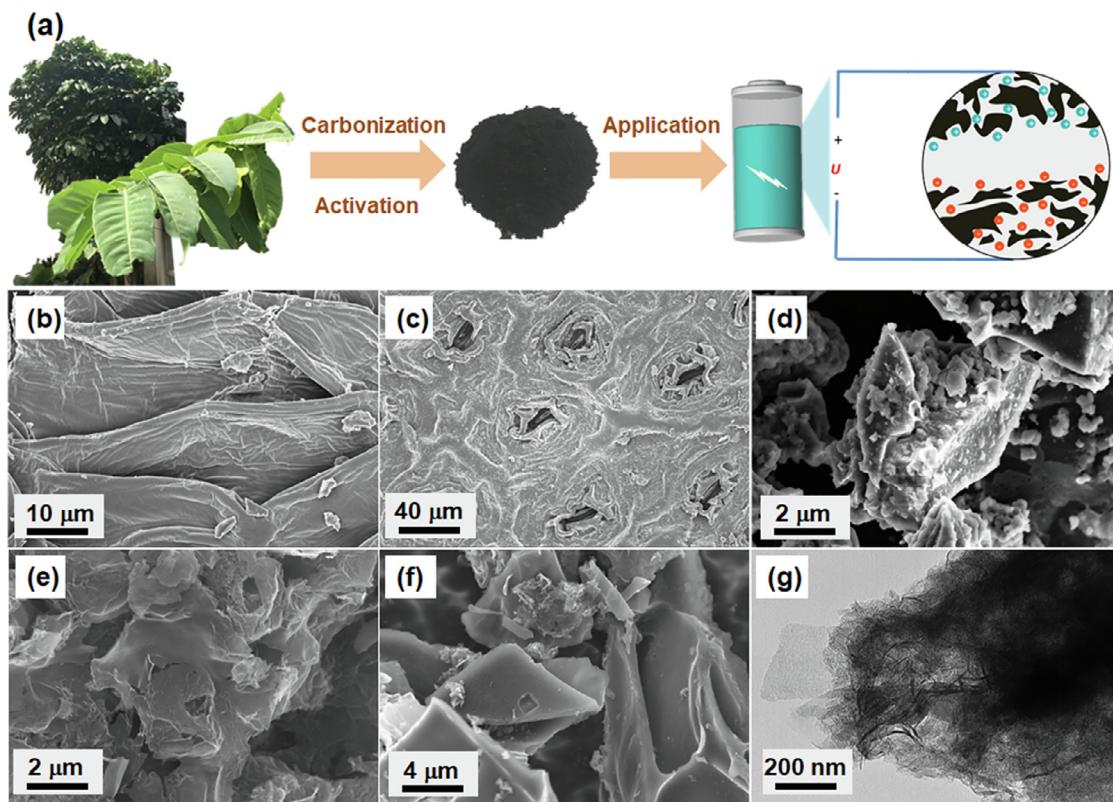


Fig. 1. (a) Overall synthesis route of HPACs; SEM images of: (b) and (c) dried Schefflera octophylla leaf; (d) C800, (e) and (f) HPAC-4.5; (g) TEM image of HPAC-4.5.

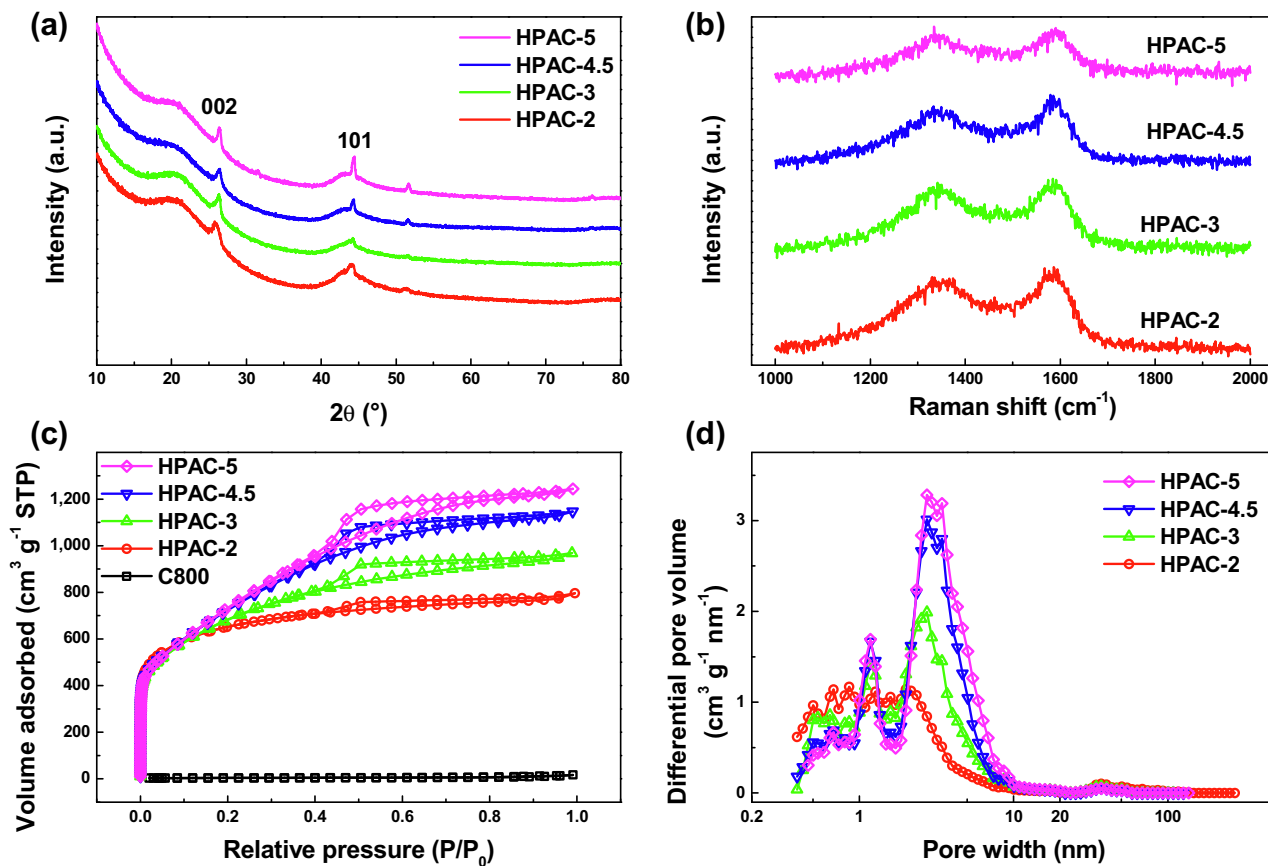


Fig. 2. (a) XRD patterns, (b) Raman spectra, (c) nitrogen adsorption/desorption isotherms, (d) corresponding pore size distribution of HPACs.

was calculated and plotted in Fig. S4. Since a lower intensity of D-band in relative to that of G-band indicates fewer defects and a higher degree of graphitization, HPAC-4.5 was expected to have the highest electrical conductivity of all HPACs.

N_2 adsorption/desorption isotherms and corresponding PSD curves are shown in Fig. 2c and d. The isotherms can be classified as type IV with a hysteresis loop, indicating the presence of mesopores [5]. PSDs confirm the presence of both mesopores and micropores. The BET specific surface area and specific pore volume are shown in Fig. S5. The BET surface area increased from $13 \text{ m}^2 \text{ g}^{-1}$ for C800 to above $2300 \text{ m}^2 \text{ g}^{-1}$ for all HPACs and HPAC-5 showed the largest value of $2643 \text{ m}^2 \text{ g}^{-1}$. The PSDs show that most pores are in the mesopore range. The microstructure of C800 inherited from the leaf contributes to the hierarchically

meso-/microporous structure of the HPACs. Since NaOH activation creates pores by etching carbon, the yield of HPACs decreased as the NaOH amount increased (Fig. S5).

The elements in the HPACs revealed by XPS include carbon (C 1s at 285 eV), oxygen (O 1s at 533 eV) and sulfur (S 2p at 164 eV) as shown in Fig S7. Detailed elemental contents are summarized in Table S1. High-resolution XPS spectra of HPAC-4.5 are shown in Fig S8. The C 1s spectrum can be deconvoluted to the C–C/C=C ($\sim 284.8 \text{ eV}$), C–O ($\sim 285.5 \text{ eV}$) and C=O ($\sim 288.9 \text{ eV}$) peaks [6–8]. The O 1s spectrum can be fitted by two peaks corresponding to C=O ($\sim 532.9 \text{ eV}$ and $\sim 535.5 \text{ eV}$) [9]. The oxygen content decreased as the NaOH amount increased, suggesting that NaOH preferred to attack the oxygen sites which can be regarded as defects in graphite. Likely, the degree of graphitization increased

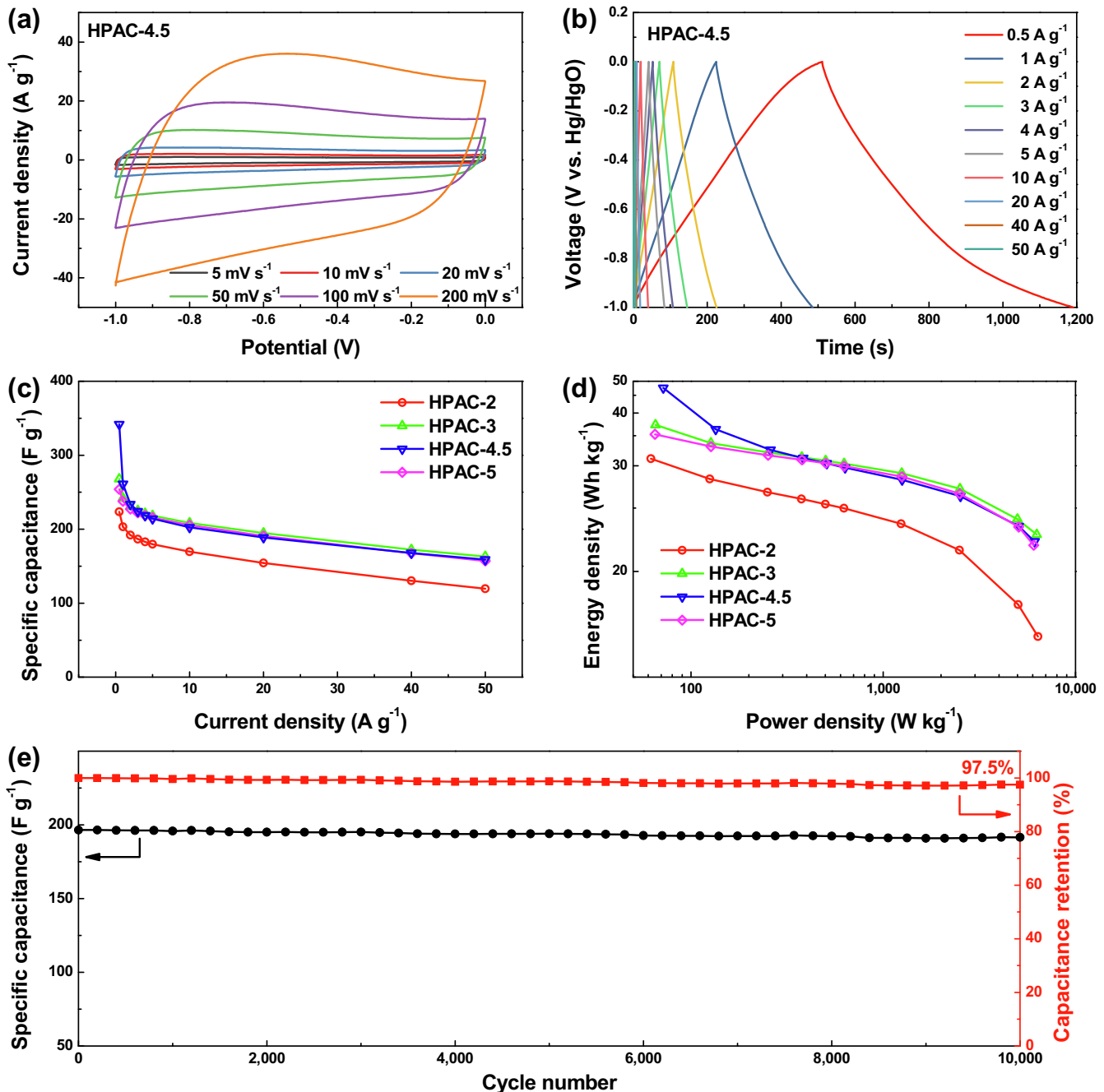


Fig. 3. (a) CV curves of HPAC-4.5 at different scan rates, (b) galvanostatic charge/discharge curves of HPAC-4.5 at different current densities, (c) Specific capacitance of HPACs, (d) Ragone plot of HPACs, (e) Cycling test of HPAC-4.5 at a current density of 10 A g^{-1} .

as more NaOH was used, which is consistent with the Raman result.

The electrochemical capacitive performance of the HPACs in 6 M KOH electrolyte was investigated using a three-electrode configuration. As shown in Fig S9, the rectangular shape at low scan rates (5–50 mV s⁻¹) suggests the typical characteristic of an EDLC. The quasi-rectangular shape of the cyclic voltammetry (CV) curves can still be maintained even when the scan rate was as high as 200 mV s⁻¹ (Figs. S9 and 3a), indicating that ion transport in these HPACs was fast. The galvanostatic charge/discharge curves at different current densities show symmetrical triangular shapes (Figs. 3b and S10), demonstrating the typical EDLC behavior. HPAC-4.5 showed the highest specific capacitance of 336F g⁻¹ at 0.5 A g⁻¹, 220F g⁻¹ at 5 A g⁻¹ and 200F g⁻¹ at 10 A g⁻¹(Fig. 3c). In the stability test, HPAC-4.5 retained 97.5% of its initial specific capacitance after 10,000 cycles (Fig. 3e). The Ragone plot derived from galvanostatic charge/discharge tests shows that the HPAC-4.5 achieved a maximum energy density of 47.5 Wh kg⁻¹ at a power density of 71.9 W kg⁻¹ and maintained an energy density of 22.1 Wh kg⁻¹ at a high power density of 6134 W kg⁻¹ in 6 M KOH electrolyte. When compared with other biomass-derived EDLC electrode materials (Table S2), HPAC-4.5 exhibits high performance, which can be attributed to its high specific surface area, hierarchical pore structure, and good electrical conductivity. The high specific surface area provides a large surface to form electric double layers for energy storage, the hierarchical pore structure facilitates ion diffusion, and a good electrical conductivity reduces electrical resistance.

4. Conclusions

In summary, leaves of *Schefflera octophylla* were carbonized and activated by NaOH, and the product was used as an electrode material for supercapacitors. The specific capacitance of HPAC-4.5 was 336 F g⁻¹ at 0.5 A g⁻¹ in 6 M KOH aqueous electrolyte and retained 97.5% of the initial capacitance after 10,000 cycles at 10 A g⁻¹. Utilizing bio-wastes such as *Schefflera octophylla* leaves to produce high performance electrode materials for EDLCs was demonstrated as a promising strategy for both effective waste management and producing high value-added energy storage materials from low-cost precursors.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.03.101>.

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